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Poly-cyclic aromatic structural study of sub-bituminous assam coal using X-ray pair distribution function

A Gogoi
Analytical Chemistry Division
CSIR-North East Institute of Science & Technology, Jorhat, Assam, India
R K Boruah
Analytical Chemistry Division
CSIR-North East Institute of Science & Technology, Jorhat, Assam, India

Abstract:

Coal is a very complex heterogeneous material. It consists of both organic and inorganic matter. The X-ray diffraction patterns of coals are produced by distinct components in the coal, which include diffraction from the organic matrix and mineral components in it. 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. X-ray scattering study is one of the most important techniques to describe the structure of coal. This paper related to the distribution of carbon atoms in a single poly-cyclic aromatic (PCA) layer (graphene) in Tirap coal from Assam, India. The pair distribution function (PDF) analysis performed indicates no evidence of any graphite like structure in this coal. The aromatic fraction in this coal is 74 % with aliphatic fraction correspondingly estimated to be 26 %. The average carbon atom has 2.6 nearest carbon atom neighbors at an average bond distance 1.50 Å. The first significant maximum of pair distribution function is at 1.5 Å which relates to the C- C aliphatic bond length. The second maximum at 2.6 Å which relates to the distance between carbon atoms of aliphatic chains that located across one carbon atom. The γ-band is observed at a d-value 4.24 Å.

Keywords: *Coal, Poly-cyclic aromatic unit, Pair-distribution function*

Introduction

Coal is a very complex natural carbonaceous material and the large variety of organic and inorganic materials involved in the formation of coal makes them highly heterogeneous. The coal structure varies from locations to location and, also, it changes with its matrix. The acceptance of coal for industrial applications depends critically on both organic and inorganic matter present in it. The technological use of the factors such as structure, mineral matter associated with coal is of more practical importance because it creates new opportunities both for widening use this raw material in coke making and conversion of coal in order to obtain liquid fuel as well as coal base chemical products.

X-ray scattering study on coal showed that x-ray diffractogram of coal could be divided into three distinct segments, each of which is dominated by a specific type of scattering from the organic matrix of the coal (Cartz & Hirsch, 1956). Out of these, the high angle region, which is due to the scattering from small condensed aromatic layers and particularly the intermediate angle which is caused by the "packing of the layers of condensed aromatic units". The x-ray radial distribution function (RDF) analysis, the estimation of aryl and alkyl fractions in coal (Grigoriew, 1990; Heek, 2000; Wertz, 1998) and molecular level structural study have received its importance in the structural study of coal. Tirap coal from North-East India has been classified as sub-bituminous type on the basis of the studies on their chemical compositions and physical characteristics. This report is an attempt to understand the short-range structural features, to determine the relationship(s) between the aryl / alkyl carbon ratio, and to determine the no. of carbon atoms present in polycyclic aromatic unit in it using X-ray scattering analysis.

Materials And Method

Coal sample was collected from Tirap coalliery of North-East India, of 60 ft seam. The sample was ground to < 150 μm and demineralised with HF-HCl following the procedure given elsewhere (Lu et.al., 2001). The x-ray diffractogram was obtained by using computer controlled X-ray diffractometer: Type Philip PW1710, with scintillator NaI single crystal at operating voltage/ current 30KV/ 20mA. The RDF calculation was carried out following the procedure given by Klug & Alexander (Klug & Alexander, 1974) from where the atom pair distribution function can be

calculated. The no. of nearest neighbor carbon atoms bonded to the average carbon (n_{cc}) and the fraction of aryl-alkyl carbon are calculated with the procedure given by Wertz (Wertz, 1998).

Result And Discussion

The x-ray diffraction pattern of the Tirap coal sample (Fig-1) shows diffuse peaks at the positions of the most prominent graphite bands. The inter-atomic distances in the coal were calculated from the atom-pair correlation curves G(r) (Fig-2), obtained after Fourier transformation of the intensity data. Using the method of Konnert & Karle (Konnert & Karle, 1973), 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 $1+2\sigma$ (Wertz, 1998), i.e., 1.02 for G(r) obtained for Tirap coal.

The small peak at about 0.3 Å comes from the non-vitrinite portion of the coal (Griegoriew, 1990) which is not seems to be statistically significant. Hence, the atom pair distribution curve G(r) indicates the first statistically significant peak P1 at r=1.50 Å caused by the bonded C-C atom pairs which relates to the C-C aliphatic bond length (Li Pai-Chi, 2002). The second maximum P2 at r=2.60 Å which relates to the distance between carbon atoms of aliphatic chains that are located across one carbon atom and third maximum P3 at r=3.90 Å which may be related to the distance between carbon atoms of aliphatic chain located across two carbon atoms. Further, the maximum in the G(r) curve is at r = 4.90 Å is found to be similar with the distance between parallel aliphatic chains of oriented Poly-ethylene (Bodoev, 1996).

For Tirap coal, the average carbon atom has 2.6 nearest atom neighbors at an average distance of 1.50 Å while 74% of the C-C bonds in the coal are between aryl carbons and 26% of the C-C bonds involve at least one aryl carbon. Combining these results indicate that the average carbon in this coal has 1.9 nearest carbon neighbors at a bond distance 1.39 Å and 0.68 carbon neighbors at a distance of 1.54 Å. The d-spacing for gamma band was found at 4.24 Å for Tirap coal.

Conclusion

The x-ray pair distribution study shows the presence of polycyclic aromatic unit of 74% and 24% aliphatic. The no. nearest neighbor carbon atoms present in this coal is 2.6. In addition, the position of the gamma band is observed at a d-value 4.24 Å, which shows the presence of aliphatic side chains linked with aromatic lamellae structure. Certain systematic errors may be present in experimental data owing to inadequate source collimation, extraneous instrumental background and incorrect absorption correction.

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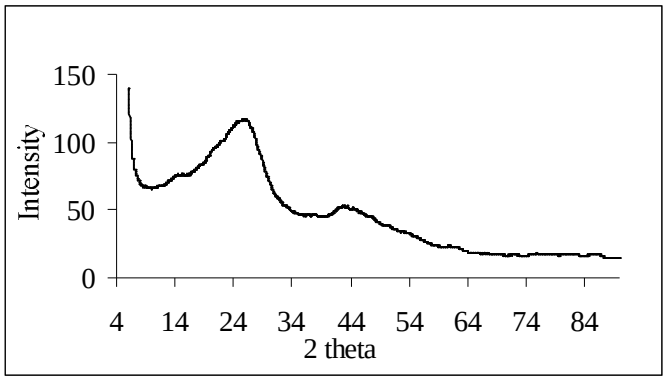

Figure 1: X-ray diffractogram of Tirap coal

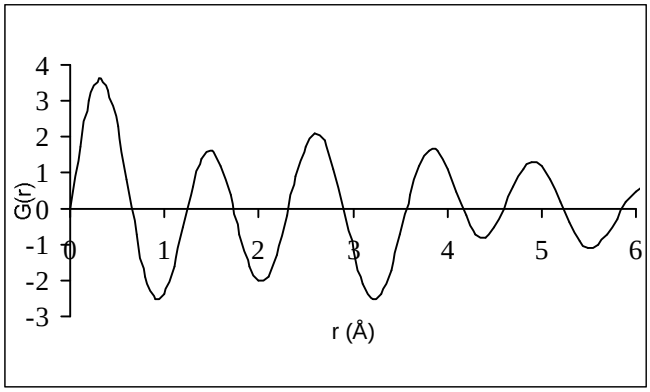

Figure 2: Pair distribution curve of Tirap coal

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