Molecular Model Construction of the Dense Medium Component Scaffold in Coal for Molecular Aggregate Simulation

Lulu Lian, Zhihong Qin, Chunsheng Li, Jinglan Zhou, Qiang Chen, Xiaoqin Yang, and Zhe Lin

ABSTRACT: Coal as an important fossil energy has been comprehensively studied in terms of its structure, reactivity, and application. However, there are few publications reported about the formation mechanism of coal. In order to explore the molecular mechanism of the formation of the dense medium component (DMC) aggregate, which is extracted from coal, the molecular model of the DMC scaffold (DMC-S) was constructed based on a number of X-ray photoelectron spectroscopy, $^{13}$C NMR, and ultimate analysis. Then, DMC-S was further optimized, and the periodic boundary condition was added for molecular mechanics and molecular dynamics simulation. The DMC-S molecule model with a density of 1.05 g/cm$^3$ and a different number of unit cells was obtained after the aforementioned experiments and simulations. When the unit cell contained 12 DMC-S molecules, the absolute value of electrostatic energy significantly increased and the peripheral branch chains in DMC-S interlaced with each other, forming a compact aggregate. The density and macrosize calculated values are all slightly lower than the true relative values because the presence of minerals or small molecules was not included in the model construction. Despite some unavoidable defects, the comparison between the simulated and experimental results validates the DMC-S aggregate model and lays a solid foundation for an in-depth study of DMC and its reactivity.

1. INTRODUCTION

Technologies for coal purification and utilization have been thoroughly studied because of its significant impacts on the economy and environment.1,2 However, there are still many problems such as specific constituents and formation mechanism3−5 existing in the process of coal utilization. Obviously, coal structure plays a decisive role in its reactivity, and significantly influencing the coal utilization. Many researchers6−8 have used the detailed coal molecular structure to construct microscopic system, which are helpful in guiding the coal utilization in adsorption and clean coal field. Molecular models of coal aid in understanding the complexity of the chemical structure of coal and exploring the microscopic property diversity of coal. Thus, many researchers have exerted enormous efforts to clarify the relationship between the coal structure and reactivity.6−12 Classical models of coal including Given,13 Wiser,14 Solomon,15 and Shinn16 highlighted the structure of coal and greatly contributed to the development of coal utilization technology. However, most of the reports published previously focused on the macromolecular structure of raw coal, which definitely cannot fully represent the highly complex structure of coal.

Based on the previous study,17 the embedded features of the structure of coal were first proposed by Qin.18−20 This theory systematically and comprehensively described the separation of the light component, loose medium component, dense medium component (DMC), and heavy component from coal, and the distribution and formation of those four components. Then, the formation of coal was speculated according to the core conception of a coal-embedded structure model. However, the formation mechanism of each component is unclear and the reason for each component having a unique feature is also unknown. For instance, the formation mechanism of nanosized particles (5 nm) in DMC is still unclear. Therefore, in order to enrich the coal-embedded structure theory and find the formation mechanism of each component, in this study, a specific and deep research on the DMC scaffold (DMC-S) was conducted.

Many researchers have utilized the simulation method to get a deep understanding of coal structure and reactivity based on the constructed coal molecular models. In these cases, the pore structure,21,22 adsorption mechanism,23,24 and coal effective...
separation were mainly explored. For example, the relationship between coal’s deformation structure and methane adsorption at different temperatures and pressures was studied by Pan, who revealed that different deformations of coal showed different adsorption capacities and adsorption isotherms. However, there are few reports focusing on the mechanisms of coal molecules’ interaction, mainly because coal’s molecular structure is very complex and difficult to analyze and requires a large-scale computation. The attractive interactions between molecules containing π systems have long been studied by theoreticians and experimentalists. Hunter has taken advantage of Coulomb’s law assuming the charge−charge interactions between two ring systems and acquired three rules as follows: π−π repulsion dominates in a face-to-face geometry; π−σ attraction dominates in an edge-on geometry; and π−σ attraction dominates in an offset π-stacked geometry. Then, the electrostatic energy was minimized when the rings were in an edge-on geometry founded by Fowler. Those research studies provided a basis for further exploration of the mechanism of the DMC-S molecule aggregation.

According to the above statement, the main purposes of this study are as follows: (1) to accurately construct the DMC-S molecule model and (2) to clarify the mechanism of the DMC-S aggregation according to the new theory about embedded features of the coal model and research studies about containing π system molecular. This study aims to provide important information for the understanding of coal structure and coal reactivity.

2. RESULTS AND DISCUSSION

2.1. Model Construction. 2.1.1. Elemental Existing State. The X-ray photoelectron spectroscopy (XPS) spectra of C (1s), O (1s), N (1s), and S (2p) were analyzed and shown in Figure 1. The attribution of each bond can be found in the literature studies. The attributions and some specific structure parameters of these bonds are shown in Table 1. It is worth mentioning that the presence of oxygen-containing compounds in minerals will affect the analysis of the O 1s spectrum, so the bond form of C and O should be analyzed based on the C 1s data.

2.1.2. 13C NMR Analysis. The nuclear magnetic resonance spectrum of DMC-S was studied by means of peak-differentiation-imitating analysis, and the attributions of each functional group were obtained according to the literature studies. The 12 structural parameters of DMC-S were the basis of the model of DMC-S construction. Because the aromaticity, aliphatic carbon number, the ratio of the aromatic

![Figure 1. XPS C 1s spectrum (a), XPS O 1s spectrum (b), XPS N 1s spectrum (c), and XPS S 2p spectrum (d) of the DMC-S sample.](image-url)
nitrogen atoms in the pyrrole-type structure, one nitrogen atom in the form of carbonyl groups. Meanwhile, there are two oxygen atoms in the form of ether oxygen, and two oxygen atoms are present in the aromatic ring. Thus, it can be concluded that two oxygen atoms are present in DMC-S.

Table 2. Structural Parameters of DMC-S

| sample | f_C | f_H | f_N | f_O | f_P | f_S | f_d | f_p | f_s | f_Hd | f_Nd | f_Od | f_Pd | f_Sd |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------|------|------|------|
| DMC-S  | 0.773 | 0.095 | 0.678 | 0.251 | 0.427 | 0.035 | 0.091 | 0.125 | 0.228 | 0.115 | 0.100 | 0.013 |

\[ f_i = f_{i, total} - f_{i, aromatic bridgehead} \]

Table 3. Types of Aromatic Structure Units in the Chemical Structural Model of DMC-S

| Types | Number |
|-------|--------|
| ![Aromatic Structure Units](image) | 6 |
| ![Aromatic Structure Units](image) | 3 |
| ![Aromatic Structure Units](image) | 3 |
| ![Aromatic Structure Units](image) | 1 |
| ![Aromatic Structure Units](image) | 1 |
| ![Aromatic Structure Units](image) | 1 |

Table 4. Energy of the DMC-S

| E_{total} (kcal/mol) | E_{vdw} (kcal/mol) | E_{el} (kcal/mol) | E_{int} (kcal/mol) |
|----------------------|-------------------|-----------------|------------------|
| 808.991              | 246.605           | −27.167         |

The oxygen functional groups in coal include a carboxyl group, phenolic hydroxyl group, methoxyl group, ether oxygen, and so on. With an increase in coalfication, the methoxyl group disappeared first, followed by the carboxyl group. The relative area percentages of C=O− and COO− were 12.15 and 2.4%, respectively, according to XPS of C 1s, and \(^1\)C NMR analysis results show that the number of oxygen atoms was 3. Thus, it can be concluded that two oxygen atoms are present in the form of ether oxygen, and two oxygen atoms are present in the form of carbonyl groups. Meanwhile, there are two nitrogen atoms in the pyrrole-type structure, one nitrogen atom in the thiophene sulfur structure according to Pietrzak and Grzybek’s research studies.\(^{30,31}\)

2.1.3. Construction and Correction of the DMC-S Molecule Structure. The DMC-S molecule model was first drawn by ChemDraw software, and then the energy and frequency of the DMC-S at the HF/3-21G level were calculated by Gaussian 09W software. The proportionality coefficient was set at 0.9085 according to the theory of a complete proportionality coefficient system, which was obtained from calculation results of the 39 known molecules at different levels.\(^37\) The DMC-S molecule model was modified repeatedly until the IR spectrum of the final model was close to the experimental spectrum. As shown in Figure 2, the comparison between the simulated and experimental spectra has a good corresponding relationship.

Figure 2. Comparing calculated and experimental spectra of DMC-S.
2.2. Optimizing the DMC-S Molecule Structure. The structure with the lowest conformational energy of the DMC-S molecule after geometry optimization and an annealing treatment is displayed in Figure 4. The optimized structure model has a compact three-dimensional structure, and the aromatic rings are arranged in an almost parallel manner. It can be seen that the conjugation of $\pi-\pi$ bonds among the aromatic rings plays an important role in the stability of the structure, leading to the decrease of van der Waals energy. Marzec38 studied the interaction between aromatic rings in carbon materials, indicating that the conjugation of $\pi-\pi$ among the aromatic rings exists in coal molecules. The specific energy parameters after optimizing are shown in Table 4.

2.3. Density of the DMC-S Molecule. Figure 5 presents the relationship between potential energy and density after adding periodic boundary conditions. It has been verified that the density of the minimum point after the lowest point energy configuration should be the density of the coal under formation conditions.39 Therefore, the simulated density of the DMC-S molecule model is 1.05 g/cm³ according to Figure 5. However, the measured density of the DMC-S is 1.15 g/cm³ because the pores in the macromolecular structure of coal are filled with a lot of small molecules, which are difficult to exclude in the process of density testing. Thus, it is reasonable that the measured density of the DMC is higher than the density of the simulated DMC-S molecule. The crystal structure model is shown in Figure 6.

2.4. Microstructure Characterizations. 2.4.1. Energy Parameters of Different Unit Cells. The intermolecular interaction energy has an important effect on the aggregation capabilities and morphology of molecules.40 In containing $\pi$ system coal macromolecular aggregates, intermolecular interactions mainly include aromatic $\pi-\pi$ stacking, $\pi-\sigma$ electrostatic interactions, Brønsted acid–base interactions, hydrogen bonding, metal coordination complexes, and interactions between cycloalkyl and alkyl groups.41
The energy parameters of different unit cells are shown in Figure 7. It shows that the bond energy, angle energy, torsion energy, and van der Waals energy increase linearly with the increase of the number of molecules. When the unit cell contains 12 DMC-S molecules, the total potential energy decreases slightly, whereas the absolute value of electrostatic interaction energy sharply increases (Figure 8). This means that the electrostatic attraction among the molecules increases, and the aggregation capabilities of the molecules increases.42

2.4.2. Radius of Gyration Analysis. It has been reported that the molecular configuration and intermolecular interaction have important effects on the mechanical hardness of polymer materials.43 However, the effect of the molecular number on the molecular flexibility has not been deeply explored. Conceptually, flexibility denotes the ability of a given structure to be deformed as a result of an external perturbation.44 Molecular flexibility is thus a crucial determinant of binding affinity in the process of intramolecular interaction.45 The theoretical definition of radius of gyration is as follows: assuming that the polymer chain contains many unit chains and the mass of each unit chain is \( m_i \), the distance from the center of gravity of the polymer chain to the \( i \) unit chain is a vector \( r_i \), so the root mean square of all the units of chain is the radius of gyration (\( R_g \)) which can represent molecular size and flexibility.46 It is defined as a squared distance between monomers in a given conformation and the molecule’s center of mass, and the formula is as follows

\[
R_g = \sqrt{\frac{\sum m_i r_i^2}{\sum m_i}}
\]

\( m_i \) represents mass of the \( i \) atom and \( r_i \) represents the position of the \( i \) atom.

The relationship between the gyration radius of the aggregate and the number of DMC-S is shown in Figure 9.

\[\text{Figure 7. Energy parameters for different unit cells (u.c. stands for the unit cell).}\]

\[\text{Figure 8. Electrostatic energy for different unit cells (u.c. stands for the unit cell).}\]

\[\text{Figure 9. Gyration radius of different numbers of DMC-S (u.c. stands for the unit cell).}\]

\[\text{Figure 10. Different dihedral angles in the DMC-S model.}\]

The \( R_g \) in different numbers of DMC-S are distributed in 8.8–10.2 Å, which indicates that intermolecular forces affect the size and flexibility of the aggregation. The gyration radius of DMC-S-12 is larger than others, indicating that DMC-S-12 has more flexibility, which benefits the formation of a cluster.

2.4.3. Torsional Angle Analysis. Conformational change in the \( \pi \) system containing molecules is mainly due to the torsion of single bonds.47 However, for the reticular structure of DMC-S, the torsion of single bonds plays an important role in molecular conformational change. Three torsional angles in the DMC-S model were chosen to deeply study the conformational change of DMC-S (Figure 10).

The range of the dihedral angle \( A \) in different unit cells can be found in Figure 11. The dihedral angle \( A \) in DMC-S-1 is in the range 46°–132°, and the range of the dihedral angle \( A \) in DMC-S-6, DMC-S-12, and DMC-S-16 is larger than in DMC-S-1 because they suffered from intermolecular interaction. The
dashed line represents the symmetry axis of the dihedral angle range curve in Figure 11. It can be found that the distance between the dashed line of DMC-S-12 and the dashed line of DMC-S-1 is the largest, which indicates that the dihedral angle A in DMC-S-12 ranges in a large scale. Meanwhile, the range of the dihedral angle C is concentrated in a narrow scale compared with the other two dihedral angles (Figure 12), indicating that the dihedral angle C located in the middle of the DMC-S molecule is difficult to reverse. The presented work shows that the peripheral branch chains of different DMC-S molecules are easier to interweave with each other, which help the aggregation become more stable and compact.

2.4.4. Density of DMC-S-12 Simulation. The DMC-S-12 aggregate added the periodic boundary conditions using the amorphous cell module under different densities. The relationship between potential energy and density can be seen in Figure 13. The simulation density of DMC-S-12 is 1.08 g/cm³, which is slightly higher than the simulated density of DMC-S, indicating that the increased intermolecular forces in DMC-S-12 make the molecules more compact. The density’s consistency validates that DMC-S-12 is a plausible aggregate.

2.5. Comparison between the Simulation and Experimental Results. Transmission electron microscopy (TEM) images of the substances extracted from coal using mixed solvents are shown in Figure 14. It can be seen that the aggregation particles belong to the DMC component whose size is approximately 5 nm. The equilibrated molecular model and supercell model of DMC-S-12 are shown in Figure 15 (37.88 Å × 37.88 Å × 37.8 Å). It can be seen that DMC-S-12 seems to have undergone a phase separation, which indicates that 12 DMC-S molecules formed an aggregate. In addition, the size of DMC-S-12 is slightly smaller than the size of a DMC particle observed by TEM, likely because of the entrained small molecules existing in the DMC particle. The comparison between the simulated and experimental results not only validates about 5 nm DMC particle containing 12 DMC-S molecules but also yields a model with periodic boundary conditions for further simulation.
3. EXPERIMENTAL MATERIALS

3.1. Preparation of DMC-S. The preparation of DMC-S can be found in the literature. DMC is the major component of coal, and it is generally acquired by extraction and back-extraction technology using CS$_2$ and N-methyl-2-pyrrolidinone (NMP) as solvents from Tongting coal extract of DMC. A small amount of DMC components was enveloped in a 450 nm Teflon film and filter paper and the samples were put into a 22 mL extraction tank of the rapid solvent extraction apparatus. DMC components were successively extracted with N-hexane, methanol, acetone, and chloroform solvents under the temperature of 100 °C and the pressure of 10 MPa. Extractions from the DMC components were named DMC-S.

3.2. Morphological Property of DMC. The copper mesh of a JEM-200CX transmission electron microscope (Japan) was covered with collodium as the supporting film in the CS$_2$ and NMP extraction liquid and moved slowly along the normal direction of the copper mesh for about 30 s. The copper mesh was taken out and put in a 30 L sealing cover for 24 h, and the morphology of DMC was observed by TEM. The accelerating voltage was 20–200 kV, and magnification was 25–1,030,000, achieving the resolution value of 0.24 nm.

3.3. Characterization of DMC-S. The ultimate analysis and density of DMC-S are listed in Table 1. XPS was conducted on a Thermo-ESCALAB 250XI photoelectron spectrometer, equipped with a monochromatized Al Ka X-ray source; the charge correction was corrected using carbon C 1s = 284.8 eV.

To examine the chemical structure features of DMC-S, $^{13}$C NMR experiments were performed on a Bruker Avance III model superconducting nuclear magnetic resonance instrument, the $^{13}$C testing frequency was 75.48 MHz, the spectral width was 500 ppm, the sampling time was 0.018 s, and the pulse width was 500 ppm, the sampling time was 0.018 s, and the pulse width was 500 ppm, the sampling time was 0.018 s, and the pulse width was 500 ppm, the sampling time was 0.018 s, and the pulse width was 500 ppm, the sampling time was 0.018 s, and the pulse width was 500 ppm. The cycle time delay was 2 s, and the scanning number was 2048.

4. THEORETICAL BASIS

4.1. Optimizing the DMC-S Molecule Structure. Geometry optimization calculations were conducted using Smart Minimizer in the Forcite module of Materials Studio 8.0 software following the Universal force field method for the calculations. The universal force field is represented as follows

$$E = E_R + E_0 + E_O + E_w + E_{vdw} + E_{el}$$

The valence interactions consist of bond stretching ($E_R$) and angular distortions. Angular distortions are composed of bond angle bending ($E_0$), dihedral angle torsion ($E_O$), and inversion terms ($E_w$). The nonbonded interactions consist of van der Waals ($E_{vdw}$) terms and electrostatic ($E_{el}$) terms. Meanwhile, the other parameter settings were as follows: the number of iterations was $1 \times 10^3$; the convergence criterion was ultratine; the energy difference was set to 0.001 kcal/mol; the Gasteiger method was chosen to balance the charge. Kulun force and van der Waals were calculated using the atom-based method. Then, the anneal item in the Forcite module taskbar was used to overcome the energy ridge of the molecular structure and make the energy of the system reach the optimum geometric state in the molecular dynamics (MD) simulation. The parameter settings were as follows: the initial temperature was 300 K, the maximum temperature was 600 K, and the heating rate was 3 K/times. The simulation time was 2000 ps under the NVT (temperature at 300 K) ensemble. The temperature control method was the Nose and the number of times for the annealing simulation was set to 20.

4.2. Density of the DMC-S Molecule. The periodic boundary conditions were added to the energy-optimized geometry of the DMC-S model, and a number of the optimal geometry configurations under periodic boundary conditions were generated using the amorphous cell module in the MS package. Then, the optimal density according to the relationship between the total potential energy and the calculated density of DMC-S was obtained.

4.3. MD Simulation Strategies of Different Configuration Units. The different configuration units (DMC-S-1 represents one DMC-S molecule in the unit cell, DMC-S-2 represents two DMC-S molecules in the unit cell, and so on) were created in an amorphous cell module, and then an annealing procedure was adopted. The parameter settings were as follows: the initial temperature was 300 K, the maximum temperature was 600 K, and the heating rate was 3 K/times. The simulation time was 2000 ps under the NVT (temperature at 300 K) ensemble and 2000 ps NPT (pressure at 0.01 GPa) later. The annealing simulation was repeated 20 times. Afterward, a further 5000 ps NVT MD simulation was performed at 300 K. In dynamic systems, Nose’s thermostat and Berendsen’s barostat were used to maintain the temperature and pressure.

5. CONCLUSIONS

The structural model of DMC-S was constructed, with a molecular formula of C$_{195}$H$_{179}$N$_3$O$_4$S in accordance with experimental elemental analysis. The density of the DMC-S molecule was 1.05 g/cm$^3$ in good agreement with the experimental measurement. The absolute value of electrostatic energy of DMC-S-12 significantly increased because the mutual attraction between the molecules increased. Meanwhile, the peripheral branch chains of different molecules were tangled up with each other forming an aggregate according to the analysis results of energy parameters, gyration radius, and torsional angle. In addition, the density of the DMC-S-12 aggregate was slightly higher (1.08 g/cm$^3$) than the density of DMC-S, indicating that DMC-S-12 was a compact and stable aggregate. The size of the DMC-S-12 aggregate was consistent with the size of the DMC particle observed by TEM. The result represents a fundamental building block from which the aggregate can be developed to permit an in-depth study of DMC, its reactivity, and coal embedded-structure theory.

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Notes
The authors declare no competing financial interest.

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