ISSN : 0974 - 7486 Volume 9 Issue 2

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 9(2), 2013 [56-62]

An x-ray scattering study of molecular level structure of tertiary originsub-bituminous Indian coal

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Received: 6th June, 2012 ; Accepted: 3rd October, 2012

ABSTRACT

An x-ray molecular level structural characterization of Tertiary origin sub-bituminous Indian coal is reported in this paper with an attempt to better understand its molecular level structure, the short-range structural features, to determine the relationship (s) between the aryl / alkyl carbon ratio and determination π and γ-bands positions of the coal. The coal was collected from Tirap colliery of Assam, North-East India has been studied. The average poly-cyclic aromatic unit in Tirap coal is a ribbon-shaped C_{14} (analogous to phenanthracene). For this coal, the average carbon atoms (n_{cc}) is found to be 1.24. Also, 73% of the C-C bonds in the coal are between aryl carbons while 27% of the C-C bond involves at least one alkyl carbon. The results indicate that the average carbon in this coal has 0.91 nearest carbon neighbors at a bond distance of 1.39 Å and 0.33 carbon neighbors at distance of 1.54 Å. The positions of π and γ-bands are observed at a d-value of 3.37 Å and 4.92 Å respectively. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Assam coal;
Coal structure;
X-ray scattering;
γ-band;
π-band;
RDF.

INTRODUCTION

Coal is a very complex heterogeneous material mainly consists of organic and inorganic matters. The structure of coals varies from locations to location. Structural characterizations of coal represent one of the most important activities in coal science owing to its utilizations. The x-ray diffraction patterns of coals are produced by distinct components in the coal, which includes diffraction from the organic matrix and mineral components in it[1-3]. The contribution from the organic component of coal shows the amorphous scattering which describes the short-range structure of the small polycyclic aromatic (PCA) unit in it. Thus, the ordering of the carbon atoms in PCA unit and the parallel packing of these units determine the x-ray scattering patterns of coals. Although the network structural modeling research on coal using various techniques like X-ray structural analysis, FT-IR, solid state NMR, UV-visible spectroscopy etc. has been carried out for more than half a century, several issues like nature of the coal structural network remain unsolved[4]. It is, however, extremely difficult and challenging to characterize the structure of coal because of its compositional heterogeneity and complexity of organic materials, largely insoluble and amorphous nature[5]. Thus, the structural properties of coal have been receiving much attention among coal scientists because of their importance in chemical reactivity during various utilizations. Also, it is worthwhile to mention that the construction of a model of the molecular structure of coal is one of the most important tasks in understanding the relationships between the coal structure and reactivity[6-7] and, hence, the structural study of coal continues to be pursued intensively.

X-ray diffraction from coal has been a subject of study among many several present and past workers[1, 8-27]. Many advances have been made in this area in the past several decades and, thus, the x-ray diffraction technique is useful for examining the molecular-level short-range structuring in non-crystalline condensed phase of coal. Many other modern methods, e.g., ^{13}CCP/MAS nmr, ^{1}H CRAMPS, FT-IR are applied in studies of coal structure which are sensitive to the phenomena occurring in the closest vicinity of the atom. However, from such studies it is impossible to draw conclusions concerning the ordering of atoms at greater distances[28-31]. The role of X-ray diffraction study in coal science is enormous and it is a fundamental method for evaluating carbon-stacking structure in coal. Thus, the Radial Distribution Function (RDF) technique using x-ray diffraction data is used to determine the structure of PCA unit in coal which does not require any assumption concerning the structure. Another advantage is that the radiation used in x-ray scattering studies is sufficiently penetrating so that the surface effects may be ignored. However, one limitation of Radial Distribution Function (RDF) method is that it provides only information on one spatial dimension and, also, it is insensitive to the presence of hydrogen atoms.

Studies of coal involving x-ray scattering analysis of the average PCA unit, the estimation of aryl and alkyl carbon fractions, the number of nearest carbon atoms bonded to average carbon etc. in coal have been carried out by many scientists[17,20,24,27,32]. Cartz and Hirsch[1,2] termed the small PCA units in coals “Lamallae” and first noted that the stacking of the lamellae produces intense peak which are the dominant feature in the x-ray diffractograms obtained from coal. The x-ray scattering study of APC 501 coal suggests an average PCA unit C_{24}[27] and favors a polycyclic unit built by circular catenation. Also, the study indicates that the average carbon has approx. 2.5 nearest carbon neighbors separated by an average C-C distance of 1.41 Å. The latter is consistent with an alkyl/aryl distribution of 14%/86%. It is, however, to be noted that the structural parameters obtained from x-ray scattering study are found to be in good agreement with the results obtained from NMR study.

As measured by x-ray scattering, the average polycyclic aromatic unit in APC401 is linearly catenated C_{14} model[24]. It is, however, impossible to construct a model containing all atomic groups found in coal, especially as their quantitative proportions are not known.

Tertiary origin Tirap coal, Assam, India have been classified as the sub-bituminous type on the basis of studies on their chemical composition and physical characteristics. The molecular level structure of Tirap coal have not been studied using X-ray diffraction techniques while works on other aspects of coal viz. demineralization, desulphurization, trace metals contents, structural parameters etc. have been reported[33-35]. This paper attempts to analyze the molecular level structure of Tirap coal by Radial Distribution Function (RDF) technique using x-ray diffraction data for the first time. It, also, includes the determination of nearest carbon neighbors, the relationship (s) between the aryl / alkyl carbon ratio, and distribution of ideal peaks of aryl and alkyl C-C atom-pairs etc.

EXPERIMENTAL

Freshly mined coal sample was collected from Tirap coalliery from North-East India and ground to < 150 ìm sample size. 5 g of the sample was demineralised[36] by dispersing in 30 ml of conc. HCl solution (36.5 wt %) and stirred for 3 h at 40 °C. Then the coal was filtered and washed with distilled water. The HCl treated samples was then mixed with 30 ml of conc. HF solution (48 wt %) and stirred for 3 h at the same temperature. Finally the treated coal was washed with hot distilled water to remove HF and dried in an air oven at ambient temperature. It may, however, be mentioned that the acid treatment used in demineralization of coal does not effect structural changes in low rank coals[37]. The proximate analysis of the coal was carried out in PA (Leco, TGA-700). The elements C, H and N were determined by the elemental analyzer: Perkin Elmer model 2400 and % of oxygen was calculated by difference method. The physico-chemical analysis of the coal sample is shown in TABLE 1.

TABLE 1 : Physico-chemical analysis of the coal sample

Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	O (by diff)
2.30	0.99	43	53.7	77.97	5.75	1.15	15.13

The x-ray diffraction data were obtained using a computer controlled X-ray diffractometer: Type Philip PW1710, with start angle: 4.02 and stop angle 89.98 and target: Cu (Fe filtered) with graphite crystal monochromator and scintillation counter with scientillator NaI single crystal. Measuring condition mode: Voltage: 30KV, Current: 20mA. The observed experimental intensities were corrected for air scatter, absorption by the sample and polarization effect. The RDF calculation was carried out following a procedure given by Klug & Alexander[38].

RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffractogram of the Tirap coal. The x-ray pattern shows diffuse peaks at the positions of the most prominent graphite bands. The atom-pair correlation function g(r) for the coal sample is shown in Figure 2. The inter-atomic distances in the coal were calculated from the g(r) curves obtained after Fourier transformation of the intensity data. Using the method of Konnert and Karle[39], the statistical uncertainty (σ) of the inter-atomic distances was calculated to be ±0.01. Thus, for a peak in g(r) to be statistically significant, its maximum must be greater than $1+2\sigma$[3], i.e., 1.02 for g(r) obtained for Tirap coal. Thus, the small peak at about 0.3 Å comes from the non-vitrinite portion of the coal[14] which is not seems to be statistically significant. Hence, the g(r) distribution curve indicates the first statistically significant peak (P1) at about 1.43 Å and further concentrations are at about 2.6 Å and 3.8 Å.

Determination of nearest carbon neighbors, aryl and alkyl carbons

It may, however, be mentioned that the six-member aromatic rings fused into polycyclic aromatic (PCA) units were proposed to be the dominant short-range structural species found in medium-rank coals[40]. In small crystalline PCA compounds, the average bonded distance between aryl carbons is 1.39 Å[41-43] while the typical bond distance between alkyl carbons is 1.54 Å[44]. For Tirap coal P1 lies in between these two distances and, hence, the area (0.9462 e^2Å) and the peak maximum (1.43 Å) under P1 may be used to estimate the number of nearest carbon atom bonded to the average carbon (n_{cc}) with 0.76 fraction of mineral free carbon atom in Tirap coal by[24]:

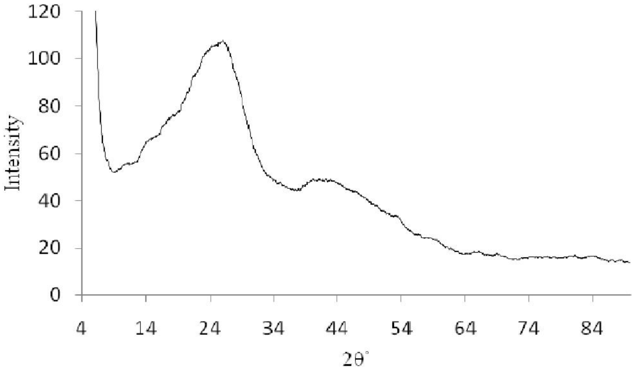

Figure 1: X-ray diffractogram of tirap coal

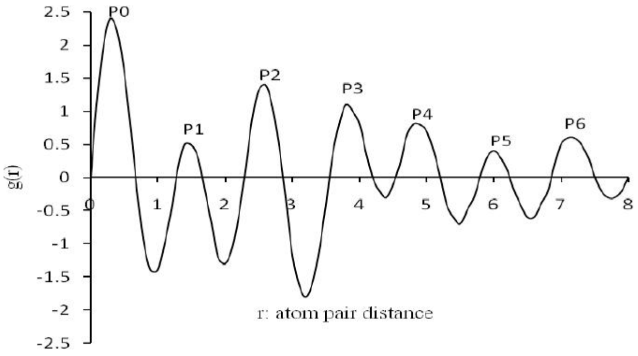

Figure 2 : G (r) obtained for tirap coal

$$n_{cc}=P1_{area}\ e^2Å\ /(0.76*36\ e^2Å) \qquad (1)$$

and the fractions of aryl and alkyl carbons in the coal by[45, 46]:

$$P1_{max}\ Å=\{x\ 1.39\ Å\}+\{(1-x)\ 1.54\ Å\} \qquad (2)$$

where x is the fraction of aryl C-C bonds and 1-x is the fraction C-C bonds that involve at least one alkyl carbon. For Tirap coal, the average carbon atoms (n_{cc}) is found to be 1.24 while 73% of the C-C bonds in the coal are between aryl carbons and 27% of the C-C bond involve at least one alkyl carbon. Combining these results indicate that the average carbon in this coal has 0.91 nearest carbon neighbors at a bond distance of 1.39 Å and 0.33 carbon neighbors at a distance of 1.54 Å.

Determination of molecular level structure

(a) Ideal peaks of aryl and alkyl C-C atom-pair distributions

The ideal peaks of aryl and alkyl C-C atom pair distribution were calculated from the equations[21]

$$IP_{arC-C}=1.6(2\pi)^{-0.5}f^2c(Q)M(Q)\{\cos(Qx^1)+\cos(Qx^2)\}\Delta s \quad (3)$$

and

$$IP_{alC-C}=0.6(2\pi)^{-0.5}f^2c\,(Q)M(Q)\{\cos(Qx^3)+\cos(Qx^4)\} \quad (4)$$

In these equations $x^1=r-1.39$ Å, $x^2=r+1.39$ Å, $x^3=r-1.54$ Å, $x^4=r+1.54$ Å

Figure 3 shows the ideal C-C peaks calculated for 0.91 C-C atom pair separated by 1.39 Å and for 0.33 C-C atom-pairs separated by 1.54 Å.

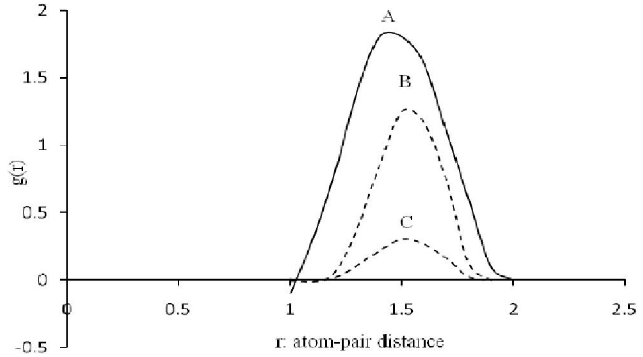

Figure 3 : A: P1 in g(r) compared with ideal C-C peak separated by B: 1.39 Å and C: 1.54 Å

(b) Simulated structure function of PCA

Many workers[20,26,27,40,47-50] have proposed the six-membered aromatic ring fused into the polycyclic aromatic units which dominants the short-range structure species found in medium rank coals. The simulated structure function for some PCA models[24] was calculated using he Kurita peak shape formalism by[51]:

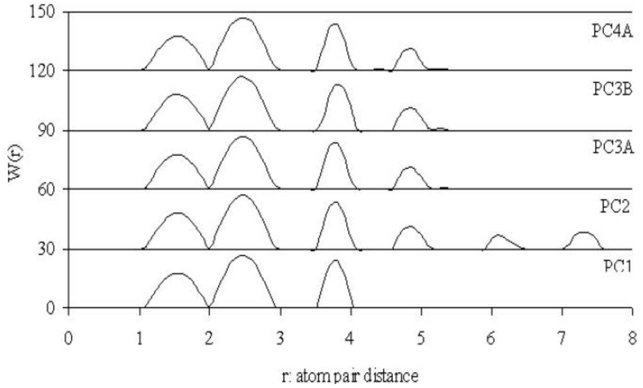

Figure 4 : The simulated structure function calculated for some PCA unit

$$W_{PCA}(r)=1+a_i\,n_{jk}[\cos\{2\pi K\delta_{jk}\}][\exp\{-\tau\delta_{jk}{}^{n}] \quad (5)$$

Where, a_i is a co-efficient that normalizes the first peak in W(r) to P1 in g(r) and k & τ are constants which shape the simulated maxima and minima in W(r). Figure 4 shows the simulated structure functions calculated for several polycyclic aromatic units. Here P1 is characterized by the bonded C-C atom pairs while P2 is caused by the nearest and the second nearest non-bonded C-C atom-pairs.

(c) R-value: The structure correlation factor and analogous structural model

The resulting structure co-relation factor for each simulated structure curve was calculated by[52]

$$R=\{\pounds\varepsilon(r)\}^2/\{\pounds g(r)\}^2 \quad (6)$$

Where ε(r)=g(r)-W(r)

TABLE 2 shows the structure co-relation factor obtained from a comparison of the atom-pair correlation function g(r), compared with the simulated structure curve W(r) calculated for each PCA compounds. The lowest R-value signifies the best correlation between g(r) and W(r). These results (with R=0.063*10^{-3}) indicate that the ribbon-shaped (linearly catenated) C_{14} structural model best agrees with the atom-pair correlation function found for Tirap coal.

TABLE 2 : Structure correlation values for the PCA models

PCA molecules			R-value (*10^{-3})
PC1	C_6	Benzene	0.165
PC2	C_{10}	Naphthalene	1.032
PC3A	C_{14}	Anthracene	0.803
PC3B	C_{14}	Phenanthracene	0.063
PC4A	C_{18}	Naphthracene	651.079

(d) Real space structural model

The ribbon-shaped linearly catenated C_{14} model, best agrees with g(r) as evident by its R-value which is lowest structure correlation factor (R=0.063*10^{-3}). It was, also, indicated previously that the maximum in the structure curve (r=1.43 Å) shows that a considerable fraction of the C-C bonds is between carbon atoms where at least one atom in the pair is an alkyl carbon. Thus the alkyl carbons are bonded to some of the secondary carbons of the PCA unit. This leads to the structural model of the C_{14} unit with alkyl carbon.

(e) Alkyl carbons associated with the PCA unit

The simulated structure curves are calculated from the non-bonding (NB-PCA) and bonding model (B-PCA). In the non-bonding model, it was assumed that the alkyl carbons are not bonded to the PCA unit while in the bonding model the alkyl carbons were assumed to be bonded to some of the secondary aryl carbons of the C_{14} unit in a proportion similar to the aryl/alkyl carbon distribution (0.73/0.27) in the coal. For the correlation between P1 in g(r) and simulated W(r) is based on 0.91 C-C atom-pairs separated by 1.39 Å and 0.33 C-C atom-pairs separated by 1.54 Å. Figure 5 shows the simulated curves for NB-PCA & B-PCA calculated from r= 0.00 Å to r=3.00 Å. Over the region from r=0.00 to r-3.00, $R=0.062*10^{-3}$ for the B-PCA model while for the NB-PCA model $R=66.589*10^{-3}$. These results indicate that most if not all of the alkyl carbons are bonded to the aryl unit.

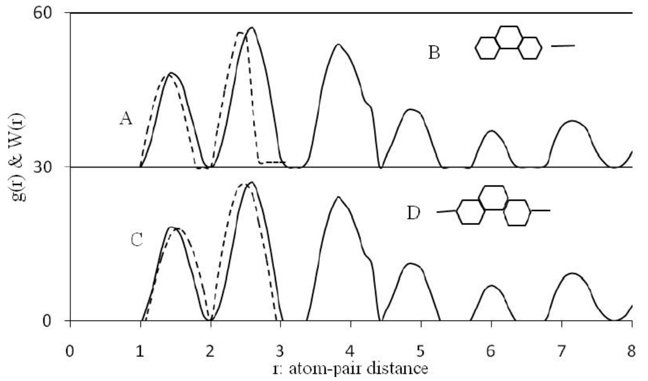

Figure 5 : A: The W(r) calculated for NB-PCA model (…) compared with g(r) B: a non-bonded model C: The W(r)

(f) Reciprocal space structural model

Figure 6 shows the J(Q) the simulated reciprocal space x-ray scattering curve J(Q) calculated from the methyl substituted anthracene model following the procedure[45, 53] given by

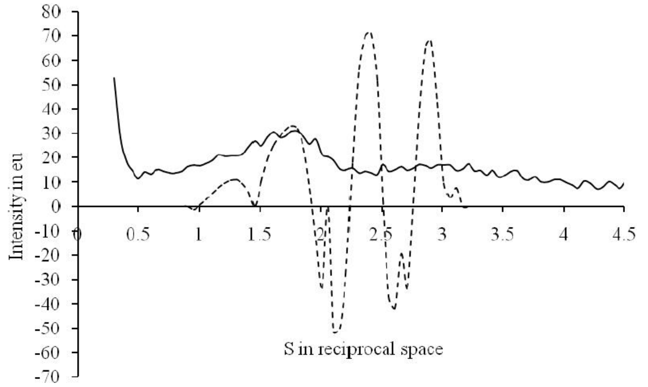

Figure 6 : The J(Q)(…) calculated from the model compared with i(Q) (__)

$$J(Q)=(n_{jk}/Q)\int 4\pi r^2\rho_0\sin(Qr_{jk})\Delta r, \qquad (7)$$

Where n_{jk} represents the number of jk C-C atom-pairs separated by the distance r_{jk}.

The reciprocal space structure co-relation factor for the comparison was calculated by

$$R=\varepsilon^2(Q)/i^2(Q) \qquad (8)$$

Where $\varepsilon(Q)=i(Q)-J(Q)$

When the maximum centered in J(Q) at 1.75 Å is included; R=0.660 and when it is excluded it becomes 0.697. Comparison of the R-value indicates that the maximum centered at 1.75 Å is caused by the atom-pair scattering within the average PCA unit in Tirap coal. Thus carbon atom in PCA unit appears to be bonded to alkyl carbons.

(g) Proposed molecular level structural model

Six-membered aromatic rings fused into polycyclic aromatic (PCA) units were proposed and thus the average poly-cyclic aromatic unit in this coal is a ribbon-shaped C_{14} model analogous to phenanthracene with most if not all of the alkyl carbons are bonded to the aryl unit.

The π and γ-bands

The carbon related peaks around 20-26° basically classified into two categories: one derived from aromatic ring stacking around 26° so-called π-band or 002 band and the other around 20° named γ-band, which is believed to be derived from aliphatic chains[54, 55]. The π and the γ-bands were observed in this coal at a d value of 3.37 Å and 4.92 Å respectively.

CONCLUSIONS

The proposed molecular level structural model for Tirap coal is a six-membered aromatic ring found into polycyclic aromatic (PCA) units and it is a ribbon-shaped C_{14} model analogous to phenanthracene with most if not all of the alkyl carbons are bonded to the alkyl unit. However whether the alkyl carbons associated with the PCA unit are methyl, methylene can not be determined from these x-ray scattering experiments. The aryl and alkyl carbons in this coal are determined to be 73% and 27% respectively. The d-values of π-band and γ-band are observed at 3.37 Å and 4.92 Å respectively. It is, also, to be noted that it does not provide direct evidence about the forces which cause the "stacking" of the poly-cyclic layers into graphene units. However, the graphene layers are distorted from planarity by the aliphatic moieties which are directed, on the average, into the spatial regions between the slightly irregular graphene units and cause the non uniform strain in their stacking. This latter effect causes the differences of the graphene layer stacking diffraction peak. Also, certain systemic errors may be present in experimental data owing to inadequate source collimation, extraneous instrument background and incorrect absorption correction. These results could be useful in chemical reaction during the various utilization processes.

ACKNOWLEDGEMENT

The authors are thankful to Dr. P. G. Rao, Director, North East Institute of Science & Technology, Jorhat-785006, India, for allowing to publishing the paper. The authors are also thankful to Mr. M. Kakoti, Department of Physics, J. B. College, Jorhat-785001, India, for providing the samples.

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