

X-ray diffraction studies of some structurally modified Indian coals and their correlation with petrographic parameters

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In order to study the X-ray structural parameters, five coals have been chosen from different coal basins of India. These coals have been demineralized by standard HF + HCl treatment and treated with nitric acid in aqueous and glacial acetic acid media. X-ray diffraction (XRD) patterns of the samples are recorded using a slow step scan (2 s/step) over an angular range $2\theta \sim 10\text{--}90^\circ$. TOPAS software has been used to determine the structural parameters like inter-layer spacing (d_{002}), crystallite size (L_c), aromaticity (f_a) and average number of aromatic layers (N_c). The structural parameters have been correlated with chemical as well as petrographic parameters of coals. Mean random reflectance (MR_r) of the studied coals varies between 0.44% and 0.54% and the vitrinite, liptinite and inertinite contents vary between 17.8% and 66.4%, 9.2% and 20.3% and 20.7% and 62.9% respectively. Nitration in both the media has increased d_{002} values. This study also shows that d_{002} and f_a values are dependent on the rank of the coal, rather than only the carbon content (C_{dmf} , dry mineral free basis). XRD rank parameter values have been directly correlated with the petrographic rank parameters. Nitration in both the media has induced similar kind of effect on individual macerals. Behaviour of the macerals to chemical treatment is also reported in this study.

Keywords: Coal, maceral, nitration, rank, XRD parameters.

COAL, a naturally occurring combustible solid, is one of the most important and abundant energy resources. It consists of organic and inorganic constituents.

Maceral groups like vitrinite, liptinite, inertinite constitute the organic part and the inorganic part consists mainly of mineral matter. Chemically, the macromolecular matrix of coal is essentially constituted of carbon, hydrogen, oxygen and relatively small proportions of nitrogen, sulphur and phosphorus¹. Due to immense heterogeneity and complex nature of coal, many structural models have been proposed². Coal is assumed to consist of a

large polymeric matrix of aromatic structure called the coal macromolecules. The macromolecule network consists of clusters of aromatic carbon that are linked to other aromatic structures mostly by aliphatic molecules; but may also include other atoms, such as oxygen, nitrogen, sulphur and phosphorus. There are other attachments to the aromatic clusters which do not form bridges. These attachments are referred to as side chains and are mainly aliphatic in nature^{3,4}. Several instrumental techniques like TEM^{5,6}, FTIR⁷, Raman spectroscopy⁸ and NMR⁹ have been used for evolving the structural models during last several decades. Moreover, coal has been used for the synthesis of several carbon-derived materials like activated carbon and humic acid and for this different kinds of structural modifications of coal (SMS) have been carried out using several methods like nitric acid treatment in acetic anhydride medium or in aqueous medium ($\sim 100^\circ\text{C}$)^{10,11}. These kinds of treatments of coals completely reorganize their spatial and chemical structures and transform them into coal-derived substances called SMCs.

The role of X-ray diffraction (XRD) is important in coal science. Initially, it was directed towards measuring the mineral matter/ash in coal. XRD analysis is a fundamental method used for evaluating carbon stacking structure. The degree of graphitization, the interlayer spacing (d_{002}), and the crystallite size (L_c) have been established as the parameters for evaluating the stacking structure of highly crystalline carbon materials^{12,13}. Using the same principle, parameters for macromolecular structure of coal are also determined by XRD, and the existence of crystallites in coal structure has been proved by the appearances of peaks corresponding to the (002), (100) and (110) reflections of graphite¹⁴.

Slow step scan XRD, 2 s/step and $0.02^\circ/\text{step}$, is used for obtaining higher resolution of diffractograms¹³. The carbon-related peaks around $20\text{--}26^\circ$ can be categorized into π (002-band) and γ bands for aromatic and aliphatic chains respectively. The π -band due to aromatic ring stacking occurs near 26° , while γ -bands (d_γ) around 20° , are believed to be derived from aliphatic chains.

X-ray structural parameters of coal are dependent on coal petrology¹⁵. The differential contents of coal maceral

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Table 1. Existing scheme of correlation of the Gondwana Formations²³

Cretaceous	Lower	Damodar-Koel valley	Rajmahal	Mahanadi	Son	Satpura	Godavari		
						Bansa bed	Jabalpur		Chikiala/ Gangapur
Jurassic	Upper	Dubrajpur							
	Middle					<i>Bagra</i>			
	Lower				Bandhavgarh		Kota		
	<i>Parsora</i>								
Triassic	Upper	SupraPanchet		Kamthi	<i>Tiki</i>		Dharmaram	Maleri Group	
	Middle						Denwa		Bhimaram Yerrapalli
	Lower	Panchet				Pali	Panchmarhi		<i>Upper Kamthi</i> Middle Kamthi
Permian	Upper	Raniganj		Raniganj	Raniganj	Bijuri	Lower Kamthi	Barakar Kamthi Group	
		Barren Measures		Barren Measures	Barren Measures	Motur	Barren Measures ? ? ?		
	Lower	Barakar	Barakar	Barakar	Barakar	Barakar	Barakar		
		Talchir	Talchir	Talchir	Talchir	Talchir	Talchir		

like vitrinite, liptinite, inertinite have a direct influence on the nature of the XRD pattern. Coal petrographic data are one of the important parameters to study the rank and maceral analysis provides detailed organic as well as inorganic association in coal. Gondwana sequences are the major resources of Indian coals. These coals were deposited in intra-cratonic basins and vary widely in their petrographic make-up and rank. It needs to be mentioned here that although many research publications are available for foreign coals, very few publications are available on XRD studies of Indian coals. In 1942, Dhar and Niyogi¹⁶ studied the XRD structural parameters of macerals of Indian coals. During the late sixties of the last century, Chandy¹⁷ performed X-ray studies of macerals and reported that the position of d_{002} band of vitrinite varied from 3.5 to 3.6 Å in the analysed samples. Recently, a few more studies have been carried out on Indian coals¹⁸⁻²¹. In this article, five coals are chosen from different coalfields of India, viz. Belpahar and Hingula coals from Ib and Talcher valleys respectively, of the Mahanadi basin, Odisha; Baranj from Wardha valley, Maharashtra; Jambad from Raniganj, West-Bengal, and Usha from Mand-Raigarh Coalfield, Chhattisgarh for the study of X-ray structural parameters using wide angle X-ray

scattering. Structural modifications have been carried out by nitric acid treatment in glacial acetic acid and in aqueous media²⁰. An attempt has been made to correlate the structural parameters of coals and their nitric acid-treated products with chemical as well as petrographic constituents of these coals.

Geological settings

Gondwana Group of the Indian Peninsula comprises a continuous sequence starting with a glacial unit at the base and red-bed facies rocks at the top²². The sediments are essentially terrigenous; occasionally thin marine horizons may be intercalated. The main lithologies are tillite/tillite, sandstone, argillaceous and carbonaceous shale and coal. A type sequence of geological formations is shown in Table 1 (ref. 23). Gondwana sedimentation occurred in rift valleys. While older sedimentary rocks of Talchir Formation have restricted development, extensive and thick deposition of coal-bearing sequence of Barakars occurred. A brief description of each basin from where the coals for the present study have been obtained is given in the following paragraphs and their locations are shown in Figure 1.

Talchir basin (Hingula (HIN) coal)

This Talchir basin constitutes the southeastern most part of the Gondwana Mahanadi Master basin and lies between lat. $20^{\circ}50'$ – $21^{\circ}15'N$ and long. $84^{\circ}09'$ – $85^{\circ}33'E$. It covers an area of about 1800 sq. km. The Palaeozoic (Lower Gondwana) basin occupies most of the area of the coalfield, whereas about 110 sq. km is occupied by the Mesozoic Middle Godwana (Triassic) sediments. The basin mainly occupies the Brahmani River valley in Dhenkanal and Angul districts, along with a small portion of the adjoining Sambalpur district, Odisha.

Wardha Valley basin (Baranj (BAR) coal)

The Wardha Coalfields are situated in the valley of Wardha River, between lat. $19^{\circ}30'$ – $20^{\circ}27'N$ and long. $78^{\circ}50'$ – $79^{\circ}45'E$ mainly in Chandrapur district. The coalfields extend in NW–SE direction over a distance of 115 km and an area of about 4130 sq. km. The main coal seam is confined to the Barakar Formation and has attained thickness of 17–20 m.

Raniganj coalfield (Jambad (JAM) coal)

This is the easternmost field of the Damodar Valley basin and is situated between lat. $23^{\circ}33'$ – $23^{\circ}52'N$ and long.

$86^{\circ}38'$ – $87^{\circ}20'E$ mainly in Burdwan district, West Bengal. It covers an area about 1550 sq. km of proved coal-bearing strata. The area is surrounded on three sides by Precambrian rock formations, but on the east, pass beneath alluvium and laterites²⁴.

Ib River basin (Belpahar (BEL) coal)

The Ib River basin is located in the southeastern part of the NW–SE trending Mahanadi master basin between lat. $21^{\circ}30'$ – $22^{\circ}14'N$ and long. $83^{\circ}32'$ – $84^{\circ}10'E$. It is named after a tributary of the Mahanadi. It embraces the Hingir sub-basin in the north and Rampur sub-basin in the south. The basin covers parts of Sundargarh, Jharsuguda and Sambalpur districts of Odisha.

Satpura basin (Usha (USH) coal)

The Satpura basin is the westernmost part of Gondwana basins exposed in the peninsular region²⁵. It is unique among all the Indian Gondwana basins in having the longest range of stratigraphic record spanning from Permian to Cretaceous²⁶. Being situated between lat. $23^{\circ}05'$ – $23^{\circ}35'N$ and long. $81^{\circ}15'$ – $83^{\circ}00'E$, it covers an area of about 4330 sq. km. It is also the largest lower Gondwana Coal Basin in India. The coalfields are partly situated in Shahdol and partly in Surguja districts of Madhya Pradesh and Chhattisgarh respectively. This basin is divided into a large number of coalfields, viz. Sohagpur, Jhagrakhand, Sonhat, Mand–Raigarh, Jhilimili, etc. Geologically all of these form a part of the continuous tracts of Barakars.

Experiments

The coals were collected from different coalfields of India following Indian Standards (IS) and were powdered ($<212\ \mu\text{m}$) for different types of treatment and analysis²⁷. Ten grams of each powdered coal sample was chemically demineralized using conventional HF + HCl acid treatment to avoid the effect of mineral matter in the XRD pattern^{18,20}. The minerals which have been leached out from these coals during demineralization are quartz (SiO_2), kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] and siderite (FeCO_3). The demineralized coals are designated as HIN (R), BAR (R), JAM (R), BEL (R) and USH (R) for the coals from Hingula, Baranj, Jambad, Belpahar and Usha coalfields respectively. Two kinds of nitration treatment were performed on each demineralized coal. In the first, coal was treated with a mixture of glacial acetic acid and concentrated HNO_3 in a 3 : 1 volume ratio and in the second type, coal was treated with 30 wt% HNO_3 in aqueous medium at 105°C in a refluxing condenser²⁰. Two grams of demineralized coal was treated with 10 ml of glacial

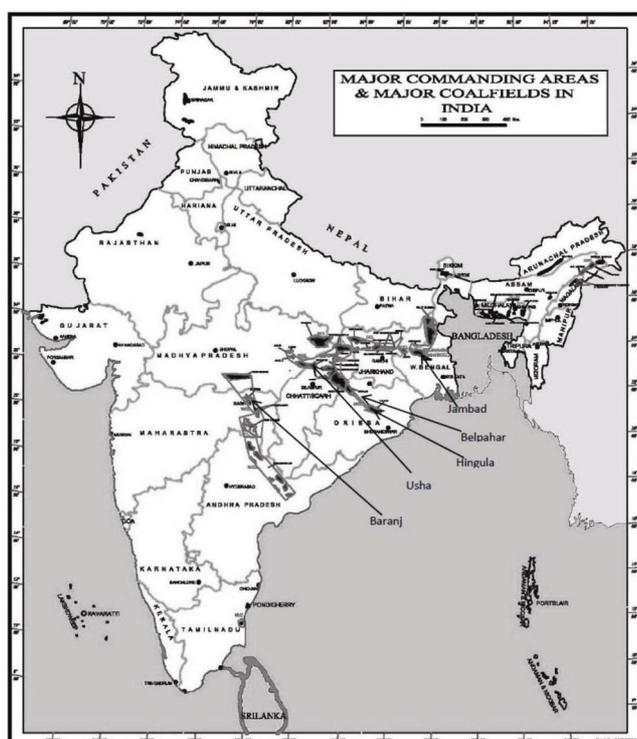


Figure 1. Locations of the coal samples collected in the present study from different coal fields of India.

acetic acid and mixed thoroughly, the flask being kept in a water bath at a temperature 15–20°C, and 3 ml of 68 wt% nitric acid was added to the mixture drop by drop for at least 30 min and was kept for 24 h. The treated mixture was diluted with 250 ml/g distilled water, left for 24 h and washed with distilled water till neutralization (pH ~ 7.0) was attained. After each type of treatment, the coal was dried in an air oven and difference in weight (Δ wt%) was calculated using the formula

$$\Delta \text{ wt}\% = (W_f - W_i)/W_i, \quad (1)$$

where W_f and W_i are the final and initial weight of the coal sample after and before treatment of coal respectively.

In the second treatment, 2.0 g of demineralized coal was treated with 60 ml of 30% nitric acid for a period of 8–10 h or until the end of any gas evolution from the coal–acid mixture. The residue was washed with warm distilled water (~60°C) for removal of any trace of nitric acid, and neutralization was confirmed by the pH test of the wash water. The calculated per cent change in weight is presented in Table 2.

The nitric acid treated coals in aqueous medium are coded with a suffix in bracket '(A)', viz. HIN(A) (i.e. demineralized Hingula coal treated with nitric acid in aqueous medium), and acetic and nitric acid-treated coals are coded with a suffix in bracket '(G)', viz. HIN(G) (i.e. demineralized Hingula coal treated with nitric acid in glacial acetic acid medium).

A D-8 ADVANCE (Bruker AXS, Germany) X-ray diffractometer was used to collect the X-ray intensities of the demineralized and treated coals in the 2θ range 10–90° with Bragg–Brentano geometry, using parallel beam $\text{CuK}\alpha$ (40 kV, 40 mA) radiation. An X-ray amorphous sample holder was used for coal sample loading, and the scan was made in locked couple in step-scan mode (0.02°/step) with 2 s at each step (Figure 2). The software TOPAS 3.0 from Bruker AXS (2005) was used for refinement of π -band and γ -band to determine d_{002} , position of γ -band, area under those bands and the average crystallite size. TOPAS 3.0 uses the fundamental parameter approach (FPA) and is therefore capable of estimating the instrumental influence. The Double–Voigt approach in TOPAS is used with both calculated (FPA) and

measured instrument functions. Employing integral breadth β_i , Stokes and Wilkinson²⁸ have developed a more generalized formula (eq. (2)) of domain-size broadening which is independent of the crystallite shape.

$$\beta_i = \lambda/L_{\text{Vol}}\cos\theta, \quad (2)$$

where λ is the wavelength of the X-ray, L_{Vol} the volume weighted crystallite size and θ the angle of diffraction.

This concept directly leads to a formula identical to the Scherrer equation, except that the constant assumes a value of unity. The semi-crystalline bumps were inserted and refined and then sharper peaks were introduced and refined. Reflections from higher intensities were refined first and smaller reflections were introduced step by step.

Proximate and ultimate analyses of coals have been carried out following IS^{29–32}. The petrographic analyses were performed following ISO^{33,34}. The maceral composition and reflectance measurements were carried out using Leitz MPV and compact Leica DMRX-P (HC) microscopes with the attached Leica QWin and msp-200 software.

Results and discussion

Proximate, ultimate and petrographic analyses of coals

The results of proximate, ultimate and petrographic analyses are shown in Table 3. Volatile matter (VM) of coals varies between 37.9% and 44.7% and fixed carbon between 55.3% and 62.1%. C_{dmf} varies from 76.51% to 84.04% and MR_r from 0.44% to 0.54%, which suggests that the coals are of low rank. VM content is a combined effect of type and content of macerals present in the coal. VM is highest in liptinite followed by vitrinite and inertinite content for the same rank of coal³⁵. VM can be successfully approximated for carboniferous coals from the petrographic compositions^{36,37}. However, Ghose *et al.*³⁸ proposed a different formula for estimation of VM for Indian coals. They used huge amounts of analytical data for VM concentration and plotted them against the respective reflectance of individual macerals and derived from following equation

$$\text{VM}_C = \frac{V \times \text{VM}_V + L \times \text{VM}_L + I \times \text{VM}_I}{100}, \quad (3)$$

where VM_C is the volatile matter of whole coal; V the percentage of vitrinite; L , the percentage of liptinite and I the percentage of inertinite; VM_V the volatile matter of vitrinite; VM_L the volatile matter of liptinite; and VM_I the volatile matter of inertinite. The volatile matter of the present coal samples has been calculated using the formula given by Ghose *et al.*³⁸ and is well in accordance with the analysed VM through proximate analysis.

Table 2. Changes in wt% after nitration

	G. Ac. + HNO ₃ wt% change	Aq. HNO ₃ wt% change
Hingula	5.34	-73.93
Baranj	8.26	-49.16
Jambad	7.00	-29.13
Belpahar	7.71	-31.12
Usha	14.81	-33.97

G. Ac., Glacial acetic acid; Aq, Aqueous.

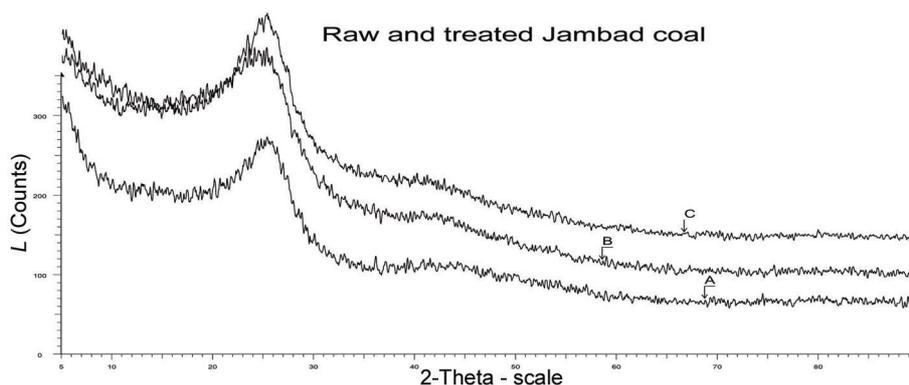


Figure 2. (A) Raw coal, (B) nitration in glacial acetic medium, and (C) nitration in aqueous medium.

Table 3. Proximate, ultimate and petrographic analyses of coals

	Proximate analysis (wt% dmf basis)				Ultimate analysis				Maceral analysis (vol%) (mineral matter free basis)			
	VM	FC	C	H	S	N	O	H/C	Vitrinite	Liptinite	Inertinite	MR _r (%)
Hingula	44.7	55.3	76.51	5.93	0.87	1.67	15.02	0.92	66.4	12.9	20.7	0.45
Baranj	37.9	62.1	81.9	4.9	2.25	1.84	9.11	0.71	33.6	14.1	52.3	0.47
Jambad	39.4	60.6	82.3	4.64	0.69	1.78	10.59	0.67	62.2	9.2	28.6	0.54
Belpahar	41.6	58.4	82.87	5.32	0.67	1.65	9.49	0.76	17.8	19.3	62.9	0.44
Usha	38.7	61.3	84.04	4.65	0.83	1.51	8.97	0.66	26.7	20.3	53	0.48

VM, Volatile matter; FC, Fixed carbon; C, Carbon; H, Hydrogen; S, Sulphur; N, Nitrogen; O, Oxygen; dmf, Dry mineral matter free basis.

Microscopic study of the coals reveals that MR_r, measured on vitrinite grains in oil immersion medium varies from 0.44% to 0.54% (Table 3). Table 3 shows that vitrinite content varies between 17.8% and 66.4%, liptinite varies between 9.2% and 20.3%, and inertinite varies between 20.7% and 62.9%. Photomicrographs of some of the macerals are shown in Figure 3. Though H₂ content of coals is said to be proportional to liptinite content, this relation is not obvious in the coals studied here. This may be due to the fact that some of the liptinites may be enveloped by gello-vitrinite.

XRD analysis

XRD analysis of coal samples exhibits high background values indicating amorphous carbon of highly disordered materials. In addition, the coals also contain some crystalline carbon corresponding to (002) plane (π -band) around 26° and (110) plane near 20° (γ -band). The spectrum was corrected for polarization³⁹. Further quantitative analysis is based on this profile rather than the observed one. The profile fitting of demineralized Jambad coal is shown in Figure 4. Theoretically, d_{002} peaks are symmetrical, but the presence of asymmetrical curve from XRD analyses confirms that another peak due to the γ -band exists. Hence, two symmetrical Gaussian peaks corresponding to π (002 bands) and γ -bands were fitted respectively.

Neither higher-order reflection of (00 l) nor (hkl) reflections were found. In the above profile-fitting neither hetero atoms nor mineral matter was considered, as the effect of mineral matter present is negligible (less than 2%).

The areas under the π - and γ -bands indicate the relative proportion of aromatic atoms (C_{ar}) and saturated carbon atoms (C_{al}) respectively. The aromaticity (f_a) of coals is measured by the following equation

$$f_a = C_{ar} / (C_{ar} + C_{al}) = A_{\pi} / (A_{\pi} + A_{\gamma}), \quad (4)$$

where A denotes the integrated area under the corresponding peak and C_{al} and C_{ar} are the number of aliphatic and aromatic carbon atoms per structure unit respectively. The average number of aromatic layers in the stacking structure, N_c , was estimated by means of the following equation

$$N_c = L_c / d_{002}. \quad (5)$$

The rank of coal is determined from the peak intensities at positions 26° and 20° by

$$\text{Coal rank} = I_{26} / I_{20}. \quad (6)$$

Based on experiments and using eqs (2)–(6), the values of d_{002} , L_c , f_a , N_c and d_{γ} were calculated for demineralized raw and treated coals (Table 4).

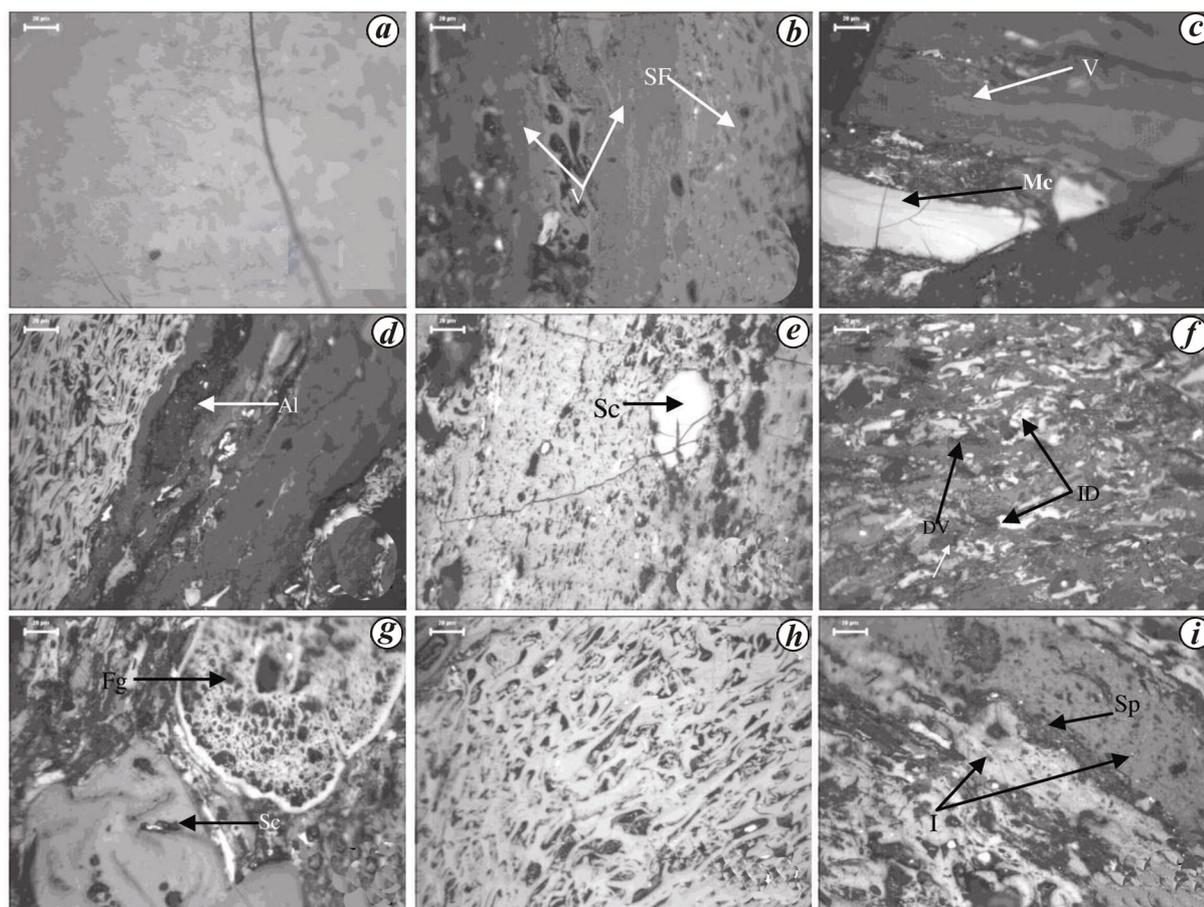


Figure 3. *a*, Collotelinite of Jambad coal; *b*, Vitrinite (V) and semifusinite (SF) of Belpahar coal; *c*, Vitrinite, macrinite (Mc) and mineral matter of Hingula coal; *d*, Algal mat (Al) in trimacerite of Jambad coal; *e*, Secretinite (Sc) in semifusinite of Usha coal; *f*, Inertodetrinite (ID) and detrovitrinite (DV) of Belpahar coal; *g*, Funginite (Fg) and secretinite (Sc) of Hingula coal; *h*, Fusinite of Usha coal; *i*, Reflectance of inertinite (I) and sporinite (Sp) of Baranj coal. All photomicrographs taken on polished section under oil immersion, $\times 500$ (scale bar $\sim 20 \mu\text{m}$).

The variation of d_{002} values with respect C_{dmf} are shown in Figure 5 *a–c*. The d_{002} values varies from 3.521 to 3.490 Å for demineralized raw coals [$d_{002}(\text{R})$]; 3.579 to 3.497 Å for nitric acid-treated coals in glacial acetic acid medium [$d_{002}(\text{G})$], and 3.526 to 3.493 Å for coals treated in aqueous nitric acid medium [$d_{002}(\text{A})$]. The variation vis-à-vis the nature of the graphs is similar for the plotting of d_{002} values against C_{dmf} . Among the five coals in the present study, Jambad has the highest rank parameter value ($\text{MR}_r \sim 0.54\%$) though its C_{dmf} is not maximum (Table 3). More structural ordering of the coal moieties leads to increase in the maturity of coal vis-à-vis vitrinite reflectance. This kind of increase of structural ordering of coal simultaneously decreases the d_{002} value. Hence, there is a sharp fall in the d_{002} value (Figure 5 *a*) in the C_{dmf} versus d_{002} plot. Similar trend is also observed for the chemically modified coals (Figure 5 *b* and *c*). Though the C_{dmf} value of Belpahar coal is higher than that of Hingula, Baranj and Jambad coals, still its rank parameter ($\text{MR}_r \sim 0.44\%$) is lowest and its d_{002} value is relatively higher (3.502 Å), which clearly confirms the fact that d_{002}

values are more dependent on the rank of the coal, rather than C_{dmf} .

The d_{002} values of coals treated with nitric acid both in glacial acetic acid and aqueous media are larger, with the only exception of Usha coal, where d_{002} value decreased in aqueous medium than in the raw coal. In general, nitric acid treatment in aqueous medium leads to oxidation as well as nitration, and improves the structural ordering, leading to decrease in the d_{002} values. However, the present study shows that the d_{002} values have increased, except in Usha coal. This may be due to the fact that nitration is the predominant phenomenon in both glacial acetic acid and aqueous media. This study shows that nitration in aqueous medium is dependent on C_{dmf} rather than the rank of the coal. Nitration has affected both aliphatic and polyaromatic hydrocarbon (PAHC) groups, which obviously leads to lowering of structural ordering of the coals having C_{dmf} less than 84.04%.

The crystallite size of the raw coals [$L_c(\text{R})$] varies from 16 to 22 Å and is plotted against C_{dmf} (Figure 6 *a*). Jambad coal is the highest ranked coal and it has the

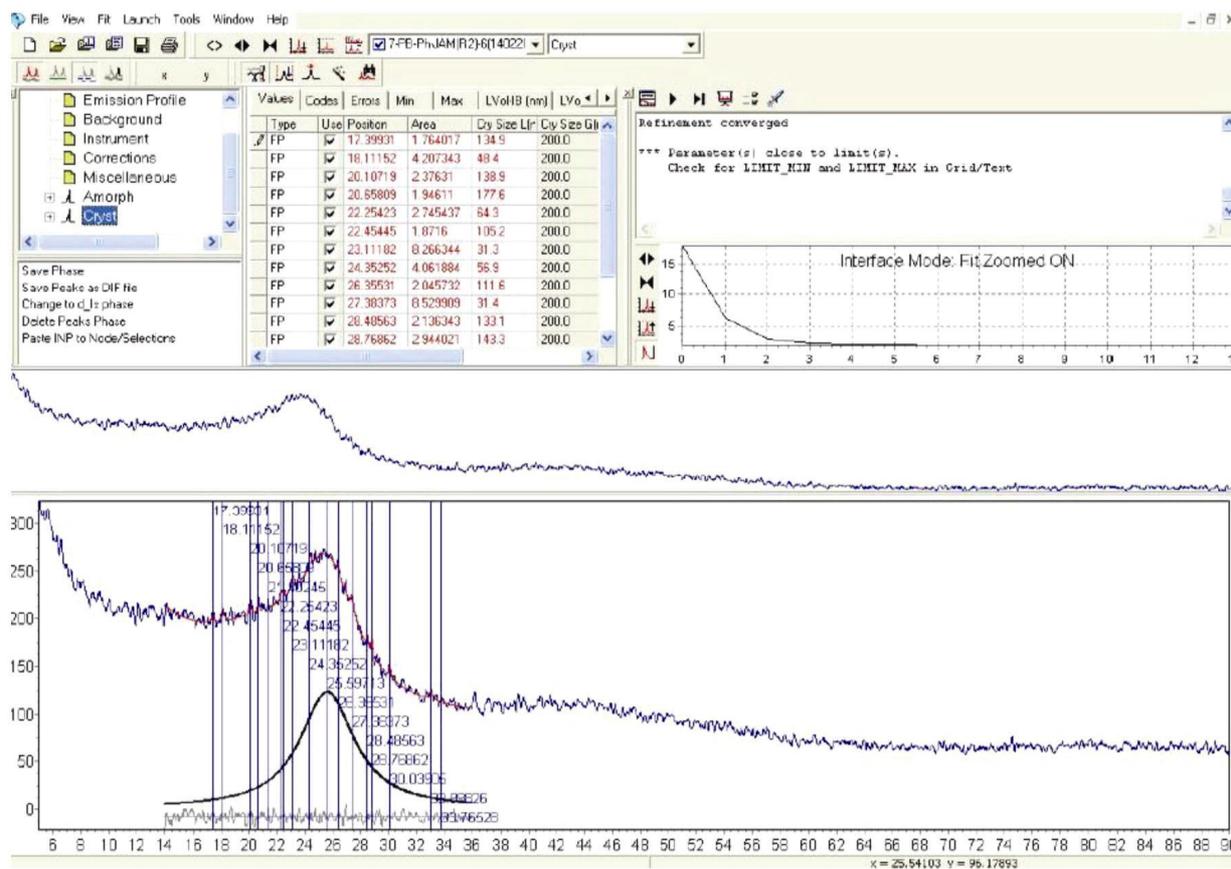


Figure 4. Profile fitting of the Jambad coal using TOPAS software.

Table 4. Values of d_{002} , L_c , f_a , N_c , I_{26}/I_{20} and d_y for the raw and treated coals

	d_{002} (Å)	L_c (Å)	f_a	N_c	I_{26}/I_{20}	d_y (Å)
Hin (R)	3.521	16	0.30	4.54	1.09	4.567
Bar (R)	3.517	17	0.37	4.83	1.20	4.392
Jam (R)	3.490	22	0.61	6.30	2.82	4.191
Bel (R)	3.502	20	0.31	5.71	1.04	4.340
Ush (R)	3.501	21	0.38	5.99	1.43	4.646
Hin (G)	3.579	13	0.39	3.63	0.88	4.519
Bar (G)	3.549	16	0.41	4.51	1.13	4.387
Jam (G)	3.497	17	0.43	4.86	1.46	4.201
Bel (G)	3.546	18	0.40	5.08	1.24	4.648
Ush (G)	3.526	21	0.42	5.96	1.14	4.087
Hin (A)	3.526	19	0.57	5.39	2.03	4.118
Bar (A)	3.526	17	0.63	4.82	2.47	4.201
Jam (A)	3.493	20	0.66	5.73	3.17	4.161
Bel (A)	3.508	19	0.56	5.42	2.77	4.184
Ush (A)	3.495	20	0.62	5.72	2.81	4.097

largest L_c value of 22 Å. Though the values of crystallite size [$L_c(G)$] of the coals treated in glacial acetic acid medium (Figure 6 b), increased gradually with increase in carbon content, the values decreased in comparison to

that of demineralized raw coals, except in the Usha coal where L_c values remained unchanged. This is due to structural disordering and the inclusion of additional heteroatoms such as nitro group and oxygen due to nitration

of coal matrix. The present study does not signify any correlation between $[L_c(A)]$ values and C_{dmf} nitric acid-treated coals in aqueous medium (Figure 6c).

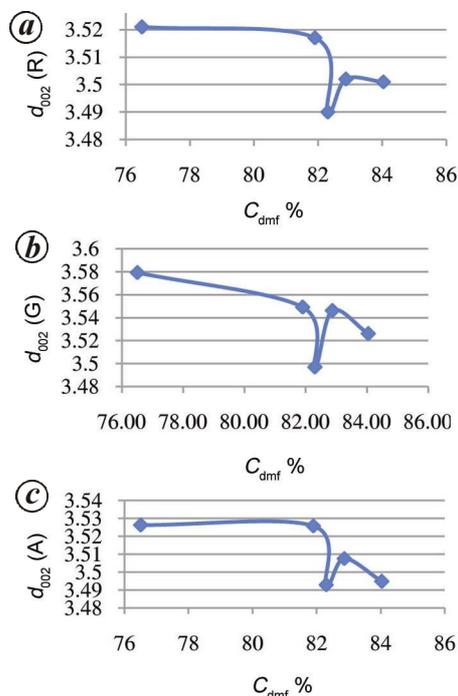


Figure 5. Variation of d_{002} with respect to C_{dmf} %: *a*, [$d_{002}(R)$]; *b*, [$d_{002}(G)$]; *c*, [$d_{002}(A)$].

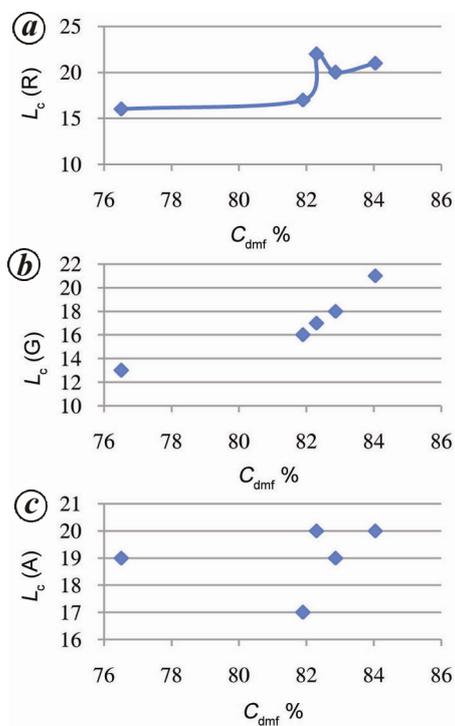


Figure 6. Variation of L_c with respect to C_{dmf} %: *a*, [$L_c(R)$]; *b*, [$L_c(G)$]; *c*, [$L_c(A)$].

The aromaticity (f_a), increased with increase in petrographic rank (MR_r ; Figure 7). With the increase of petrographic rank, the aliphatic content decreases which results in the increase in aromaticity of the coal. XRD study also corroborates this fact. However, a plot of f_a against C_{dmf} (Figure 8a-c), does not show a simple increasing trend, but sharp increase in f_a value is observed

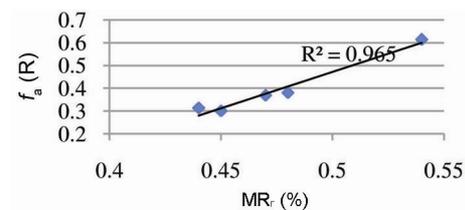


Figure 7. Relation of petrographic rank MR_r and $f_a(R)$ of demineralized raw coals.

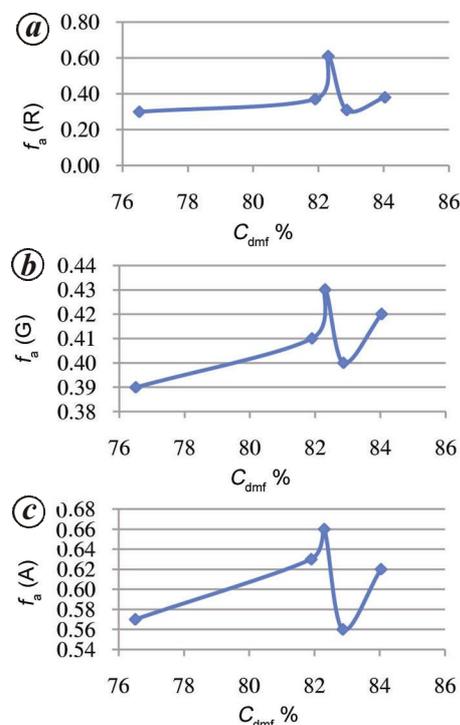


Figure 8. Variation of f_a with respect to C_{dmf} %: *a*, [$f_a(R)$]; *b*, [$f_a(G)$]; *c*, [$f_a(A)$].

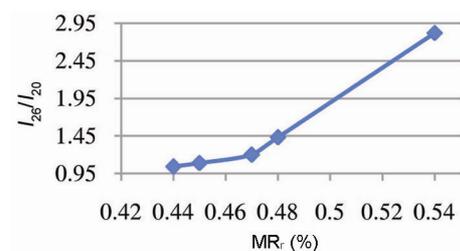


Figure 9. Variation of I_{26}/I_{20} with respect to MR_r (%) for demineralized raw coals.

for Jambad coal for raw as well as treated coals. This signifies the fact that f_a is a parameter dependent more on maturity of the coal rather than C_{dmf} . The nature of all three graphs is similar.

Nitric acid treatment in glacial acetic acid and water media has increased the aromaticity values of the coals with the exception of Jambad coal, which shows that f_a value has decreased in glacial acetic acid medium. This study clearly shows that rank of coal is the most important parameter for chemical treatments. It also signifies that nitration in mild condition such as in glacial acetic acid medium, removes the aliphatic side chains, consequently leading to increase in the aromaticity. As the Jambad coal is of the highest rank, its aromaticity has not increased in the glacial acetic acid medium, rather it has

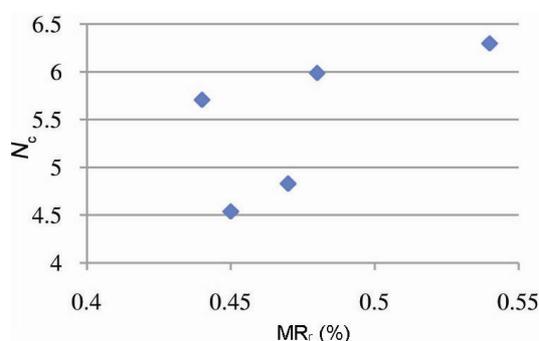


Figure 10. Variation of N_c with respect to MR_r (%) for demineralized raw coals.

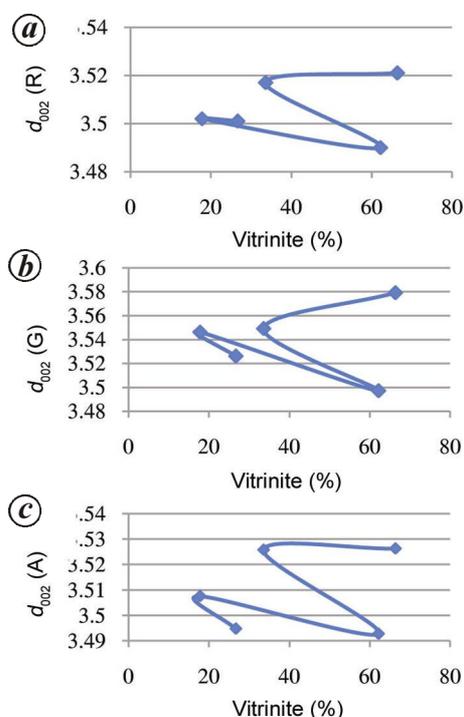


Figure 11. Variation of d_{002} with respect to vitrinite percentage: *a*, [$d_{002}(R)$]; *b*, [$d_{002}(G)$]; *c*, [$d_{002}(A)$].

decreased due to predominance of nitration phenomenon in the aliphatic side chains.

In Figure 9, rank of the raw coals as determined from XRD analysis I_{26}/I_{20} (Table 3) is plotted against rank

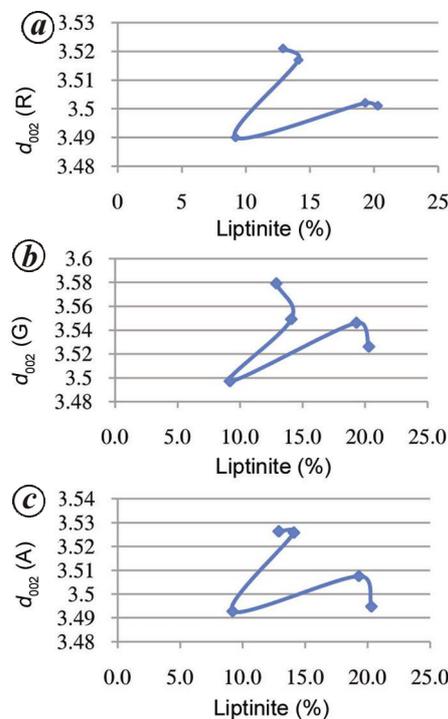


Figure 12. Variation of d_{002} with respect to liptinite percentage: *a*, [$d_{002}(R)$]; *b*, [$d_{002}(G)$]; *c*, [$d_{002}(A)$].

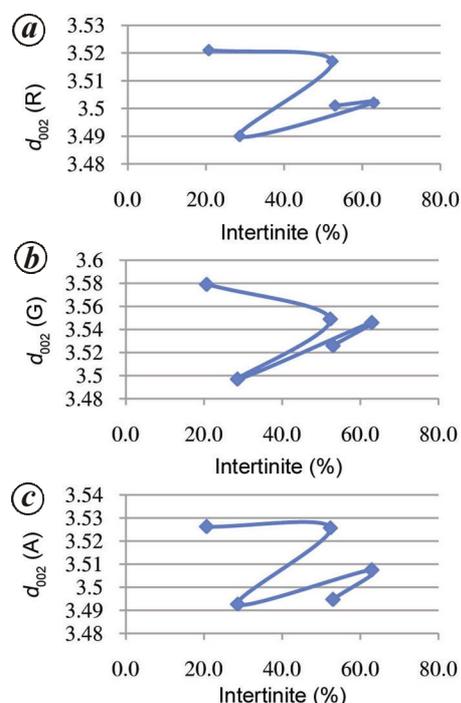


Figure 13. Variation of d_{002} with respect to inertinite percentage: *a*, [$d_{002}(R)$]; *b*, [$d_{002}(G)$]; *c*, [$d_{002}(A)$].

parameter values (MR_r) determined from petrographic analysis. This plot shows coherent relationship between the two parameters. The study shows that XRD can be used as a quick tool to determine the rank of coals. In Figure 10, the average number of aromatic layers in the stacking structure N_c , is plotted against MR_r . For raw coals, it shows that number of stacking layers increases with the rank of the coal. Only Belpahar coal deviates from this relation, as it shows slightly higher value of N_c with respect to MR_r . It is also further noted that the Hingula coal has the highest d_{002} and H/C ratio and Usha coal has the least H/C (0.67) ratio (Tables 2 and 3).

The petrographic characteristic of coal is dependent on the combination of its major macerals constituents, namely vitrinite, liptinite and inertinite. Each maceral has been plotted against the d_{002} values for raw and treated coals. Hingula coal with vitrinite content of 66.4% and Jambad coal with 62.2% vitrinite show the highest and the lowest d_{002} values both in raw and nitric acid treated conditions respectively (Figure 11 a–c). Lowest d_{002} values are recorded for Jambad coal with 9.2% liptinite and 28.6% inertinite (Figures 12 a–c and 13 a–c). The nature of the graphs is similar with respect to the individual macerals. This signify the fact that independently vitrinite, inertinite and liptinite responded similarly to the nitration treatment both in acetic acid and aqueous media.

Tamarkina *et al.*¹¹ prepared SMCs by acetic anhydrite treatment. In the present study structural modifications of coal were carried out by nitric acid in glacial acetic acid and aqueous media¹¹. The present study shows that structural modifications are more dependent on rank parameter rather than only the C_{dmf} (%), as coal rank is a function of structural compaction vis-à-vis maturity. Hence X-ray structural parameters of coal in the present study could not be directly compared with C_{dmf} (%).

Conclusion

X-ray structural parameters of Indian coals and their structural modifications through nitric acid treatment in acetic acid and aqueous media show that the changes in the structural parameters and the aromaticity of the treated coals are dependent upon coal rank and the medium of treatment. In general, weight increase is observed in acetic acid medium due to significant nitration simultaneously with oxidation of the coal matrix removing the aliphatic side chains. Thus the loss of aliphatic side chains increases the relative content of aromatic moieties leading to the relative increase of aromaticity. However, the d_{002} values in nitric acid-treated coals have increased with respect to the raw coals signifying the fact that treated coals are getting a more disordered structure. A significant observation in the present study is that nitration in a milder medium like glacial acetic acid is capable of removing the aliphatic side chains from the

coals. The highest ranked Jambad coal among the coals studied was the only exception. The significant weight loss occurred in low-rank coal due to the predominance of the oxidation phenomenon in aqueous medium which removed the aliphatic side chains. In aqueous medium, nitration occurred simultaneously with oxidation of the aliphatic side chains. An important observation of the present study is the behaviour of macerals like vitrinite, inertinite and liptinite to nitric acid treatment. The nature of variation of d_{002} values for the macerals is similar irrespective to the nature of the medium of treatment. X-ray structural parameters are more dependent on coal rank than C_{dmf} .

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