ABSTRACT: The detailed investigation of the chemical structure of vitrinite-rich Karharbari coal was performed utilizing advanced analytical techniques. The salient objective of this work is the evaluation of various structural properties of coal, which is necessary for identifying the chemical and physical interactions between coal and various reactants during its utilization. Karharbari coal is a poorly organized coal with high aromatic content. The value of corrected aromaticity ($f_a'$) was found to be 0.82 by 13C NMR spectroscopy and was also confirmed by XRD (aromaticity = 0.84) and FT-IR analysis (aromaticity = 0.82). The average molecular weight of the aromatic cluster was found to be 507 amu by the NMR result, which is closer to the result obtained by HRTEM (MW = 530 amu). The structural and lattice parameters of Karharbari coal were obtained by NMR spectroscopy and then compared with the similar rank Argonne Premium coal. The molecular weight distribution was obtained by LD-TOF-MS and compared with HRTEM fringe model analysis. The presence of different heteroatoms like carbon, oxygen, nitrogen, and sulfur with their functionalities was determined by using the XPS technique. Different carbon/oxygen functionalities present in the Karharbari coal were found to be (C−C) and (C−H) 68.5%, (C−O) 23.4%, (COO−) 1.9%, and (C=O) 6.0%. Nitrogen functionalities such as pyridine, pyrrolic, quaternary, and oxidized nitrogen and their compositions (mol %) were 19.3, 45.6, 31.2, and 3.7%, respectively. Different forms of sulfur were also found to be present, namely, thiophenes, sulfones, sulfuric acid, and sulfates with the molar contents of 16.4, 41.6, 21.3, and 20.5%, respectively. This information will be useful in improvising coal utilization techniques.

1. INTRODUCTION

Coal is a heterogeneous material and has a three-dimensional macromolecular structure, which consists of maceral and minerals.1,2 Carbon, hydrogen, and oxygen are the main constituents of macerals with some amount of sulfur and nitrogen. The maceral is a combination of different inputs and depositional environments, which can be distinguished as liptinite, vitrinite, and inertinite. Liptinite has the highest hydrogen to carbon (H/C) atomic ratio, whereas vitrinite and inertinite have a comparatively lower H/C atomic ratio. The amount, chemical structure, and distribution of various macerals in coal are highly dependent on the condition of coalification and chemical nature of the coal-forming materials.3,4 A typical maceral structure of coal consists of alkyl-substituted aromatic and polyaromatic bonded by covalent and non-covalent bonds (van der Waals interaction, hydrogen bond, electrostatic interactions, and $\pi-\pi$ interaction, etc.).5,6−8 Incumbent coal conversion processes and inefficient utilization of coal prompted researchers to understand its structure at a fundamental level and represent a molecular model.

The first partial coal structure developed by Wender13 shows 92 atoms (molecular formula, $C_{42}H_{40}O_{10}$), consisting of a single aromatic ring cross-linked by aliphatic chains. Nishioka proposed two models stating that coal has networking structures, namely, non-associative and associative.16,17 The former signifies coal as macromolecules, which are not soluble in organic solvents, whereas the latter defines it as individual molecules linked to each other by non-covalent bonds.14,15 Due to these variations, different ranks of coal yields different percentages of the product.18,19 Out of all networking structures, associated structure yields higher extraction by breaking the secondary interactions with alkylation, acetylation, and silylation.20−22 Cody et al.23 suggested that entwined chains may also be present in the coal network structure. Therefore, coal might be assumed to be a combined structure of associated, non-associated, and entwined chains.
Modern instrumental analytical techniques such as X-ray diffraction (XRD), solid-state $^{13}$C nuclear magnetic resonance ($^{13}$C NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, laser desorption ionization time-of-flight mass spectroscopy (LD-TOF-MS), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM) are some non-destructive techniques that are helpful in obtaining more structural parameters of coal without destroying it by converting into small molecules, whereas flash-pyrolysis gas chromatography—mass spectroscopy (py-GC/MS) tends to produce small molecules.

Solid-state $^{13}$C NMR spectroscopy has unique capabilities and is non-destructive in nature, making it ideal for analyzing a carbon skeletal structure of a coal sample by applying cross-polarization (CP) magic-angle spinning (MAS), cross-polarization (CP) total sideband suppression (TOSS), single pulse excitation (SPE), dipolar decoupling, and variable contact time techniques. FT-IR spectroscopy is widely used to study the structure, geochemical, and other relevant characteristics of coal. Peaks in FT-IR spectrograms of coal samples are composite and highly dispersed due to the high complexity of the coal. Apart from these techniques, X-ray diffraction (XRD) is also a useful tool to determine different structural parameters of coal with good reproducibility.

Flash-pyrolysis gas chromatography—mass spectroscopy (py-GC/MS) is another technique that can be utilized to investigate coal. The limitation with py-GC/MS analysis of coal is that only a small percentage of coal is pyrolyzed, and the size of the GC column is limited for the fragments that can transverse the column. In laser desorption ionization time-of-flight mass spectroscopy (LD-TOF-MS), the molecular weight distribution of various groups present in coal can be determined, but quantitative analysis of individual compounds cannot be performed. Much of the coals (except anthracite) consist of very small size aromatic layers, which are poorly oriented. These aromatic layers can be obtained by using high-resolution transmission electron microscopy (HRTEM) in the form of lattice fringes. The aromatic stacking and alignment of the lattice fringes could be obtained by HRTEM images, which help to represent the molecular size and spatial arrangement of coal macromolecules that can also be calculated by the fringe length. Most layers in bituminous coal are single, and very few layers are stacked on to each other.

The study of coal structure and chemical behavior of its macromolecules is very challenging to the investigators with various physical and analytical techniques developed for the structural characterization of coal. The main objective of these techniques is to provide a better understanding of the structure of coal. Coal is the primary energy source in India, and in view of this, the structural study of Karharbari coal (a vitrinite-rich low-volatile bituminous coal) from the Talcher Coalfield, Orissa, India, was performed with the help of previously discussed techniques in order to avoid any ambiguities and complications that are involved with efficient coal utilization. The improved understanding of the chemical structure of coal at a molecular level has been effectively used in the prediction of coal behavior (reactivity and reaction mechanism) in its various utilization processes. These new investigations have also led to the utilization of coal for converting it into different products.

2. EXPERIMENTS

2.1. Coal Sample Preparation. The coal sample was crushed and ground to 200 mesh size and demineralized to reduce the amount of mineral matter present. Demineralization is carried out to minimize the effect of mineral materials during analytical analysis. A combination of HCl (CAS no. 7647-01-0) and HF (CAS no. 7664-39-3), as supplied by Sigma-Aldrich, was used for the demineralization process because HF and HCl do not disrupt the molecular structure of the coal as a lixiviant. A 5 M dilute solution of HCl was prepared from a 32% concentrated solution (provided), and HF (48% concentrated) was used without any purification. An amount of 50 g of the 200 mesh coal sample was stirred with a magnetic stirrer continuously into 200 mL of 5 M HCl solution (maintaining a 4 mL (HCl):1 g (coal) ratio) in a polytetrafluoroethylene (PTFE) beaker covered by Perspex lid for 24 h. The acid was separated by centrifugation, and the precipitate was dissolved in lixiviant HF (maintaining a 4 mL (HF):1 g (precipitate) ratio) and stirred for 24 h. The precipitate was separated from the acid solution by centrifugation and then dissolved in 5 M HCl (maintaining a 4 mL (HCl):1 g (precipitate) ratio) and stirred for 24 h. The resulting solution of the precipitate and acid was then placed in a centrifuge for separation of acid, and the precipitate was washed with hot deionized water until a pH of 7.0 was obtained for the filtrate. At last, the demineralized coal sample was dried in a vacuum oven at 105 °C for 6 h and subsequently stored in a desiccator.

Proximate analysis of the demineralized coal sample was performed by standard methods (IS: 1350 (Part I-1984)). Carbon, nitrogen, and hydrogen were analyzed by means of a Perkin Elmer elemental analyzer (model 2400). The sulfur determinator (Leco, SC132) was used to determine the sulfur, and the percentage of oxygen was calculated by difference. The maceral group compositions were determined by the standard method (ASTM D 2799-05a, 2005). The true density value of the demineralized coal sample was obtained using a JW-M100A helium pycnometer.

The free radicals were formed during demineralization of the coal due to the removal of inorganic cations constituted in the coal functional groups such as the carboxylic acid functionalities. These free radicals can influence the intensity of some of the $^{13}$C NMR analysis. This problem can be eradicated by treating the demineralized coal sample with samarium(II) iodide (SmI$_2$) in tetrahydrofuran (0.1 M) to reduce the paramagnetic character without reducing the diamagnetic character of organic coal compounds. The demineralized coal sample was mixed with 0.1 M SmI$_2$ (maintaining an 8 mL (SmI$_2$):1 g (coal) ratio) in a beaker and stirred continuously with a magnetic stirrer for 12 h. After this treatment, the reaction was cooled with 30 mL of deionized water, and THF was evaporated. The remaining residue was washed with 500 mL of diluted HCl (2 M) to remove the lanthanide ions. The residual coal sample was washed with boiled deionized water until the pH of 7.0 for the filtrate was achieved. At last, the residual coal sample was dried further in a vacuum oven at 105 °C for 6 h and subsequently stored in a desiccator.

2.2. Coal Sample Characterization. 2.2.1. Solid-State $^{13}$C Nuclear Magnetic Resonance ($^{13}$C NMR) Spectroscopy. The solid-state $^{13}$C NMR analysis was carried out on a Bruker AVANCE III 500 MHz two-channel spectrometer at the institutional instrumentation lab, IIT Roorkee. The NMR apparatus operated at the resonant frequency of $^{13}$C nucleus of 100.13 MHz with a 5 mm probe and ZrO$_2$ rotor (outer diameter of 6 mm). The $^{13}$C NMR experiment was conducted with cross-polarization (CP) magic-angle spinning (MAS) with a combination of variable contact time and dipolar dephasing.
Cross-polarization (CP) experiments were carried out at ambient temperature. The CP-MAS experiments were carried out at a MAS speed of 8 kHz with a sampling time of 0.05 s, a pulse width of 4 μs, and a cycle delay time of 5 s. A total of 7000 scans per spectrum were collected.

The peak position of every functional group and its relative percentage were assigned as discussed by Trehwella et al. Various lattice and structural parameters were calculated by using the method of Solum et al.12十二^{13}C parameters, which are aromaticity ($f_a$), carbonyl carbon ($f_c$), corrected aromaticity ($f_s$), aliphatic carbon ($f_al$), aliphatic carbon-containing sp and sp$^2$ carbon ($f_sp$, protonated carbon ($f_{sp}^p$), nonprotonated aliphatic carbon ($f_{sp}^n$), aromatic carbon (whose carbon is bond to oxygen) ($f_{sp}$), and bridgehead carbons ($f_{B}$) of coal macerals obtained by the method given by Solum et al.12

The lattice parameters such as the average number of aromatic carbon atoms per cluster ($X_o$) and mole fraction of bridgehead carbon ($X_b$) were calculated from the structural parameters as follows:

$$X_b = \frac{f_{B}}{f_{a}}$$

$$X_o = 0.5\left\{\left[1 - \tanh\left(\frac{C - C_o}{m}\right)\right] \times \left(\frac{1}{2} - \frac{3}{C}\right)\right\} + \left\{\left[1 + \tanh\left(\frac{C - C_o}{m}\right)\right] \times \left(1 - \frac{\sqrt{6}}{\sqrt{C}}\right)\right\}$$

Where $C_o$ and $m$ are constant parameters with a value of $C_o = 19.57$ and $m = 4.15$, respectively, obtained by Solum et al.12

The average number of attachment ($\sigma + 1$) and the fractional amount of all bridges intact ($P_o$) are described by the following equations:

$$\sigma + 1 = \frac{f_{sp}^p + f_{sp}^n - f_{sp}^n}{f_{a}}$$

$$P_o = \frac{f_{sp}^p + f_{sp}^n - f_{sp}^n}{f_{sp}^p + f_{sp}^n}$$

The determination of the last four lattice parameters including the number of bridges and loops per cluster B.L., the number of side chains per cluster S.C., the average molecular weight of a cluster MW, and the average molecular weight of a side chain or half of a bridge mass $M_b$ are defined as follows:

$$B. L. = P_o(\sigma + 1)$$

$$S. C. = (\sigma + 1) - B. L.$$

$$MW = \frac{12.01C}{f_{a}} \times (\%carbon/100)$$

$$M_b = \frac{MW - 13M_o}{\sigma + 1}$$

The carbon % is taken from the elemental analysis of the coal (dmmf), and $M_o$ is the initial magnetization, which is taken as 2.4.

Equation 2 determines the aromatic cluster size in compounds for which $X_o$ is known even when the structure is unknown. For a low-rank coal average, the aromatic cluster size is one to three linear aromatic rings containing less than nine carbons, whereas for higher-rank coals the average aromatic cluster size is four to five nonlinear aromatic rings containing more than 15 carbons.12 B.L. and S.C. obtained from eqs 5 and 6, respectively, indicate the attachment or cross-linking through an aromatic culture obtained by eq 2. B.L. indicates the number of connections between clusters (bridges-B.L.) and connections back to the same cluster (loops-B.L.). S.C. indicates the number of attachments mainly the number of aliphatic side chains terminating in methyl groups.

The^{13}C CP/MAS NMR analysis was conducted with the combination of variable contact time and dipolar dephasing techniques to improve the result accuracy. The demineralized Karharbari coal was treated with samarium(II) iodide to eliminate free radicals. Elimination of free radicals is required to improve the quantitative reliability of the NMR spectrum.

2.2.2. Fourier Transform Infrared (FT-IR) Spectroscopy. The FT-IR spectra of the demineralized coal was obtained using a ShimadzuIRAffinity-1S FTIR spectrometer at the chemical engineering department, MANIT Bhopal. The transmittance and wavelength requirement was equal to 0.1 and 0.1 cm$^{-1}$, respectively. The spectra were recorded at a resolution of 5 cm$^{-1}$ within 4000–400 cm$^{-1}$ over 32 scans.

Work done by Machnikowska et al.32 was used for the FT-IR spectral qualitative interpretation. The band region (3000–2800 cm$^{-1}$) belongs to the aliphatic C–H stretching, and the band region (3100–3000 cm$^{-1}$) can be attributed aromatic C–H stretching. The bands at 2930 and 2850 cm$^{-1}$ from the aliphatic C–H stretching were assigned to asymmetric CH$_2$ vibrations and symmetric CH$_3$ and CH$_2$ vibrations, respectively. The band at 1600 cm$^{-1}$ corresponds to C–C stretching vibration of the aromatic rings. The band on the left-hand side of the C=C stretching vibration at 1680 cm$^{-1}$ was assigned to C=O stretching. From C=O stretching vibrations, it could be concluded that esters, aldehydes, ketones, or –COOH may be present in the Karharbari coal. The bands at 1450 and 1170 cm$^{-1}$ correspond to CH$_2$ and CH$_3$ vibrations, respectively. The strong intensity band at 1110–1000 cm$^{-1}$ was associated with C=O stretching vibration (ether groups) and O–H band groups. The 800–680 cm$^{-1}$ band region was assigned to out-of-plane aromatic C–H vibration. The band region (3250–3750 cm$^{-1}$) was assigned to the various H-bond combinations, which suggest the presence of different OH groups. The bands at 3700, 3650, 3619, 3511, and 3320 cm$^{-1}$ were assigned to OH–ether hydrogen bonds, OH–OH bonds, free OH groups, OH–π hydrogen bond, and cyclic OH groups, respectively.

2.2.3. X-ray Diffraction (XRD). X-ray diffraction was carried out on a Bruker D8 Advance diffractometer at the Indian Institute of Technology Roorkee. The diffractograms of a demineralized coal sample were determined by using a Cu anode Kα radiation ($\lambda = 1.54059$ Å) at 40 kV voltage and 40 mA current. The X-ray intensities were calculated in the range of 2$^\circ$ ≤ 2θ ≤ 120$^\circ$ with a step size of 0.019$^\circ$2θ. The phase quantification method was applied to the resulting diffractograms for further analysis and smoothening. After processing the diffractograms, the average structural parameters were calculated from the peak widths at half-maximum intensity (β) and
the peak position ($\theta$) by using the empirical expression obtained from Scherrer (eqs 9–12). 42,43

The average number of layers per carbon crystallite ($N_{ave}$), the interlayer spacing between aromatic sheets ($d_{002}$), average crystallite diameter ($L_{a,10}$) and average crystallite height ($L_{c}$) were calculated using the following equations:

$$d_{002} = \frac{\lambda}{2 \sin \theta_{002}}$$  \hspace{1cm} (9)

$$L_{c} = \frac{K_{c}\lambda}{\beta_{002} \cos \theta_{002}}$$  \hspace{1cm} (10)

$$L_{a,10} = \frac{K_{a}\lambda}{\beta_{100} \cos \theta_{10}}$$  \hspace{1cm} (11)

$$N_{ave} = 1 + \frac{L_{c}}{d_{002}}$$  \hspace{1cm} (12)

where $K_{c}$ is a constant that depends upon the X-ray reflection plane of Cu Kα (0.89 for Cu Kα). Other structural parameters include the fraction of amorphous carbon ($x_{a}$), degree of disorder index (DOI), and aromaticity ($f_{a}$), which can be calculated by using the following equations:

$$X_{a} = \frac{S_{a}}{S_{a} + S_{c}}$$  \hspace{1cm} (13)

$$f_{a} = \frac{S_{002}}{S_{002} + S_{\gamma}}$$  \hspace{1cm} (14)

$$DOI = X_{a} + (1 - X_{a})(1 - f_{a})$$  \hspace{1cm} (15)

where $S_{a}$ and $S_{c}$ are the corresponding areas of the separated peaks, and $S_{002}$ and $S_{\gamma}$ are the area under the (002) band and the $\gamma$ band, respectively. It was assumed that ($S_{002}$ and $S_{\gamma}$) $S_{002}$ and $S_{\gamma}$ were equal to the number of aromatic carbon and aliphatic carbon atoms, respectively.

2.2.4. Flash-Pyrolysis Gas Chromatography–Mass Spectroscopy (py-GC/MS). Flash-pyrolysis gas chromatography–mass spectroscopy (py-GC/MS) analyses of different compounds by partial destruction of macromolecules can be investigated by thermal splitting (pyrolysis, py) of their peripheral fragments, and the obtained pyrolysates can be investigated by an analytical GC/MS apparatus.33 The aromatic portion of the structure is given by fringe lengths, which were estimated by the carbon ring catenation and angle of viewing. The series of aromatic skeletons were constructed assuming fringe depth equal to the fringe width.37

The aromatic portion of the structure is given by fringe lengths, which were estimated by the carbon ring catenation and angle of viewing. The series of aromatic skeletons were constructed assuming fringe depth equal to the fringe width.37

Cut-off length values for some small aromatic molecules are as follows: <3 Å for benzene, <4.4 Å for naphthalene, and <5.4 Å for anthracene/phenanthrene. Other fringe lengths ranging from 5.5 to 34.5 Å were taken according to the work by Okolo et al.:41 5.5–8.4 Å for 2 × 2, 8.5–13.4 Å for 3 × 3, 13.5–17.4 Å for 4 × 4, 17.5–21.4 Å for 5 × 5, 21.5–25.4 Å for 6 × 6, 25.5–29.5 Å for 7 × 7, and 29.5–34.5 Å for 8 × 8. The aromatic raft structures ranging from 2 × 2 to 8 × 8 were assumed to be taken as parallelogram-shaped sheets. All fringes below 3 Å were ignored because they could not be clearly distinguished from the background noise. Mathews et al.43 developed a set of equations (eqs 16–18) for calculating the minimum ($C_{min}$) and maximum ($C_{max}$) carbon atoms in the parallelogram-shaped aromatic fringes and the molecular weight of an individual fringe:

$$C_{max} = 0.7981 \times \text{fringe length}^{1.7964}$$  \hspace{1cm} (16)

$$C_{min} = 0.4312 \times \text{fringe length}^{1.7132}$$  \hspace{1cm} (17)

$$MW = 12.106 \times C_{\text{avg}} + ((0.1806 \times C_{\text{avg}}) + 8.98)$$  \hspace{1cm} (18)
3. RESULTS AND DISCUSSION

3.1. Information from Quality Analysis. The quality analysis of Karharbari coal is summarized in Table 1. The proximate analysis of Karharbari coal provides the overall percentage (weight percentage on air-dry basis) of volatile matter (33.6%), moisture (7.1%), ash (11.2%), and fixed carbon (48.1%). The proximate analysis is subdivided into the smaller carbon species: vitrinite (57.8%), inertinite (29.5%), and liptinite (12.7%). The values of the mean vitrinite reflectance (0.59%) and volatile matter (33.6%) indicate the coal as a low-volatile bituminous higher-rank coal. The ultimate analysis (% weight on dry mineral matter free basis) of carbon, hydrogen, nitrogen, sulfur, and oxygen is 80.1, 6.7, 3.2, 0.8, and 0.7, respectively. The corrected aromaticity ($f_a$) of the Karharbari coal was 0.82. The amount of nonprotonated carbon ($f_a^H$) is more (0.56) than protonated carbon ($f_a^N$, 0.26), phenolics or phenolic ether ($f_a^P$, 0.08), and alkylated aromatic carbons ($f_a^S$, 0.19). It shows that more number of carbons were present in the aromatic ring than side chains, and few carbons were also present in different functional groups. Furthermore, it was observed that the bridgehead carbons ($f_a^H$) present was 0.29, which is more than that of functional groups. This result indicates that the coal macromolecules mainly consist of aromatic ring structures, which are connected to aliphatic carbons and a few side chains. The results of the determination of the lattice parameters indicate that every cluster consists of 17 aromatic carbon atoms with 0.337 mole fraction of bridgehead carbon, 3.7 bridges and loops, and 0.82 side chains. Furthermore, the attachments to every cluster are 4.5. The molecular weight of every average aromatic cluster is 507. The NMR results are similar with the same-rank Argonne Premium coal (low-volatile bituminous Pocahontas coal).

3.2. Solid-State $^{13}$C Nuclear Magnetic Resonance (NMR) Spectroscopy Analysis. The CP/MAS NMR spectrum of the demineralized Karharbari coal sample was obtained and is shown in Figure 1. A small degree of a graphite-like structure was observed and shown in the XRD section (002) and (10) at $-31.5^\circ$ and $-50^\circ$, respectively. The intensity of the (002) band was very high because the aromatic ring carbon layers are arranged in a spatial manner with some interlayer distance ($d_{002}$). The intensity of (10) and (11) bands that correspond to the graphite position were very low or invisible. A $\gamma$-band was observed and shown in the XRD spectrum at the left-hand side of the (002) band. The $\gamma$-band represents the aliphatic side chains that are attached to crystalline carbon (aromatic carbon).

The average structural parameters were calculated and are represented in Table 2. The value of $d_{002}$ for the Karharbari coal was found to be 4.63 Å, which is more than vitrinite-rich Waterberg coal ($d_{002} = 3.97$ Å), whereas the $L_e$ value was 13.96 Å, which is also lower than the value for vitrinite-rich Waterberg coal (4.27 Å). The average number of layers per carbon crystallite ($N_{ave}$) was 2.54, which is comparable with the same-rank vitrinite-rich low-volatile bituminous coal. The value of the average crystallite diameter ($L_{ave}$) was 16.32 Å, which might...
have some error due to a weak (10) band in the XRD diffractograms. Other structural parameters were fractions of amorphous carbon-containing ($x_a$) 0.56 and aromaticity ($f_a$) 0.72, which were lower than the value (0.84) obtained by $^{13}$C NMR CP/MAS, and the degree of disorder index (DOI) was found to be 0.68. These values also establish the fact that Karharbari coal has a poorly organized structure.

3.5. Flash-Pyrolysis Gas Chromatography–Mass Spectroscopy (py-GC/MS) Analysis. The demineralized Karharbari coal sample analyzed by py-GC/MS resulted in the pyrolysis profile as shown in Figure 4. The presence of alkylindenes, alkynaphthalenes, alkynaphthoals, phenanthrene, alkylbenzenes, alkylphenols, polyaromatic, and homologous series of $n$-alkanes and $n$-alk-1-enes can be clearly identified by the pyrolyte distribution of the Karharbari coal sample. The higher aromatic content of the Karharbari coal obtained by the FT-IR and NMR spectra was confirmed by the pyrograms. The distribution of the major compositions obtained by py-GC/MS is shown in Figure 5. The flash-pyrolysis GC/MS analysis of the coal sample has a limitation that a small percentage of the coal can be pyrolyzed, and the GC column has a size limit in regard to the fragments that can be inserted.

3.6. Laser Desorption Ionization Time-of-Flight Mass Spectroscopy (LD-TOF-MS) Analysis. Laser desorption

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**Table 3. Relative Parameters of the Karharbari Coal**

| relative parameters | calculation       | value |
|---------------------|-------------------|-------|
| $H_a/H_y$           | $A_{3200-3000}/A_{680-800}$ | 0.79  |
| aliphatic/aromatic  | $A_{3200-3000}/A_{1600}$   | 1.23  |
| $\alpha(CH_2)/\alpha(CH_3)$ | $A_{1450}/A_{1170}$       | 0.52  |

**Table 4. XRD Structural Parameters of the Karharbari Coal**

| structural parameters | respective value |
|-----------------------|------------------|
| interlayer spacing between aromatic sheets ($d_{002}$) | 4.63 Å |
| average crystallite height ($L_c$)                  | 13.96 Å |
| average number of layer per carbon crystallite ($N_{av}$) | 2.54 |
| average crystallite diameter ($L_{a,10}$)            | 16.32 Å |
| fraction of amorphous carbon contain                 | 0.56  |
| aromaticity                                           | 0.79  |
| degree of disorder index                              | 0.68  |

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Figure 2. FT-IR spectrogram of the Karharbari Coal.

Figure 3. XRD spectrogram of the Karharbari coal.
ionization time-of-flight mass spectra was obtained in the range of 75 to 4000 m/z in reflector mode for the demineralized Karharbari coal sample and are presented in Figure 6. The laser power was varied to get maximum molecular masses present in the coal sample. The higher laser power results in higher-molecular-weight components to be observed, whereas lower laser power extents result in lower-molecular-weight components. An effective molecular mass distribution of coal can be obtained by using LD-TOF-MS but is less effective toward the quantitative estimation or the amounts of individual masses present. The spectra of the demineralized Karharbari coal shown in Figure 6 shows the molecular weight distribution ranging from 4000 m/z with a maximum abundance in the range of 1000–1500 m/z.

3.7. X-ray Photoelectron Spectroscopy Analysis. The qualitative analysis, based on surface elements or heteroatoms present in the coal, was obtained by using X-ray photoelectron (XPS) spectroscopy. A spectrum in the range of binding energies of 0−1350 eV was collected, and the results are shown in Figure 7. The peak heights in Figure 7 reveal the composition of surface elements, in which C and O are present in majority, whereas the peaks associated with N and S are in minority due to their low content. The XPS spectrogam at C 1s, O 1s, N 1s, and S 2p are split and fitted by XPS PEAK software, and the curves are plotted using Origin software, presented here in Figure 8a–d. The quantitative analysis of the XPS spectrogam was carried out by Gaussian peak shapes using Origin software.

The presence of different heteroatoms like carbon, oxygen, nitrogen, and sulfur were obtained in the XPS spectrum at the binding energies of 289.6, 532.8, 400, and 162.3 eV, respectively. The surface elemental concentration (atomic %) was obtained by quantitative analysis of the peaks present in the spectrum, which were 82.6% C 1s, 12.3% O 1s, 1.2% N 1s, and 1.7% S 2p.

It was observed that four peaks were obtained by evaluation of the C (1s) signal shown in Figure 8b, with the quantitative distribution (mol %) of the different carbon forms present in coal given in Table 5. The constituents are aromatic graphitized carbon (C=C) and aliphatic carbon (C−H) 68.5%, phenolic and ether carbon (C−O) 23.4%, carboxyl (COO−) 1.9%, and carboxide (C==O) 6.0%.

The constituent evaluation of N (1s) also yielded four peaks, which are represented in Figure 8c, and they are at binding energies of 399.3, 400.8, 401.5, and 402.9 eV corresponding to the different nitrogen forms pyridine, pyrrolic, quaternary, and oxidized nitrogen, respectively. The molar distribution of pyridine, pyrrolic, quaternary, and oxidized nitrogen are 19.3, 45.6, 31.2, and 3.7%, respectively, as presented in Table 5.

The constituent evaluation of the O (1s) spectrum and correspondent distributions were also calculated and is presented in Figure 8a and Table 5. The O (1s) peak fitting provided five peaks at binding energies of 530.2, 531.8, 532.3, 533.4, and 535.1 eV, which can be assigned to inorganic oxygen, C==O, C−O, COO−, and absorbance oxygen with the molar percentages of 2.3, 23.1, 39.6, 31.2, and 3.5%, respectively.

Different sulfur species were also studied by the peak evaluation of S (2p) spectra in the region of 160–175 eV binding energy. It can be concluded that the peaks at binding energies of 166.1 and 167.2 eV can be assigned to sulfoxides with 16.4% on molar basis, and the peaks at binding energies of 164.9, 168.4, and 169.8 eV were assigned to sulfoxides, thiophenes, sulfones and, sulfuric acid and sulfates with the molar contents of 16.4, 41.6, 21.3, and 20.5%, respectively.

Figure 4. py-GC/MS spectrum of the Karharbari coal.

Figure 5. Composition of pyrolytes of the Karharbari coal.
3.8. High-Resolution Transmission Electron Microscopy (HRTEM). The sequence of extraction of aromatic fringes is presented in Figure 9. Five areas were selected from the HRTEM image for the extraction of the lattice fringes to obtain the actual distribution of aromatic fringes in the demineralized Karharbari coal. The skeletonized images of all five areas are shown in Figure 10, and the distribution and grouping of all the aromatic fringes was done according to their fringe length and molecular weight as presented in Table 6.

The skeletonized image of HRTEM aromatic fringes from Figure 10 clearly indicates that the fringes or layers in Karharbari coal are poorly oriented, and most of these are nonplanar. It was observed that a maximum of four-layer stack and an average of three-layer stack were observed by HRTEM, which is close to the value of the stacking number \( N_{\text{ave}} = 2.54 \) obtained by XRD. The maximum fringe count was observed in the range of fringe length of 5.5–13.4 Å, which is comparable to the average crystallite size obtained by XRD. A good agreement was found from the comparison of structural parameters obtained by XRD and HRTEM.

A total of 680 fringes were extracted from all five HRTEM images, which can be distributed in the coal sample according to their fringe length. All the fringes were assumed to be parallelogram-shaped aromatic sheets with two characteristic lengths, namely, maximum length (MaxL) and minimum length (MinL). The series of parallelogram-shaped aromatic sheets started from a single benzene-shaped fringe to an 8 \( \times \) 8 parallelogram fringe. All parallelogram-shaped aromatic fringes are shown in Figure 11. Results show that the average molecular weight of the HRTEM analyzed aromatic fringes was 530 amu comparable with the molecular weight (507 amu) obtained by \(^{13}\)C NMR results.

A fringe length of <3.0 Å was neglected in the HRTEM image due to noise and association with the same fringe length. A total of 50 fringes were assumed as less than 3.0 Å fringe length to get an accurate distribution of all fringe sizes in the coal sample. The fringe lengths of <4.4 and <5.4 Å were assigned to naphthalene

![Figure 6. LD-TOF mass spectra of the Karharbari coal.](image)

![Figure 7. XPS full spectrum scan of the demineralized Karharbari coal.](image)

### Table 5. XPS O (1s), C (1s), N (1s), and S (2p) Data of the Demineralized Karharbari Coal

| XPS C (1s) data | binding energy (eV) | carbon form | content (mol %) |
|----------------|------------------|-------------|----------------|
| 284.5          | aromatic graphitized carbon (C−C) and aliphatic carbon (C−H) | 68.5         |
| 286.3          | phenolic and ether carbon (C−O) | 23.4         |
| 287.7          | carboxyl (COO−) | 1.9          |
| 288.9          | carboxide (C═O) | 6.0          |

| XPS N (1s) data | binding energy (eV) | nitrogen form | content (mol %) |
|----------------|------------------|-------------|----------------|
| 399.3          | pyridine nitrogen | 19.3        |
| 400.8          | pyrrolic nitrogen | 45.6        |
| 401.5          | quaternary nitrogen | 31.2        |
| 402.9          | oxidized nitrogen | 3.7         |

| XPS O (1s) data | binding energy (eV) | oxygen form | content (mol %) |
|----------------|------------------|-------------|----------------|
| 530.2          | inorganic oxygen | 2.3         |
| 531.8          | C═O              | 23.1        |
| 532.3          | C−O              | 39.6        |
| 533.4          | COO−             | 31.2        |
| 535.1          | absorbance oxygen | 3.5         |

| XPS S (2p) data | binding energy (eV) | sulfur form | content (mol %) |
|----------------|------------------|-------------|----------------|
| 166.1, 167.2   | sulfoxides       | 16.4        |
| 164.9          | thiophenes       | 41.6        |
| 168.4          | sulfones         | 21.3        |
| 169.8          | sulfonic acid and sulfates | 20.5 |

https://dx.doi.org/10.1021/acsomega.9b03674
ACS Omega 2020, 5, 6336–6347
and anthracene, respectively, with an abundance of 17.6 and 14.1%, respectively. The contribution of naphthalene and anthracene in the average molecular weight of the HRTEM aromatic fringes was about 22.0 and 24.7 amu, respectively. The Karharbari coal sample mainly consisted of a $2 \times 2$ aromatic structure, which was assigned in the range of 5.5−8.4 Å fringe length due to their maximum content of 22.1%, with a contribution of 61.0 amu in average molecular weight of the HRTEM aromatic fringes. From the HRTEM image analysis, their proportion of $3 \times 3$, $4 \times 4$, $5 \times 5$, $6 \times 6$, $7 \times 7$, and $8 \times 8$ parallelogram aromatic sheets in Karharbari coal was obtained as 19.4, 8.6, 5.2, 3.2, 1.6, and 0.9%, respectively, with the contribution of 97.2, 84.1, 80.6, 72.1, 48.3, and 35.04 amu in average molecular weight of HRTEM aromatic fringes.

Table 6. Data Obtained by Analysis of HRTEM Images

| aromatic sheet | grouping by fringe length (Å) | MinL (Å) | MaxL (Å) | molecular weight range (amu) | counts in model | frequency (%) |
|----------------|-------------------------------|----------|----------|-----------------------------|----------------|---------------|
| benzene        | <3.0                          |          |          | 50−99.99                    | 50             | 6.8           |
| naphthalene    | 3.0−4.4                       | 2.8      | 4.7      | 100−149.99                  | 129            | 17.6          |
| anthracene     | 4.5−5.4                       | 2.8      | 5.9      | 150−199.99                  | 103            | 14.1          |
| $2 \times 2$   | 5.5−8.4                       | 4.9      | 8.6      | 200−349.99                  | 162            | 22.1          |
| $3 \times 3$   | 8.5−13.4                      | 7.4      | 14.2     | 350−649.99                  | 142            | 19.4          |
| $4 \times 4$   | 13.5−17.4                     | 11.3     | 18.8     | 650−1299.99                 | 63             | 8.6           |
| $5 \times 5$   | 17.5−21.4                     | 16.9     | 22.3     | 1300−1799.99                | 38             | 5.2           |
| $6 \times 6$   | 21.5−25.4                     | 20.8     | 27.6     | 1800−2599.99                | 24             | 3.2           |
| $7 \times 7$   | 25.5−29.4                     | 24.1     | 32.5     | 2600−3299.99                | 12             | 1.6           |
| $8 \times 8$   | 29.5−34.5                     | 27.9     | 35.7     | 3300−4000                   | 7              | 0.9           |
respectively. Mathews et al. were the first to compare molecular weight distribution results of HRTEM and LD-TOF-MS, and a similar approach was used here to compare the molecular weight distribution in the interval of 200 amu with the frequency in the number of aromatic fringes for Karharbari coal and is presented in Figure 12.

4. CONCLUSIONS

The Karharbari coal is a poorly organized amorphous coal with a disordered index of 0.68, \( d_{002} \) of 4.63 Å, and \( L_c \) of 13.59 Å. The aromaticity of the Karharbari coal was found to be 0.79 from the XRD result, which was similar to the NMR result (corrected aromaticity = 0.82). The elemental analysis obtained by CHNS analysis (80.1% C, 5.5% H, 1.9% N, 3.1% S, and 9.2% O) was confirmed by using XPS spectroscopy (82.6% C 1s, 12.3% O 1s, 1.2% N 1s, and 1.7% S 2p). Different forms of carbon, oxygen, nitrogen, and sulfur were also obtained by XPS spectroscopy, and their functionalities were presented. The average molecular weight of the aromatic cluster is 507 amu as obtained by the NMR result, which is relatively closer to the result obtained by HRTEM analysis (MW = 530 amu). The molecular weight distribution of the Karharbari coal ranged to approximately 4000 amu by LD-TOF-MS and HRTEM results. The maximum contributors (38.1%) of 5.5—8.4 Å fringe length were obtained in the Karharbari coal with a molecular weight in the range of 250—750 amu, which was in agreement with the maximum abundance at 700 m/z, as obtained by LD-TOF-MS analysis. This structural information will aid in a better understanding of the conversion behavior of this coal in current processes and the development of future processes.

Figure 9. HRTEM image analysis sequence.

Figure 10. Skeletonized image of HRTEM aromatic fringes.
Figure 11. Different fringes with minimum length (MinL) and maximum length (MaxL).

Figure 12. Comparison of molecular weight distribution of Karharbari coal determined by HRTEM model (purple) and LD-TOF-MS (solid black).

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
Funding for this work from Maulana Azad National Institute of Technology, Bhopal (MP) 462003 is gratefully acknowledged. We also express our gratitude to the Department of Chemical Engineering Indian Institute of Technology, Roorkee, for providing required facilities for completion of this research work.

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