

## X-ray structural parameters of some Indian coals

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**Five Indian coals of different ranks (C% ~ 73.6–92.8) have been demineralized by chemical method. Very slow scan X-ray scattering studies have been performed and coal structural parameters determined by a semi-quantitative method. The present study reveals that coal consists of a semi-crystalline turbostratic structure. Also, the high background of the diffraction profiles clearly shows that coal has amorphous carbon in its structure.  $d_{002}$  value decreases and  $f_a$  increases with increase in coal rank. There is a strong linear relationship between C% and volatile matter content with  $d_{002}$  values of coal.**

**Keywords:** Coal, molecular structure, turbostratic structure, XRD.

THE compositional heterogeneity and complexity of coal organic materials require a complex approach for studying their molecular structure. Coal consists of primary macromolecules of polyaromatic–polynuclear structure with some heteroatom groups and their secondary network. The secondary network is made up of aromatic ring-stacking, aliphatic side-chain entanglement, hydrogen bonds, cation bridges, and charge–transfer interactions through oxygen functional groups<sup>1–3</sup>. Many structural models have been proposed for coal considering the presence of aliphatic and aromatic species, amount of oxygen containing functional groups, and several other factors. Instrumental techniques like TEM<sup>4,5</sup>, FT-IR<sup>6</sup>, Raman spectroscopy<sup>7</sup> and NMR<sup>8</sup> have been used for coal molecular structure determination. The role of X-ray diffraction (XRD) study in coal science is enormous. It was initially directed towards measuring the minerals and/or the low- and high-temperature ash in coal. XRD analysis is a fundamental method for evaluating carbon-stacking structure. The degree of ordering, interlayer spacing ( $d_{002}$ ) and crystallite size ( $L_a$ ,  $L_c$ ) have been established as the structural parameters for evaluating the stacking structure of highly crystalline carbon materials<sup>9</sup>. The structure of coal has also been characterized by XRD, and the existence of crystallites in coal structure has been proven by the appearances of the peaks corresponding to the 002, 100, and 110 reflections of graphite<sup>10</sup>. It has an intermediate structure between graphitic and amorphous state, so-called turbostratic structure or random layer lattice structure. Coal also contains significant amount of highly disordered material, amorphous carbon, which is responsible for the background intensity

of the diffractogram. However, the vagueness of the XRD profile of coal with low crystallinity often makes quantitative evaluation of the stacking structure difficult. Fifty years ago, Hirsch<sup>11</sup> and Diamond<sup>12</sup> proposed the statistical interpretation of XRD profiles for carbon materials with low crystallinity, but the recent development of computer techniques has enabled more accurate calculations and detailed analysis of XRD profiles. In the last two decades, extensive X-ray scattering studies<sup>13,14</sup> have been performed on coal for its structure determination.

Slow step scan XRD<sup>15</sup> analysis has been used to give higher resolution of the diffractograms, classifying the carbon-related peaks around 20–26° basically into two categories: one derived from aromatic ring stacking around 26° (so-called  $\pi$ -band or 002 band) and the other around 20° named  $\gamma$ -band, which is believed to be derived from aliphatic chains. The intensity ratio ( $I_{26}/I_{20}$ ) of the two peaks appears to reflect the coal rank<sup>16</sup>.

In this context, structural parameters of Indian coals using XRD have not been attempted. In the present study, a semi-quantitative approach has been used to determine  $d_{002}$ , aromaticity and coal rank ( $I_{26}/I_{20}$ ) of five Indian coals ranging from sub-bituminous to high volatile bituminous. Very slow step scan X-ray scattering studies have been performed on the demineralized coals and deconvolution has been made on the broad hump in the 2 $\theta$  range of 15–32°. This broad hump is fitted into two Gaussian peaks around 20 and 26° and the  $d$ -spacings are taken as the positions of the  $\gamma$ -band and  $d_{002}$  ( $\pi$ -band) respectively. Heights and areas under these two peaks have been used to determine their relative coal ranks and aromaticity ( $f_a$ ). These parameters have been compared with the elemental carbon and volatile matter content of the coals.

Five coal samples covering the range sub-bituminous to high volatile bituminous, collected from different coalfields, namely Muraidih, Mohuda, Sounda, Sirina and Kamptee of India are coded as MH, MO, SO, SI, and KA. Elemental constituent and volatile matter (VM) content were estimated for the coals on dry ash free (daf) basis (Table 1). All coal samples were chemically demineralized to avoid the effect of mineral matter in the diffractogram. Effect of very low content of mineral matter in the demineralized coal is neglected and the effect of heteroatom is insignificant<sup>17</sup>.

Ten grams of each powdered (72 mesh) coal was demineralized by dispersing in 60 ml of conc. HCl solution

**Table 1.** Compositional analysis of coals

	Ultimate analysis (dry ash free basis, %)				
	C	H	N	O by diff	S
MH	92.8	3.5	1.8	1.4	0.5
MO	87.8	5.1	2.4	4.3	0.4
SO	79.2	5.1	2.2	12.7	0.8
SI	75.0	4.4	1.7	16.5	2.4
KA	73.6	4.1	1.8	20.0	0.5

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(36.5 wt%) and stirred for 3 h at 60°C in a water bath. Then the coal was filtered and washed with distilled water. The HCl-treated coal samples were then mixed with 60 ml of conc. HF (48 wt%) and stirred for 3 h at the same temperature. Finally, the treated coals were washed with hot distilled water to remove HF and dried in an air-oven at 100°C. Weight loss was then checked to see that demineralization had occurred to at least less than 1% effective mineral matter.

A D-8 ADVANCE (Bruker AXS, Germany) X-ray diffractometer was used to collect X-ray intensities of the demineralized coals in the  $2\theta$  range of 10–115° with Bragg–Brentano geometry using parallel beam  $\text{CuK}\alpha$  (40 kV, 40 mA) radiation. Zero background sample holder was used for coal sample loading and the scan was made in locked couple, step scan mode (0.1°/step) with 6 s at each step.

A Windows NT™-based Diffrac Plus Profile fitting software (M/s Bruker AXS, Germany) was used for deconvolution of the diffractograms in the  $2\theta$  region of 15–32°. This software is used to obtain line positions, intensities, widths and shapes from both resolved and unresolved XRD spectra using least square refinement technique. To get rid of the systematic error related to the least square fitting for the peak positions and intensities, alignment of the X-ray diffractometer was checked before every scan by running standard quartz specimen. The  $2\theta$  scan was refined with  $K_{\alpha 1}$  and  $K_{\alpha 2}$  doublet and the  $K_{\alpha 2}/K_{\alpha 1}$  relative intensity. The least square algorithm refines the background intensities and peak intensities, positions and widths. Two symmetrical Gaussian peaks were fitted to corroborate the  $\pi$ -band and  $\gamma$ -band. Initial guess values for the peak positions and half width were chosen and the profile was fitted. Goodness-of-fit was measured by minimizing four statistical parameters, namely reliability (R), reliability index (RI), Weighted reliability (WR) and theoretical reliability (TR) by several trials. They are expressed as

$$R = 100\% \sqrt{\frac{\sum w(l_o - l_c)^2}{\sum w l_o^2}}, \quad \text{RI} = 100\% \frac{\sum |l_o - l_c|}{\sum l_o},$$

$$\text{RW} = 100\% \frac{\sum \sqrt{w} |l_o - l_c|}{\sum \sqrt{w l_o}}, \quad \text{TR} = 100\% \sqrt{\frac{\sum w l_o}{\sum w l_o^2}},$$

where  $l_o$  and  $l_c$  are observed and calculated intensities and  $w$  is the weighting factor.

A good profile fit is achieved when error values are less than 5% for crystalline materials. In the present study, profile fitting was performed on diffused humps for 170 intensity points and error value could be minimized up to 6.5%, except in one case where error is 4.4%. Considering the nature of the diffractograms, this is the best possible Gaussian fit in the region of study (Figure 1). The minimum error value of 4.4% is achieved for the MH coal, as it has relatively sharper hump in the  $2\theta \sim 15\text{--}32^\circ$  than the other four coals.

Theoretically, the areas under the  $\pi$ - and  $\gamma$ -peaks should be equal to the number of aromatic atoms ( $C_{\text{ar}}$ ) and saturated carbon atoms ( $C_{\text{al}}$ ), respectively<sup>18</sup>. Therefore, the aromaticity ( $f_a$ ) of coal, the ratio of carbon atoms in aliphatic chains vs aromatic rings can be defined as

$$f_a = \frac{C_{\text{ar}}}{C_{\text{ar}} + C_{\text{al}}} = \frac{A_{002}}{A_{002} + A_{\gamma}},$$

where  $A$  is the integrated area under the corresponding peak, and  $C_{\text{al}}$  and  $C_{\text{ar}}$  are the number of aliphatic and aromatic carbon atoms per structure unit respectively. Using this relation,  $f_a$  values for all examined coals have been calculated; however, relative intensity ratio ( $I_{26}/I_{20}$ ) for these two peaks is taken as coal rank. The results have been summarized in Table 2.

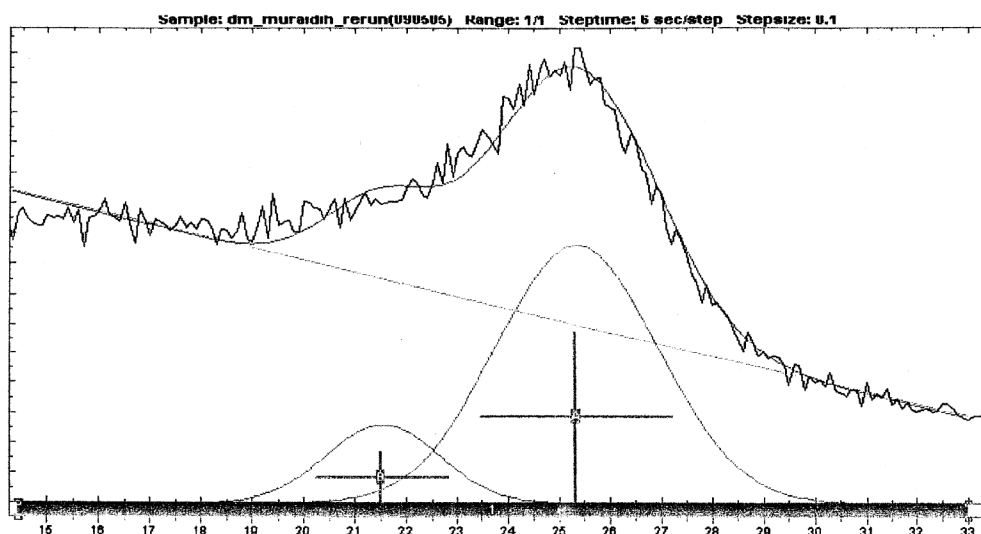


Figure 1. Fitting of two Gaussian peaks for the Muraidih demineralized coal in  $2\theta \sim 15\text{--}32^\circ$ .

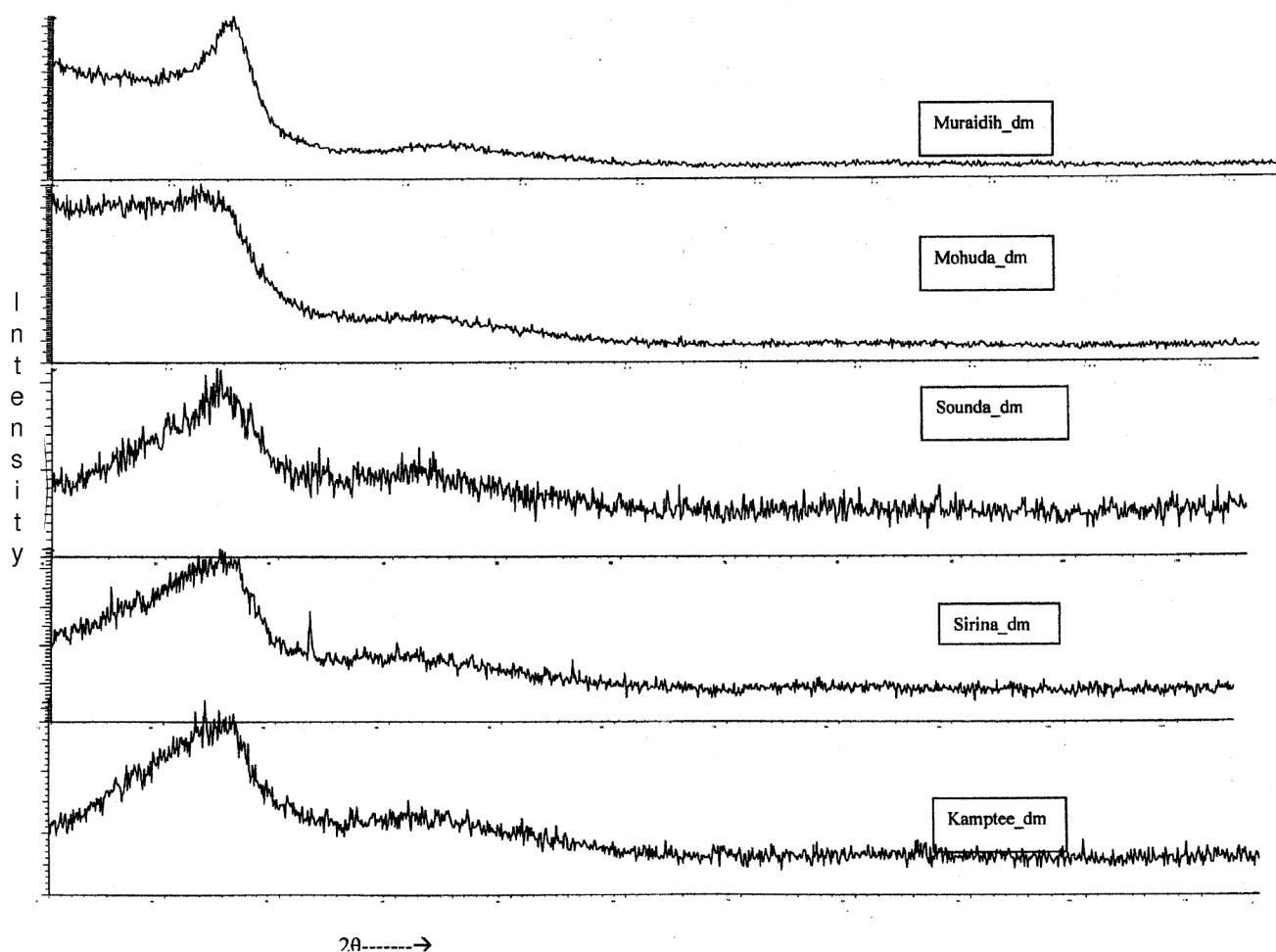


Figure 2. X-ray diffractograms of demineralized coals.

Table 2. Structural parameters extracted from the profile fitting of XRD spectra

Coal type	VM (%)	$d_{002}$ (Å)	$d_{11}$ (Å)	$f_a$	$I_{26}/I_{20}$	$R$ (%)
MH	16.5	3.51	4.13	0.83	3.91	4.4
MO	31.9	3.52	4.17	0.80	3.07	6.0
SO	34.4	3.54	4.45	0.77	2.85	7.9
SI	32.7	3.55	4.20	0.75	2.42	6.5
KA	32.8	3.56	4.29	0.70	2.14	6.5

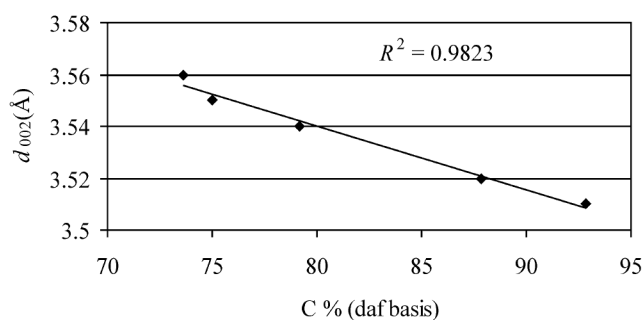


Figure 3. Variation of  $d_{002}$  vs elemental carbon of coals.

A careful study of the diffraction profiles of coals shows the presence of high background intensity (Figure 2) in all the profiles. This is due to the fact that not all carbon atoms are in aromatic structures and a significant amount exists in the form of amorphous carbon. Moreover, all coals contain a clear (002) band and two two-dimensional reflections, (10) and (11). Neither higher order reflections of (00 $l$ ) band nor ( $hkl$ ) reflections are found.

Quantitative comparison has been made for the XRD profile results for the five coals. The  $d_{002}$  has been plotted versus elemental carbon (daf basis) for the coals (Figure 3). It is observed that  $d_{002}$  which ranges from 3.51 to 3.56 Å, decreases with increase in elemental carbon content of the coals and maintains a linear relationship with high correlation coefficient ( $R^2$ : 0.98). It is known that  $d_{002}$  value decreases with increase in coal maturity *vis-à-vis* coal rank<sup>19</sup>. VM values of the demineralized coals have been compared with the  $f_a$ ,  $d_{002}$  and  $I_{26}/I_{20}$  ratio (Table 2). Increase in  $f_a$  is not so prominent for four of the coals with high VM content, but overall it is found to increase with decrease in VM content. This relation is obvious as volatile matter of coals comes from the saturated hydrocar-

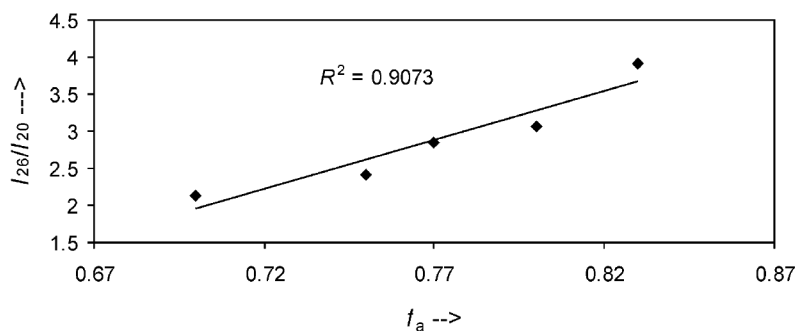


Figure 4. Relation between  $f_a$  and  $I_{26}/I_{20}$ .

bons and hence the decrease of aliphatic side chains increases the aromaticity of coal. A similar relationship exists between VM content and  $d_{002}$  and  $f_a$  values. It is clear from Figure 4 that aromaticity increases with increase in relative ratio of  $I_{26}/I_{20}$  and there is strong linear relationship between  $f_a$  and  $I_{26}/I_{20}$  values ( $R^2$ : 0.91).

Position of the  $\gamma$ -band varies between 4.13 and 4.45 Å and  $d_a$  does not show any correlation to any of the other parameters in this study. Moreover, no earlier researcher has reported any details about the  $\gamma$ -band and established any correlation with other structural parameters of coal.

The present study, aimed towards the determination of X-ray structural parameters of some Indian coals by a semi-quantitative approach, reveals that coal consists of a semi-crystalline turbostratic structure. High background of the diffraction profiles clearly proves that coal has amorphous carbon in its structure. The study reveals that  $d_{002}$  value decreases and  $f_a$  increases with the increase in coal rank, and hence the degree of ordering also increases. This is an initial step towards application of XRD technique to determine X-ray structural parameters of Indian coals. Further studies are in progress on several other Indian coals of varied rank and geological occurrences to determine X-ray structural parameters *vis-à-vis* molecular level understanding of Indian coals.

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