Structural Characterization and Molecular Simulation of Baoqing Lignite

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ABSTRACT: The molecular structure of Baoqing lignite was analyzed by ultimate analysis, Fourier transform infrared spectroscopy, X-ray diffraction spectroscopy, $^1$C solid-state nuclear magnetic resonance, and X-ray photoelectron spectroscopy. The results revealed that the aromaticity of Baoqing lignite is 27.64%, and the aromatic structure mainly contains benzene and naphthalene. The aliphatic structure consists of alkyl side chains and cycloalkyl. Oxygen atoms are present in phenol, ether, carbonyl, and carboxyl groups; nitrogen atoms are chiefly in pyridine and pyrrole; sulfur atoms mainly exist in sulfoxide sulfur. The molecular structure model of Baoqing lignite was constructed based on experimental data, and the molecular formula is $\text{C}_{184}\text{H}_{199}\text{O}_{50}\text{N}_{2}\text{S}$. The molecular configuration was optimized by adopting the M06-2X basis set in the framework of density functional theory. Moreover, the simulated FTIR spectrum was in good agreement with the experimental spectra, proving the accuracy of the molecular structure. The molecular model of Baoqing lignite contains a majority of aliphatic structures and aromatic rings with a poor condensation degree. Moreover, the aromatic layers irregularly arrange in space.

1. INTRODUCTION

Lignite is a kind of fossil energy with a large content and is spread all over the world. In recent years, the thermal transformation of lignite, such as pyrolysis, liquefaction, and gasification, has attracted wide attention. However, the development and utilization of lignite have been greatly restricted in the energy field for its high moisture, high volatile matter, and low calorific value. It is worth noting that the molecular structure of lignite plays a vital role that determines the path and the activity of the reaction in the thermal transformation process. Therefore, it is of great significance to study the molecular structure model of lignite for comprehensive applications.

Investigations indicated that the molecular structure of coal is a highly complex molecular network, including a series of organic structural units connected by covalent and non-covalent bonds. Constructing a molecular structure model of lignite can face challenges due to its diversity and heterogeneity. In previous studies, coal was generally pyrolyzed or extracted, and its production was analyzed to obtain information regarding the molecular structure. However, with the advent of NMR, X-ray diffraction and other technologies, a large number of coal structural parameters can be obtained without pyrolysis or extraction of coal. These technologies have the advantages of high sensitivity and minimal damage to the molecular structure. They can obtain information about the detected object in its original state and are beneficial for studying the carbon skeleton structure, functional groups, and side chain groups of coal.

Analytical techniques for studying the structure of lignite mainly include solid-state $^1$C nuclear magnetic resonance ($^1$C NMR), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), etc. Previous studies have proven that multiple characterizations are an effective method for a complete understanding of the chemical structures of lignite. Xiao et al. employed XPS to study nitrogen atoms in the soluble organic matter of Xianfeng lignite and claimed that nitrogen is mainly in pyridine and pyrrole. Yan et al. adopted solid-state $^1$C NMR, XRD, and FTIR to study the molecular structure of various rank coals. The results demonstrated that with an improved coal rank, the percentage of aliphatic functional groups and oxygen-containing functional groups decreases, and the aromatic cluster size and mean coal molecular mass increase; moreover, side chains of each aromatic ring decrease, and the degree of graphitization of...
Table 1. Proximate and Ultimate Analysis Results of BL\textsuperscript{a}

| sample  | \(M_{\text{ad}}\) | \(A_d\) | \(V_{\text{daf}}\) | \(F_{C,\text{ad}}\) | \(C\) | \(H\) | \(O^{\text{a}}\) | \(N\) | \(S\) | H/C | O/C | N/C | S/C |
|---------|-----------------|--------|-----------------|----------|-----|-----|-------|-----|-----|-----|-----|-----|-----|
| BL      | 6.12            | 25.02  | 62.52           | 33.21    | 66.69| 6.08| 24.75 | 0.77| 0.71| 1.08| 0.27| 0.01| 0.004|

\textsuperscript{a}d, dried base; ad, air-dried base; daf, dry and ash-free base; M, moisture; A, ash; V, volatile matter; FC, fixed carbon; \(^{\text{a}}\), by difference.

As shown in Figure 2, a number of disordered frizzy peaks implied that there existed a certain percentage of disordered carbon. Moreover, the 002 peak (26°) represents the aromatic carbon component in coal molecules.\textsuperscript{27} The 002 peak value not only reflects the spatial arrangement of the aromatic ring carbon network layer but also shows the distance between the aromatic ring carbon and the aromatic ring layers. The \(\gamma\) peak (19.20°) represents the aliphatic carbon in coal. The 100 peak (41°) is related to the condensation degree of aromatic rings and the size of the aromatic carbon network layer.

The microcrystalline structure parameters of the BL were calculated based on the XRD peak fitting results (Table 2). For BL, the aromaticity \(f_\gamma\) of BL is 0.27, the layer stacking height \(L_c\) is 7.69 Å, and the interlayer spacing \(d_{002}\) is 3.42 Å. These are the key parameters for constructing its molecular structure. Compared with medium- and high-rank coals, \(I_{002}/I_\gamma\) (the intensity ratio of the 002 peak to the \(\gamma\) peak) of BL is smaller, while \(d_{002}\) is larger. This indicated that the BL molecular structure contains more aliphatic structures and has a poor condensation degree of aromatic rings. In addition, the aromatic layers irregularly arrange in space.\textsuperscript{11,17,30}

\section*{2. RESULTS AND DISCUSSION}

\subsection*{2.1. Proximate and Ultimate Analyses}

Table 1 lists the proximate and ultimate analysis results of Baoqing lignite (BL). The atomic ratios of H/C, O/C, N/C, and S/C were calculated to be 1.08, 0.27, 0.01, and 0.004, respectively. This is an important parameter for calculating the BL molecular formula.

\subsection*{2.2. FTIR Analysis}

Figure 1 shows the FTIR spectrum of BL lignite. It can be divided into four sections: 700–900, 1000–1800, 2700–3000, and 3000–3600 cm\(^{-1}\). These sections correspond to aromatic structures, oxygen-containing functional groups, aliphatic carbon structures, and hydroxyl functional groups, respectively.\textsuperscript{9,24–26} The broad and strong peak near 3413 cm\(^{-1}\) represents –OH; a sharp peak at approximately 1623 cm\(^{-1}\) should be the skeleton of the aromatic ring; the acromion at 1701 cm\(^{-1}\) is C=O/COOH.\textsuperscript{9,18} The C–H stretching vibration in the alkane structure makes three absorption peaks appear at 1384, 2850, and 2921 cm\(^{-1}\). Meanwhile, 1037 cm\(^{-1}\) is the absorption peak of aliphatic ether/alcohol. In this study, the FTIR spectrum of BL is mainly used to conclude the type of functional group, and then, it was compared with the calculated infrared spectrum of the molecular model to verify the model accuracy.

\subsection*{2.3. X-ray Diffraction Analysis}

XRD is an important tool for analyzing structures, and it has been widely employed in cognizing the coal physical structure.\textsuperscript{27} As shown in Figure 2, a number of disordered frizzy peaks implied that there existed a certain percentage of disordered carbon. Moreover, the 002 peak (26°) represents the aromatic carbon component in coal molecules.\textsuperscript{27} The 002 peak value not only reflects the spatial arrangement of the aromatic ring carbon network layer but also shows the distance between the aromatic ring carbon and the aromatic ring layers. The \(\gamma\) peak (19.20°) represents the aliphatic carbon in coal. The 100 peak (41°) is related to the condensation degree of aromatic rings and the size of the aromatic carbon network layer.

The microcrystalline structure parameters of the BL were calculated based on the XRD peak fitting results (Table 2). For BL, the aromaticity \(f_\gamma\) of BL is 0.27, the layer stacking height \(L_c\) is 7.69 Å, and the interlayer spacing \(d_{002}\) is 3.42 Å. These are the key parameters for constructing its molecular structure. Compared with medium- and high-rank coals, \(I_{002}/I_\gamma\) (the intensity ratio of the 002 peak to the \(\gamma\) peak) of BL is smaller, while \(d_{002}\) is larger. This indicated that the BL molecular structure contains more aliphatic structures and has a poor condensation degree of aromatic rings. In addition, the aromatic layers irregularly arrange in space.\textsuperscript{11,17,30}

\subsection*{2.4. \(^{13}\text{C}\) NMR Analysis}

Figure 3 shows the \(^{13}\text{C}\) NMR peak fitting curve of BL, and Table 3 lists the structural parameters obtained therefrom. The \(^{13}\text{C}\) NMR spectrum of BL was divided into 19 peaks by an Origin 2018 peak fitting module, representing different existence forms of carbon.\textsuperscript{13,31–34} The \(^{13}\text{C}\) NMR peak fitting curve of BL can be divided into 3 chemical shift regions:\textsuperscript{25,35} 0–90 ppm (peaks 1–10) is the aliphatic carbon; 90–170 ppm (peaks 11–17) is the aromatic carbon; 170–220 ppm (peaks 18 and 19) is the carbonyl carbon. The peaks of aliphatic carbon are high and sharp, indicating that the aliphatic carbon amount is dominant in BL, with methylene (26–37 ppm) and aromatic methyl (15–26 ppm) the most. Aromatic carbons are second to aliphatic carbons in the number of structures in BL. Particularly, protonated aromatic carbons (95–124) and aliphatic substituted aromatic carbon (137–149 ppm) account for most. The amount of carbonyl carbon is the least.
Table 2. XRD Peak Fitting Data of BL

| sample | 2θ(002) | 2θ(100) | f_s | I_{002}/I_f | d_{002} | L_2 | L_s | N |
|--------|---------|---------|-----|-------------|---------|-----|-----|---|
| BL     | 26.00   | 19.20   | 41.00 | 0.27        | 0.38    | 3.42 | 7.69 | 15.76 | 2.25 |

![Raw spectrum vs. Fitted spectrum](image)

Figure 3. $^{13}$C NMR peak fitting curve of BL.

Table 3. Structural Parameters of BL

| peak | chemical shift (ppm) | carbon type | symbol | molar content (%) |
|------|-----------------------|-------------|--------|-------------------|
| Aliphatic |                   |             |        |                   |
| 1     | 0–15                  | aliphatic methyl | f_a^1 | 4.86              |
| 2     | 15–26                 | aromatic methyl | f_a^2 | 13.84             |
| 3 and 4 | 26–37                | methylene | f_a^3 | 22.60             |
| 4–6   | 37–50                 | quaternary sp^3C | f_a^4 | 10.18             |
| 7–10  | 50–95                 | oxy-methylene | f_a^11 | 13.06             |
| Aromatic |                   |             |        |                   |
| 11–13 | 95–124                | protonated aromatic carbon | f_a^18 | 13.66             |
| 14    | 124–137               | aromatic bridgehead carbon | f_a^b | 3.22              |
| 15 and 16 | 137–149            | aliphatic substituted aromatic carbon | f_a^1 | 7.92              |
| 17    | 149–164               | oxy-aromatic carbon | f_a^22 | 2.84              |
| 18    | 164–195               | carbonyl in carboxyl and ester | f_a^12 | 2.96              |
| 19    | 195–220               | carbonyl in ketone and aldehyde | f_a^2 | 4.86              |

Table 4 summarizes the structural characteristics obtained by $^{13}$C NMR in order to understand the carbon skeleton of BL better. Among these, $f_a$ and $f_d$ are 27.64 and 64.54%, respectively. That is, there are 28 aromatic carbons and 65 aliphatic carbons in every 100 carbon atoms. This is consistent with the XRD analysis results. Further, the $X_b$ of BL is 0.13, between benzene (0) and naphthalene (0.25), suggesting that the aromatic carbon skeleton of BL mainly includes benzene and naphthalene. The average length ($C_n$) of the methylene chain in BL is 2.85. Also, the substituted degree ($\sigma$) of the aromatic ring is 0.88, implying that each aromatic ring has 5 or 6 substituents.

2.5. XPS Analysis. XPS is able to analyze the elemental composition of coal. Figure 4 displays the XPS peak fitting spectra about the carbon, oxygen, nitrogen, and sulfur in BL. The identification of peak position and binding energy refers to related literature.

Table 5 lists the peak fitting results of carbon, oxygen, nitrogen, and sulfur. The C 1s spectrum suggested that C mainly exists in C–C/C–H with the content of 76.6%, which is consistent with classical theory of coal molecular structure. The O 1s spectrum indicated that oxygen in C–O accounts for 66.6%, corresponding to the broad and strong –OH absorption peak in FTIR at 3413 cm$^{-1}$ followed by COO accounting for 13.3%. The resonance signal of $^{13}$C NMR between 170 and 220 ppm also proved the COO presence. According to the N 1s spectrum, nitrogen exists by the form of pyridine nitrogen, pyrrole nitrogen, quaternary nitrogen, and nitrogen oxides, corresponding to 399.5, 400.4, 401.4, and 403 eV in binding energies, respectively. Among these, the highest content is in pyrrole nitrogen (49.6%) followed by pyridine nitrogen (25.7%). In light of the S 2p spectrum, sulfoxide sulfur is dominant in organic sulfur, accounting for 45.1% of the total sulfur.

2.6. Molecular Structural Characteristics of BL. Excessive molecular weight will greatly prolong the calculation time due to limited running speed of Gaussian 09. This study assumed BL molecular weight to be 3000, for it is enough to reveal the complexity and diversity of the coal structure.

2.6.1. Structure of Aromatic Carbon. The ratio of aromatic bridge carbon to aromatic peripheral carbon ($X_b$) reflects the aromatic structure units in coal molecules. According to the calculation results, the $X_b$ of benzene and naphthalene are 0 and 0.25, respectively. The $X_b$ of BL is 0.13 (Table 4), between benzene (0) and naphthalene (0.25), implying that the aromatic carbon skeleton of BL mainly includes benzene and naphthalene. The XPS spectra show that there are pyrrole and pyridine structures in the BL molecule. Therefore, pyrrole and pyridine are essential in establishing the molecular model. As shown in Table 6, the types and numbers of aromatic structures were determined by constantly adjusting the number of aromatic rings to make the ratio of aromatic bridge carbon to aromatic peripheral carbon close to 0.13. After calculation, there are 51 aromatic carbon atoms. Based on XRD and $^{13}$C NMR analysis, the aromaticity of BL is 27.64%; thereby, the total amount of carbon atoms is 184. According to ultimate analysis in Table 1, the atomic ratios of H/C, O/C, N/C, and S/C are 1.08, 0.27, 0.01, and 0.004, respectively. Therefore, it is easy to calculate that the amount of hydrogen, oxygen, nitrogen, and sulfur are 199, 50, 2, and 1, respectively. Based on the above analysis, the molecular formula of the BL molecular structure model was acquired as $C_{184}H_{199}O_{50}N_{2}S$. 2.6.2. Structural of Aliphatic Carbon. $^{13}$C NMR analysis results show that aliphatic carbon structures include methyl,
methylene, quaternary carbon, and oxygen aliphatic carbon. According to each kind of aliphatic carbon content (Table 3), the amount of methyl, methylene, quaternary carbon, and oxygen aliphatic carbon was calculated to be 34, 41, 19, and 25, respectively.

2.6.3. Structure of Heteroatoms. Oxygen, nitrogen, and sulfur are dominating heteroatoms in BL. Specifically, oxygen takes up the most proportion. Nitrogen and sulfur are harmful elements to the transformation and utilization of BL. According to 13C NMR and XPS analysis results, the oxygen-containing functional groups mainly include methyl ether oxygen, phenolic hydroxyl, carbonyl, and carboxyl groups. The 50 oxygen atoms of the BL molecule are allocated in proportion to each functional group, and the amounts of ether oxygen, phenolic hydroxyl, carbonyl, and carboxyl groups were calculated to be 29, 2, 9, and 5, respectively. The XPS spectrum shows that BL has trace amounts of sulfur and nitrogen, and there are only two nitrogen atoms and one sulfur atom in the molecular formula. Thereby, as shown in Table 6, this study selected the components with higher content to represent the whole based on the method of constructing an average molecular model.

2.7. Molecular Simulation of BL. According to the types and numbers of structural parameters in Table 6, the aromatic ring skeleton and side chain groups of the BL molecule are connected to construct the initial structure model. In order to ensure that the H/C atomic ratio is consistent with the ultimate analysis, the types and amounts of aliphatic carbons need appropriate adjustment in constructing the molecular model. Since the molecules in nature are under the lowest energy, the molecular model can only represent real properties of coal when it stays in the lowest energy. Therefore, the molecular system must be optimized to minimize the energy. In this work, the M06-2X basis set of density functional theory was used to optimize the structure of the initial molecular model. Also, the resulting BL molecular structure model is shown in Figure 5. Then, the experimental FTIR spectrum was compared with the simulated FTIR spectrum calculated by the B3LYP/6-31+G basis set. As shown in Figure 6, the two spectra agree well. Specifically, the difference in 1000–1800 cm⁻¹ may be caused by the stretching vibration of oxygen-containing functional groups. Further, in 3000–3600 cm⁻¹, the experimental FTIR spectrum is wide and strong, while the simulated FTIR spectrum is sharp since only a single molecule was considered without calculated hydrogen bonding between molecules in molecular calculation.

3. CONCLUSIONS

(a) The aromaticity of BL is 27.64%, the ratio of aromatic bridge carbon to aromatic peripheral carbon \( \chi_b \) is 0.13, and the aromatic rings are mainly benzene and naphthalene. The \( L_c \) and \( d_{002} \) are 7.69 and 3.42 Å, respectively. The aliphatic carbon is mainly in the
methyl, methylene, quaternary carbon, and oxygen aliphatic carbon. Oxygen is the most abundant heteroatom in BL, while nitrogen and sulfur are less.

(b) The molecular structure model of BL was successfully constructed, and its molecular formula is C_{184}H_{199}O_{50}N_{2}S. The spatial configuration of the structural model is optimized by the M06-2X functional in density functional theory. The calculated FTIR spectrum is in good agreement with the FTIR spectrum obtained from the experiment, which proves the accuracy of the BL structural model.

(c) The structural model has a majority of aliphatic carbon structures and the poor condensation degree of aromatic rings. The aromatic layers irregularly arrange in space. Each aromatic cluster contains 1–2 rings on average; each aromatic ring has 5 or 6 substituents; the methylene average chain length is 2.85. The aromatic rings are mainly connected by bridging bonds (methylene bond, methoxy, etc.) and aliphatic rings.

4. EXPERIMENTAL METHODS

4.1. Materials. BL was obtained from Baoqing County, Heilongjiang Province, China. Preparation of samples was according to the Chinese national standard GB/T 474-2008. The proximate analysis of coal samples was based on the

| types               | assignment | symbol | number |
|---------------------|------------|--------|--------|
| aromatic carbon     | benzene    |        | 2      |
|                     | naphthalene|        | 3      |
| structure           | pyridine   |        | 1      |
|                     | pyrrole    |        | 1      |
| aliphatic carbon    | methyl     | -CH₃   | 34     |
| structure           | methylene  | -CH₂-  | 41     |
|                     | quaternary | -CH⁻⁻⁻| 19     |
| oxygen aliphatic    | R-O-R      |        | 25     |
| carbon              | ether oxygen| C-O  | 29     |
| heteroatomic        | phenolic hydroxyl | OH | 2      |
| structure           | carbonyl   | RCOOH  | 9      |
|                     | carboxyl   | RCOR   | 5      |
|                     | sulfoxide sulfur | O | 1      |
Chinese national standard GB/T 212-2008. The content of C, H, N, and S in coal was measured using a Multi EA 4000 ultimate analyzer and an SDS 601 sulfur analyzer, and O content was obtained by difference.

4.2. Characterization of Coal Samples. The FTIR experiment was carried out using a German Bruker ALPHA Fourier infrared spectrometer. It was obtained by collating 100 scans with wavenumbers ranging from 400 to 4200 cm\(^{-1}\) at a resolution of 0.06 cm\(^{-1}\).

The XRD spectra of BL were observed by adopting a PANalytical X-ray diffraction analyzer (X’Pert3 Powder) with a copper anode at 40 kV. The X-ray intensities are measured in the range of 5\(^\circ\)–90\(^\circ\) with the scan speed of 2\(^\circ\) min\(^{-1}\). The resulting diffractograms are further smoothened and analyzed by employing a phase quantification method.

The \(^{13}\)C NMR analysis results of BL were acquired from a Bruker AVWB III600, manufactured by Germany Bruker, a cross-polarization magic-angle nuclear magnetic resonance spectrometer (\(^{13}\)C CP/MAS NMR). The cross-polarization (CP) experiments were conducted at ambient temperature with proton decoupling using a relaxation or recycle delay of 3 s. The chemical shift of \(^{13}\)C was calibrated by adamantane (an external standard substance). A total of 4000 scans were collected for increased signal to noise resolution.

4.3. Molecular Structure Model Construction. The construction process of the BL structural model is shown in Figure 7. The computational part was carried out on the Gaussian 09 platform.\(^ {39}\) The M06-2X basis set of density functional theory was employed to optimize the molecular structure. The B3LYP/6-31\(^*\) basis set was used for frequency analysis.\(^ {40}\)

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### Notes
The authors declare no competing financial interest.

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![Figure 6. Calculated FTIR spectrum and experimental FTIR spectrum.](image)

![Figure 7. BL molecular structure model construction flow chart.](image)
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