Molecular Model Construction and Evaluation of Jincheng Anthracite

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ABSTRACT: Despite its importance, limited representations of the anthracite models have been developed. The first molecular representation of Chinese Jincheng anthracite with the incorporation of diverse molecular structures was constructed based on the available analytical data. Three hundred individual aromatic sheets were first built based on the aromatic fringe distribution obtained from high-resolution transmission electron microscopy. Alkyl chains and nitrogen, sulfur, and oxygen heteroatoms were added in the aromatic skeletons to form diverse anthracite structural units based on 13C NMR, X-ray photoelectron spectroscopy, and ultimate analyses. Fifty-five different anthracite molecules were formed by covalent cross-linking considering the constraint imposed by the molecular weight distribution of the Jincheng anthracite obtained from laser desorption time-of-flight mass spectrometry (LD-TOF MS). These molecules were packed into a three-dimensional cell to form a Jincheng anthracite model (C7730H3916O133N123S25). We showed that the proposed model can provide a reasonable representation of the Jincheng anthracite by comparing the simulated and experimental magnetic resonance spectroscopy, LD-TOF MS, density, and X-ray diffraction data. Because of the large, molecularly diverse structure, many anthracite behavioral processes can be further explored using this model in the future.

1. INTRODUCTION

Anthracite is the highest rank coal, which has been used as a raw material for power generation and metallurgical applications. In addition, it has also widely been used to provide various coal-based carbon materials, such as carbon electrodes and activated carbon. At the molecular level, the structure of anthracite will influence its conversion and utilization process. For example, when anthracite is used to produce synthetic graphite, carbon atoms in different chemical environments in the original anthracite would have different microstructures after the graphitization process of anthracite. As a filler, the internal structure and differences in the surface characteristics between the pristine and thermally treated anthracite had an effect on the curing behavior, viscoelastic properties, and thermal stability of epoxy resin compositions. A microscopic understanding of the organic structures of anthracite will aid its conversion processes.

Various experimental methods have been employed to investigate the coal structural properties. An anthracite from New England was examined using the X-ray radial distribution method and it was found that its mean structural unit is around 80% aromatic and consists of polycyclic six-membered rings. A detailed structural analysis of three typical anthracites in China was conducted with a temperature-programmed oxidation approach to obtain the hydrogen content. The identification of the C/H ratio and the heteroatom (oxygen, nitrogen, and sulfur) content allowed the elemental composition, and thus the average size of the aromatic sheets that form the anthracite, to be evaluated. Aso et al. found that the average aromatic layer size is from 2.1 to 3.7 nm. Their study is based on the assumption that the heteroatoms are present along the edges of the sheets and that no defects occur along the basal plane of the aromatic layers. High-resolution transmission electron microscopy (HRTEM) images were also applied to obtain the size of the aromatic layers. The representative organic structure in the Jincheng anthracite was characterized by solid state 13C nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and mass spectrometry (MS). The most likely forms of oxygen in anthracite are assumed as an open ether, closed ether, or carbonyl, while pyrrolic nitrogen, and thiophenic sulfur are the main organic heteroatom species like other ranks of coals discussed in the literature.
A molecular model provides a better understanding concerning the structure–performance relationships of coal. The structural characterization models of coal published exceeded 130. However, most of them are bituminous coal models, such as the computational models for two South Africa bituminous coals and the model for Illinois no. 6 Argonne Premium coal. Limited models of anthracite have been developed despite its importance and it is estimated as the easiest coal to model because of its high rank. The statistically averaged anthracite representation has been designed by Spiro and Kosky to integrate to parameters ally, the molecular weight distribution of coal can be identified by the Jincheng anthracite model. These two models can help better understand the structure of these coals, providing insight into the coal behavior in various areas such as froth flotation and coal dust control at the molecular level, which will be reported on in due course.

2. RESULTS AND DISCUSSION

2.1. Aromatic Skeleton Model Construction. Figure 1 presents the occurrence frequency of the aromatic sheets in the anthracite sample. From Figure 1, it could be found that a 2 × 2 (45.5%) aromatic sheet was present in the highest frequency in the Jincheng anthracite. This is different from the Henan anthracite in which a 1 × 1 aromatic sheet was the most abundant component. At the same time, the small size-condensed aromatic rings, such as the contents of naphthalene and anthracene, are only 1.6 and 2.6%, respectively. Van Niekerk et al. investigated the models of two South Africa bituminous coal samples. They found that the most abundant aromatic moiety in these two models is naphthalene. Castro-Marcano et al. found that the most abundant structural entity in Illinois no. 6 Argonne Premium coal is also naphthalene. Thus, anthracite is generally more aromatic than bituminous coal. Three hundred parallelogram-shaped aromatic sheets were applied to establish the aromatic skeleton of the Jincheng anthracite model based on the aromatic sheet distribution achieved by HRTEM. Using molecular simulations, the number of aromatic sheets characterizes the structural variety of coal, but it is also small enough to manage. The number of different sizes of aromatic sheets is also given in Figure 1. From this figure, it can be found that the number of different sizes of aromatic sheets is a close match to the HRTEM results.

In this stage, the ratio of aromatic bridgehead carbons to aromatic carbons (f_{ar}/f_{at}) in the constructed aromatic skeleton model can be preliminarily estimated. The f_{ar}/f_{at} ratio in the model is 0.48, which is higher than that measured by NMR experiment (0.46) according to Table 1. To match the experimental value, the aromatic sheets in the model were trimmed randomly, which was implemented on aromatic sheets 3 × 3 and greater. It should be noted that the reason for trimming has been explained by Niekker and Mathews.
Parameters: $f^\alpha$, total sp$^2$ carbons; $f^\beta$, carbonyl/carboxyl carbons; $f^\gamma$, aromatic carbons; $f^\delta$, protonated aromatic carbons; $f^\epsilon$, nonprotonated aromatic carbons; $f^\zeta$, phenols and phenolic ethers; $f^\omega$, alkylated aromatic carbons; $f^\varphi$, aromatic bridgehead carbons; $f^\omega$, total sp$^3$ carbons; $f^\Pi$, CH or CH$_2$; $f^\omega$, methyl or methoxyl groups; and $f^\omega$, bonded to oxygen.

### 2.2. Incorporation of Aliphatic Groups

To obtain the desired total sp$^2$ carbon value ($f^\alpha$) derived from NMR (Table 1), aliphatic groups were grafted to the aromatic skeleton randomly through replacing hydrogen atoms in the edge of aromatic sheets using a Perl script. The $f^\delta$ value reveals the number of aliphatic carbons, while the alkylated aromatic carbon value ($f^\omega$) indicates the available sites for the incorporation of aliphatic groups. From Table 1, it can be calculated that the proportion of $f^\omega/f^\delta$ is about 1.2, meaning that the averaged carbon atom number of side chains attached to the aromatic sheet is smaller than 2. This excludes the obvious presence of long-chain alkyl substituent groups in coal molecules. Thus, only methyl groups were considered at the beginning stage. The –CH$_2$– and –CH$_3$– units in bridges could be formed by adjusting these methyl groups to achieve a satisfactory agreement with the experimental results during the cross-linking process of these structural units analyzed below. In this manner, the construction of the main carbon skeleton of the Jincheng anthracite was decided.

### 2.3. Nitrogen, Sulfur, and Oxygen Heteroatom Addition

Because the carbon skeleton of the Jincheng anthracite model has been constructed basically, the number of carbon atoms can be determined. It was found that there were 8348 carbon atoms in the model. Accordingly, the content of oxygen, nitrogen, and sulfur heteroatoms can be determined from the ratio of oxygen, nitrogen, and sulfur to carbon (Table 2). In addition, the distribution of different chemical forms of these heteroatoms in the Jincheng anthracite can be obtained from XPS analysis.

As for the oxygen-containing groups, 144 oxygen atoms should be inserted into the anthracite model according to the O/C ratio. Here, it is noted that the sulphoxide, sulphone, and sulphate groups contain the oxygen atoms. Thirty-six oxygen atoms have been added into the model during the insertion process of sulfur-containing groups. These oxygen atoms should be subtracted from 144 oxygen atoms. Therefore, only 108 oxygen atoms are available to insert into the model. Jincheng anthracite has 86.3% C=O and 13.7% C=O based on XPS analysis, as shown in Figure 2c. The oxygen atoms in the C–O forms can be attributed to ether or hydroxyl groups. Unlike bituminous coal and brown coal, it seems that only ether-type groups exist in anthracite.

### 2.4. Generation of Cross-Linked Molecules and Anthracite Model Construction

After incorporation of alkyl groups and nitrogen, sulfur, oxygen heteroatoms, 300 different anthracite structural units have been constructed. To form coal molecules in the constructed anthracite model, the chemical bonds connecting these structural units were needed. LD-TOF MS can approximate the molecular weight distribution of coal molecules, which can be used to constrain the cross-linking process.

Table 2. Ultimate Analysis and Helium Density of the Jincheng Anthracite

| Elemental Analysis (mol %, d.m.m.f.) | Atomic Ratio | Density (g/cm$^3$) |
|-------------------------------------|--------------|-------------------|
| C | H | O | N | S | H/C | O/C | N/C | S/C | 1.43 |
| 64.8 | 32.8 | 1.1 | 1.0 | 0.2 | 0.51 | 0.017 | 0.015 | 0.0031 |

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Ultimate analysis is a widely used method for quantification of C, H, O, N, and S in coals. The molar percentages of C, H, O, N, and S in Jincheng anthracite sample were 64.8, 32.8, 1.1, 1.0, and 0.2%, respectively. The elemental data were considered to be one of the most critical parameters for coal model construction.30 Thus, the number of C, H, N, S, and O atoms in the anthracite model was modified on the cross-link coal molecules by adding and subtracting operation on account of achieving ultimate analysis. Especially, an initial representation was first found to be too rich in carbon. Thus, the number of carbon atoms was reduced. Finally, a Jincheng anthracite model of 55 molecules with a chemical formula C7730H3916O133N123S25 was reached, which is matched with its experimental elemental composition.

These molecules were incorporated into a cubic periodic cell. After structural relaxation, as observed from Figure 4, the energy-optimized packed model was constructed. The detailed structural model can be found in the Supporting Information.

2.5. Model Evaluation. The structural parameters of the proposed model were evaluated and compared to those obtained from NMR measurements (Table 1). The structural parameters of the molecular representation are consistent with

Figure 3. Comparison of the molecular weight distribution for the Jincheng anthracite determined from LD-TOF MS (pink line) and the constructed molecular model (green bars) after cross-linking and heteroatom addition.

Figure 2. Comparison of (a) nitrogen, (b) sulfur, and (c) oxygen distributions of the Jincheng anthracite based on XPS analysis (pink bar, %) and their final number (blue line) in the proposed molecular model.

Figure 4. Proposed 3D molecular model of the Jincheng anthracite (C7730H3916O133N123S25) composed of 11,927 atoms in a periodic cubic box (for clarification, hydrogen not shown).
the data obtained from experiments. A slight discrepancy is observed in the bridgehead carbon component (\(f_{\text{al}}^B\)), the alkylated aromatic carbons (\(f_{\text{al}}^A\)), and the methyl or methoxyl groups (\(f_{\text{al}}^M\)). The \(f_{\text{al}}^B\) value obtained from the model is higher than the measured one, while the \(f_{\text{al}}^A\) and \(f_{\text{al}}^M\) values derived from the model are lower than the NMR results. This is attributed to the constraint of low H/C ratio (0.51) obtained from the ultimate analysis. This means that one hydrogen atom would be shared by nearly 2 carbon atoms. It is well known that the H/C ratio in the aliphatic chain is about 2.0, which is remarkably higher than the measured H/C ratio. However, the H/C ratio in the aromatic structure is lower: the H/C ratio of the peripheral carbon in the aromatic structure bonded to hydrogen is 1.0, while no hydrogen atoms attach to bridgehead carbon. To match the low experimental H/C ratio, the percentage of total sp\(^3\) carbons (anthracite model, especially the percentage of bridgehead carbon. To match the low experimental H/C ratio, the percentage of aromatic carbon atoms in the proposed anthracite model, especially the percentage of bridgehead carbon atoms should be increased. Correspondingly, the percentage of total sp\(^3\) carbons (\(f_{\text{al}}\)) in the model should be decreased. The decrease of \(f_{\text{al}}\) in the model mainly comes from the contribution of methyl or methoxyl groups (\(f_{\text{al}}^M\)), while the percentage of CH or CH\(_2\) (\(f_{\text{al}}^A\)) is nearly identical to the experimental value because the cross-linking of coal structural units needs the presence of CH and CH\(_2\) groups. The decrease of \(f_{\text{al}}^M\) also leads to the reduction of \(f_{\text{al}}^B\).

The final distributions of the nitrogen, sulfur, and oxygen of the proposed model are also compared with those measured by XPS (Figure 2), and a relatively good coincidence was obtained.

Because the previous models\(^{16-18}\) are represented by only one coal molecule, many important structural characteristics, such as stacking, curvature, and porosity, cannot be included. Thus, the application areas of these models are very limited. Unlike these, anthracite models incorporating molecular diversity from the LD-TOF MS data were an important objective during model generation of the Jincheng anthracite. This is required to capture the continuum of the structural properties. The final molecular weight distribution of the coal molecules present in the proposed model was verified through the comparison with the results of LD-TOF MS, as shown in Figure 3. As depicted in Figure 3, the overall shape and distribution of both the model and experimental data are reasonable.

Density of coal is an important physical property, which can be used to verify the proposed model. The estimated density of the proposed model is 1.47 g/cm\(^3\), which is consistent with the experimentally measured value of 1.43 g/cm\(^3\) (Table 2). Gan et al.\(^{54}\) have measured the helium density data of twelve American anthracite samples, whose range is between 1.25 and 1.53 g/cm\(^3\). The density of our model is also in this range. In addition, the density of the South Africa bituminous coal models\(^{14}\) is 1.28 g/cm\(^3\). The density of the Illinois no. 6 Argonne Premium coal model\(^{1}\) is 1.32 g/cm\(^3\). The densities of two char models derived from South Africa coals\(^{55}\) are 1.82 and 1.87 g/cm\(^3\). It is reasonable that the density of our anthracite model is higher than that of the bituminous coal models and is lower than that of char models, which should be attributed to their different degrees of coalification.

In addition, the structure of our model was also evaluated by comparing the simulated and experimental XRD profiles (Figure 5), which has never been done in the construction process of coal and char models before. The Jincheng anthracite contains a short-range graphite-like construction and this was obvious from the (002) and (10) band positions at the experimental XRD profile that reflect the degree of order of the aromatic sheets. The observed intensity curve, especially the high intensity in the low-angle range, can be influenced by various factors, such as sample packing, cracks, micropores, and other heterogeneities existing in the anthracite because of its structural complexity and heterogeneity.\(^{56}\) Meanwhile, the limited scale and simulation time for the constructed model also influence the simulated XRD spectrum. Therefore, the quantitative comparison between these two patterns cannot be achieved. However, the simulated XRD pattern can capture the main profile of the real anthracite sample despite the slight deviations of the (002) and (10) peaks, implying that the aromatic orientation and stacking can be well reproduced in the model, which further validates the physical structure of our model.

Finally, despite the difference between the statistically averaged model and our model, we also compare our model with two single molecule anthracite models, GBW(E)110031\(^{17}\) and Henan\(^{58}\) anthracite models, published recently too. Both our model and these two models can capture the information obtained from the elemental analysis and NMR spectra. However, unlike our model, the molecular weight distribution of anthracite and the diverse interaction of molecules cannot be represented obviously by these two models. In addition, two key parameters to evaluate coal, sulfur content and aromaticity, are compared here. We found that the S/C atomic ratio in GBW(E)110031 and Henan anthracite models is 0.0099 and 0.0038, respectively, which is higher than that of our model (0.0031). As far as aromaticity is concerned, it should be noted that \(f_J\) values of GBW(E)110031 and Henan anthracite models are 0.81 and 0.83, which are lower than that of our model (0.92), suggesting our model can represent a more mature low-sulfur anthracite.

3. CONCLUSIONS

A molecular model for the Jincheng anthracite has been developed based on a variety of experimental characterization results. An aromatic skeleton model was initially generated based on the aromatic sheet distribution determined by HRTEM. The carbon skeleton was constructed through the
introduction of alkyl side chains into the aromatic layers with the structural parameters derived from $^{13}$C NMR. Organic nitrogen, sulfur, and oxygen heteroatoms were randomly added to the carbon skeleton to form 300 anthracite structural units according to the XPS and elemental composition data. These structural units were cross-linked to meet the constraint of molecular weight distribution indicated by LD-TOF MS, resulting in the formation of 55 structurally diverse anthracite molecules. These individual molecules were finally modified to match the results of ultimate analysis, which were then assembled into a 3D periodic box to form a large scale Jincheng anthracite model ($C_{7758}H_{9360}O_{1331}N_{123}S_{52}$). The reasonable consistency between the model parameters and chemical and physical structural parameters obtained experimentally (NMR, LD-TOF MS, density, and XRD) validated the model. This is the first Chinese anthracite model, which incorporates a molecularly diverse structure and captures the meaningful molecular weight distribution, allowing more accurate behavioral modeling in the future.

4. MATERIALS AND METHODS

4.1. Materials and Preparation. The anthracite was collected from the Jincheng coalfield (Jincheng, Shanxi, China). The coal sample was crushed, comminuted, and screened to pass a 74 μm sieve. The sample was treated employing a HCI/HF/HCl demineralization procedure$^{37}$ to remove the mineral matter. The treated sample was washed using DI water and dried under vacuum.

4.2. $^{13}$C NMR Spectrum Analysis. In order to obtain a quantitative estimation of its carbon skeleton structure parameters, the anthracite sample was subjected to $^{13}$C CP MAS NMR experiments using a Bruker AVANCE III 600 spectrometer with a 3.2 mm MAS probe under 25.152 MHz resonance frequency. For increasing accuracy in the results, a combination of variable contact time and dipolar dephasing techniques was applied.$^{38,39}$

4.3. XPS Analysis. The XPS experimental analysis of samples was carried out using a PerkinElmer PHI−5000C ESCA X-ray photoelectron spectrometer. An excitation source of monochromatic Al Kα X-rays with a power of around 250 W was used. The high voltage was kept at 14.0 kV with a detection angle of 54°.$^{40}$ Electron binding energies were calibrated based on the graphite C 1s peak at 284.6 eV.

4.4. LD-TOF MS. LD-TOF MS is a Micromass MALDI mass spectrometer equipped with a N$_2$ UV laser. A reflectron mode pulse voltage of 2300 V, a source voltage of 15,000 V, and a reflectron voltage of 2000 V were used. The anthracite sample was mixed with Milli-Q water. A sample plate was used to deposit the dispersed slurry and the water was removed by vacuum before measurements. The detailed instrumentation and procedures have been described elsewhere.$^{41}$

4.5. Helium Pycnometry. The true density of the anthracite sample was determined using a JW-M100A helium pycnometer by measuring the pressure change of the probe gas in a calibrated volume.$^{42}$ The sample was degassed at 353 K under vacuum for about 24 h prior to measurement. The helium density of the anthracite model was evaluated based on the mass and the occupied volume of the anthracite molecules in the model with a 1.29 Å helium probe$^{43}$ using the zeo++ software.$^{44}$

4.6. XRD Analysis. The XRD data of the anthracite sample were obtained using a Bruker D8 Advance X-ray powder diffractometer with Cu Kα as an X-ray source. The anthracite sample was scanned from 3 to 90° in the 2θ range with a 0.01° step interval and a 0.1 s/step counter time. To calculate the X-ray diffractogram of the model, the algorithm$^{45}$ implemented in LAMMPS software$^{46}$ has been used in which a 3D mesh of reciprocal lattice nodes is built on a rectangular grid. The diffraction intensity at each reciprocal lattice node has been computed by performing spherical integration and the corresponding normalization of the intensity data using modeled radiation of wavelength lambda.

4.7. HRTEM Analysis. To acquire a statistically representative fringe composition, three HRTEM images of the Jincheng anthracite were converted to binary images and the lattice fringes were extracted and analyzed using an in-house MATLAB-based graphical user interface program. HRTEM is the only analytical method that can investigate the coal structure intuitively at present. The method reported by Mathews et al.$^{30,45}$ was used to quantify the aromatic fringes assuming that the aromatic fringes are of parallelogram catenation. Structural defects in the aromatic sheets of anthracite$^{46}$ were not considered in the present work.

4.8. Molecular Model Construction. Individual molecules were constructed with the structural data based on elemental analyses, XPS, HRTEM, solid-state $^{13}$C MAS NMR, and LDTOF-MS. Among them, elemental, XPS, HRTEM, and solid-state $^{13}$C MAS NMR data were previously applied to achieve the molecular structural data for this coal and the results are available elsewhere.$^{21}$ The structure of the individual molecules was achieved via aromatic skeleton model construction, incorporation of aliphatic groups, heteroatom addition, and generation of cross-linked molecules exploiting several Perl scripts, which was similar to Mathews’ group.$^{29,30}$ To obtain a bulk model of the Jincheng anthracite, the individual molecules were initially enclosed in a 3D periodic cubic cell with the Packmol package$^{47}$ with an initial density of 0.1 g/cm$^3$. Then, a 2.0 ns isothermal-isobaric (NPT) molecular dynamics calculation was conducted at 1.0 atm and 298 K with a time step of 1 fs to combine molecules together to obtain a stable conformation with the Berendsen thermostat and barostat.$^{48}$ Finally, energy minimization was accomplished on the structure to ensure a low-energy configuration. The van der Waals interactions were cut off at 15.5 Å. The long-range cumbic interactions were computed with the PPPM algorithm, with a convergence parameter of 10$^{-5}$. All the molecular mechanics and dynamics simulations were carried out with LAMMPS software$^{44}$ using the improved version of the PCFF force field.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03894.

3D molecular model of Jincheng anthracite (PDB)

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Notes

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