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Article

Molecular Model Construction and Optimization Study of Gas Coal in the Huainan Mining Area

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1. Introduction

Coal is an important basic energy source and industrial raw material in China, and it accounts for more than 90% of the fossil resource reserves [1,2]. The gradual depletion of shallow coal resources has increased the depth of coal mining. Fire in mines caused by coal spontaneous combustion often occurs and becomes one of the main disasters in coal mine production [3], which seriously affects economic development and threatens the lives of coal miners [4,5]. The prevention of coal spontaneous combustion fires has been major topics of research in the field of coal mine safety [6–8]. At present, many studies generally agree that coal spontaneous combustion is caused by coal–oxygen recombination [9]. However, coal–oxygen recombination is a complex process. The adsorption mechanism of oxygen in coal is difficult to reveal by experimental means. A mutual reflection relationship exists between the properties and structure of coal [10]. As a result, the construction and optimization of the coal macromolecule model is the theoretical basis for revealing the mechanism of coal spontaneous combustion.

The construction of the coal molecular model provides foundation for molecular simulation. The research methods are mainly divided into physical and chemical methods [11–15]. ^{13}C nuclear magnetic resonance spectroscopy (^{13}C -NMR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and other physical methods were used to obtain relevant information on the construction of the molecular structure model [16–18]. Early coal chemical structure models, such as the Wiser, Given, and Shinn models [19–21], were widely recognized by scholars. The rapid development of computer technology in recent years has encouraged scholars to use modern analysis methods combined with computer-aided software in building coal molecular models. The mechanism and reaction

characteristics of coal spontaneous combustion were investigated by molecular simulation [22–25]. Carlson [26] simulated the three-dimensional structures of four bituminous coal models using computer software and concluded that molecular modeling is an effective means to study coal structure. Wu et al. [27] systematically investigated the competitive adsorption characteristics of smoke from coal-fired power plants using molecular dynamics (MD) simulation software and on the basis of the construction of the molecular structure of coal. The results showed that the absolute adsorption decreases with the increase in temperature and water content in coal. However, the absolute adsorption increases with the rise in pressure and the corresponding volumetric mole fraction. Hong et al. [28] structured the coal char model and studied the combustion and gasification properties of coal char using the reaction MD (ReaxFF MD) simulation method. Hao et al. [29] investigated the adsorption characteristics of different gasses ($\text{CH}_4/\text{CO}_2/\text{N}_2$) on the coal surface by establishing the molecular model of anthracite coal and revealed the thermodynamic parameters of coal surface adsorption using the molecular simulation. The results showed that the adsorption amounts of the three gases on the coal surface are shown in descending order: $\text{CO}_2 > \text{CH}_4 > \text{N}_2$, according to adsorption affinity and thermodynamic parameters. Meng et al. [30] revealed the relationships between different grades of coal and methane adsorption using the method of the grand canonical Monte Carlo and the density functional theory based on studying four different grades of coal models. Wei et al. [31] constructed a macromolecular structure model of Zaoquan coal using proximate analysis, ultimate analysis, XPS, ^{13}C solid-state NMR, and other physical methods together with computer software. They determined the effects of different final temperatures and heating rates on pyrolysis behavior. Chai and Zeng [32] probed the changes in macroscopic and microscopic characteristics of Wucuiwan coal at different temperatures by constructing a molecular model. Ping et al. [33] analyzed the mirror and inert groups of Shanghai Miao bituminous coal by using ^{13}C solid-state NMR, Fourier-transform infrared spectroscopy, and XPS. The differences between the structure and functional groups in the molecules were explored to construct molecular structure models.

The studies of the abovementioned scholars indicate that the characteristics of coal oxygen adsorption were deeply explored by molecular simulation. The accuracy of the coal molecular model is the focus of our subsequent research, which has an important effect on the research results. The coal macromolecular model was a collection of analytical results of experimental data based on the characterized coal microstructure parameters, which must be further analyzed or verified. However, the verification methods used by the abovementioned scholars need to be further improved. The authors are mainly engaged in the research on coal spontaneous combustion fire prevention and control and coal mine safety. Thus, the gas coal in the Huainan mining area was further studied in this work based on comprehensive research methods. Proximate analysis, ultimate analysis, ^{13}C -NMR, XPS, and XRD were used to realize the information characterization of gas coal. The rationality of the macromolecular structure model based on the characterization information was verified by the carbon spectrum and density simulation of coal molecules. A more stable and accurate molecular structure model was obtained using the Materia Studio (MS) software optimization, which provided a method for predicting the macromolecular model of coal and theoretical support for preventing the occurrence of coal spontaneous combustion fire at the molecular level.

2. Experimental Section

2.1. Elemental and Industrial Analysis Tests

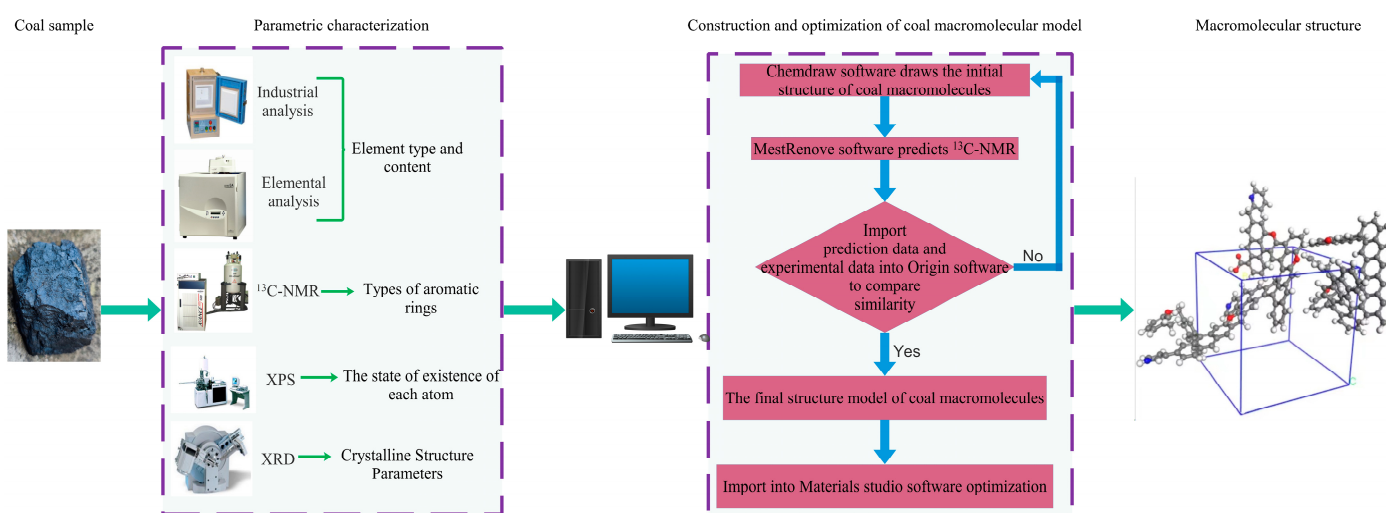
The elemental and industrial analysis tests were carried out by SX2-2.5-10 apparatus of Beijing Zhongxing weiye and Thermo Scientific Flash 2000 apparatus based on Chinese national standards GB/T212-2008 and GB/T476-2008. The experimental results are shown in Table 1.

Table 1. The results of elemental and industrial analysis tests.

Proximate Analysis (w%, daf)				Ultimate Analysis (wt%, daf)				
M _{ad}	A _{ad}	V _{daf}	FC _{ad}	C _{ad}	H _{ad}	O _{ad}	N _{ad}	S _{t,d}
0.79	8.288	17.3	70.922	66.12	4.56	4.37	1.28	0.18

2.2. Experimental Protocol

The gas coal samples were taken from the Huainan mining area in Anhui Province. The samples were crushed and sieved into 60–80 mesh particles before the experiments. The information on each carbon atom, the structural parameters of microcrystals, and the occurrence modes of C, O, N, and S atoms in the samples was obtained by ¹³C-NMR, XPS, and XRD tests. The macromolecular model of coal was constructed and optimized by the Materia Studio (MS) software. The specific process is shown in Figure 1.

**Figure 1.** Gas coal macromolecular modeling flow chart.

(1) ¹³C-NMR spectroscopy (¹³C-NMR)

The carbon atoms information was obtained using the Bruker400m solid-state NMR (¹³C-NMR) instrument. The experiment used high-resolution solid-state nuclear magnetic resonance spectroscopy. The MAS spin rate was 10 kHz, the recovery time was 4 s, and the pulse width was 4.5 μs. The pre-scan delay was 6.5 μs, and the scanning number was 3000.

(2) X-ray diffraction (XRD)

The microstructure parameters of coal were obtained using the German Bruker D8 Advance X-ray diffractometer (XRD) with Cu target radiation. The specified parameters were as follows: the counting time was 19.2 sec/step, the step size was 0.02034°, the scan range was 5°–80°, the voltage was 40 kV, and the current was 40 mA.

(3) X-ray photoelectron spectroscopy (XPS)

The occurrence modes of C, O, N, and S atoms were obtained using the X-ray photoelectron spectrometer from Thermo Fisher Scientific, and the parameters were as follows: the monochromatic was Al Ka, the energy was 1486.6 eV, the angle of electron emission was 45°, the beam spot was 500 μm, the number of scans was 5, and the charge correction was corrected using carbon C1s = 284.8 eV.

3. Results and Discussions

3.1. The Analysis of the Elemental Normalization and the Atomic Ratio

The content of elements, types, and the atomic percent were determined by proximate and ultimate analysis. The contents of oxygen in Table 1 were calculated by deducting the

moisture and ash. The ultimate analysis was normalized to calculate the atomic ratio of each atom. The results are shown in Table 2. Based on the atomic ratios, if the number of C atoms in coal is n , the molecular formula of coal can be expressed as $C_nH_{0.828n}O_{0.05n}N_{0.017n}S_{0.001n}$.

Table 2. The results of the elemental normalization and the atomic ratio.

Normalization (w%, daf)					Atomic Ratio			
C	H	O	N	S	H/C	O/C	N/C	S/C
86.42	5.96	5.71	1.67	0.24	0.828	0.050	0.017	0.001

3.2. ^{13}C -NMR Test Results and Analysis

The ^{13}C -NMR spectrums were fitted to obtain carbon atoms information by using Peak Fit software. In Figure 2, the main carbon signal peaks of coal were located with the chemical shift between $0\text{ ppm} - 50 \times 10^{-6}\text{ ppm}$ and $100 \times 10^{-6}\text{ ppm} - 170 \times 10^{-6}\text{ ppm}$, which belonged to aliphatic carbon and aromatic carbon, respectively [34]. Each peak was classified based on peak position attribution results in the literature [35], and the classified results are shown in Table 3. According to the calculation method of the 12 structural parameters in the literature [36] (the ascribing positions of different peaks were determined by the results of ^{13}C -NMR peak fitting, and the peak values were substituted into the formula to calculate the structural parameters of coal molecules) and the chemical shift attribution of carbon in Table 3, the 12 structural parameters of coal were calculated, and the results are shown in Table 4. In Table 4, the proportion of aromatic carbon (f_a') in gas coal was 87.70%, which was the main body of a constituting macromolecule. The proportion of aliphatic carbon (f_{a1}) was 12%, and carbonyl and carboxyl carbon (f_a^C) were 0.3%, unprotonated aromatic carbons bridged with aromatic carbon (f_a^B) was 25.3%. $X_{BP} = f_a^B / (f_a^H + f_a^P + f_a^S) = 0.407$, which was the ratio of aromatic bridge carbon to circumferential carbon, and the X_{BP} value reflected the size of aromatic clusters in coal [37]. The types and numbers of aromatic rings in the macromolecule structure were inferred by the size of aromatic clusters in combination with the ultimate analysis.

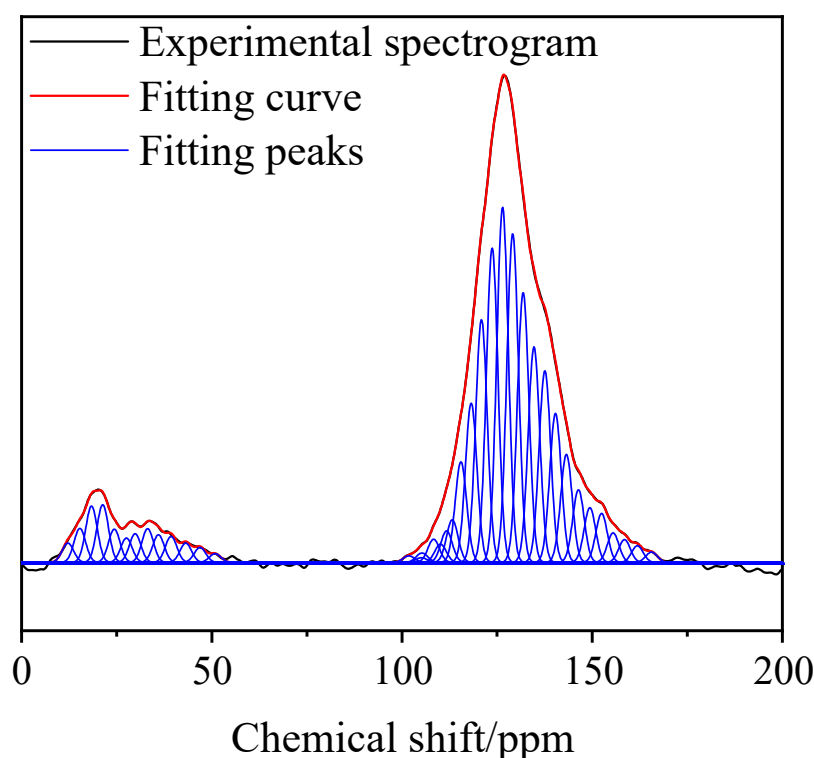


Figure 2. ^{13}C -NMR split-peak-fitting spectrum of gas coal.

Table 3. Carbon structure attribution and proportion.

Peak	Area	Center (ppm)	Relative Area	Attribution	Peak	Area	Center (ppm)	Relative Area	Attribution
1	0.5375	12.16	0.006	A ₁	20	0.1183	113.22	0.013	A ₆
2	0.9461	15.30	0.011	A ₁	21	0.279	115.48	0.031	A ₆
3	1.565	18.37	0.018	A ₂	22	0.4417	118.19	0.050	A ₆
4	1.603	21.32	0.018	A ₂	23	0.6737	120.89	0.076	A ₆
5	0.9237	24.36	0.010	A ₃	24	0.8716	123.70	0.098	A ₆
6	0.6759	27.55	0.008	A ₃	25	0.9847	126.44	0.111	A ₆
7	0.7956	29.85	0.009	A ₃	26	0.9119	129.09	0.102	A ₇
8	0.9374	33.14	0.011	A ₃	27	0.7487	131.85	0.084	A ₇
9	0.7669	35.97	0.009	A ₃	28	0.5977	134.70	0.067	A ₇
10	0.723	39.29	0.008	A ₄	29	0.5317	137.56	0.060	A ₈
11	0.5363	43.15	0.006	A ₄	30	0.4133	140.35	0.046	A ₈
12	0.4164	46.89	0.005	A ₄	31	0.2996	143.23	0.034	A ₈
13	0.243	50.88	0.003	A ₅	32	0.2015	146.39	0.023	A ₈
14	0.1836	101.81	0.002	A ₆	33	0.152	149.39	0.017	A ₉
15	0.1305	105.13	0.001	A ₆	34	0.1359	152.47	0.015	A ₉
16	0.2635	105.25	0.003	A ₆	35	0.08195	155.50	0.009	A ₉
17	0.6444	108.31	0.007	A ₆	36	0.06333	158.49	0.007	A ₉
18	0.5065	110.12	0.006	A ₆	37	0.0462	161.88	0.005	A ₉
19	0.8758	111.72	0.010	A ₆	38	0.02881	165.59	0.003	A ₁₀

Note: A₁—lipid methyl carbon; A₂—aromatic cyclic methyl carbon; A₃—methylene carbon and methine carbon; A₄—methine carbon and quaternary carbon; A₅—oxygen-conjugated methylene and oxygen-conjugated methylene carbon; A₆—protonated aromatic carbon; A₇—bridgehead aromatic carbon; A₈—side branch aromatic carbon; A₉—oxygen replaces aromatic carbon; A₁₀—carboxy carbon.

Table 4. Structure parameters of gas coal.

Type	Symbol	Value	Type	Symbol	Value
Total aromatic carbon	f_a	0.880	Alkylated aromatic	f_a^S	0.179
Carbonyl groups	f_a^C	0.003	Aromatic bridgehead	f_a^B	0.253
In an aromatic ring	f_a^I	0.877	Total aliphatic carbon	f_{a1}	0.120
Nonprotonated and aromatic	f_a^N	0.470	CH ₃	f_{a1}^*	0.046
Protonated and aromatic	f_a^H	0.407	CH or CH ₂	f_{a1}^H	0.065
Phenolic or phenolic ether	f_a^P	0.037	Bonded to oxygen	f_{a1}^0	0.009

3.3. XRD Test Results and Analyses

To obtain the microcrystalline structure parameters of samples, the XRD test results were fitted by using the Jade software, and the results are reported in Figure 3. The characteristic peaks of 002 and 100 were located at 24.879° and 43.254°, respectively. According to the calculation method in the literature [38,39] and combined with the calculation results in Figure 3, the parameters including L_a (the mean diameter of aromatic ring lamellar in a stacked cluster), L_c (the effective stacking height of aromatic ring layers along the vertical direction of aromatic core), d_{002} (the layer spacing of aromatic ring lamellar), and N_{ave} (the effective stacking layer number of aromatic ring layers) were calculated, and the L_a , L_c , and d_{002} were 11.77, 6.62, and 3.575 nm, respectively. The calculated microcrystalline structure parameters provided effective data for the subsequent construction of the coal macromolecular structure model and the stacking mode of each aromatic layer in the model.

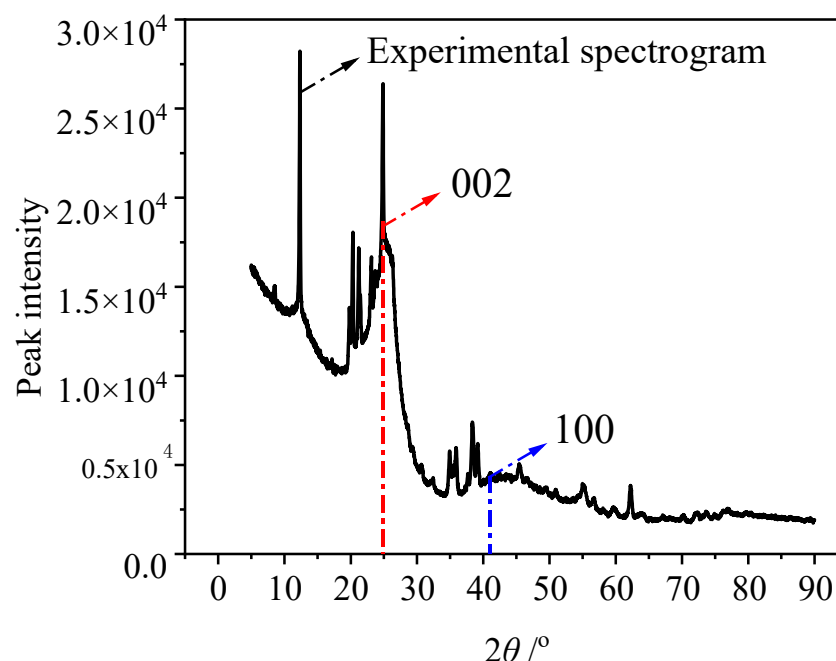


Figure 3. XRD spectrum of gas coal.

3.4. XPS Test Results and Analyses

The modes of occurrence of C, O, N, and S atoms in coal were performed by the XPS test to infer the connection patterns of aromatic rings. The result of XPS test is presented in Figure 4a. The spectrum was fitted by the Avantage software, and the fitting results are shown in Figure 4b–d. According to the results of the ultimate analysis, the content of S was only 0.18%, which was not enough for one S atom. Thus, it was not considered in the molecular structure. The molecular formula of gas coal was expressed as $C_nH_{0.828n}O_{0.05n}N_{0.017n}$.

The results of C fitted spectra are shown in Figure 4b. There were four peak positions in the C split peak spectrum, which indicated that the carbon in coal mainly existed in four forms. The centers of the four peaks were 284.45 eV, 284.8 eV, 285.18 eV, and 290.06 eV. These different peaks were assigned to C–C, C–H, C–O, and C=O, respectively. Among them, the content ratio of C–C, C–H, C–O, and C=O was 0.56:0.29:0.11:0.05.

The results of O fitted spectra are shown in Figure 4c. From Figure 4c, ether oxygen bond (C–O), carbonyl (C=O), and carboxyl (COOH) existed in the oxygen spectrogram. The proportions of oxygen were 52%, 46.0%, and 2%, respectively. The centers of the three peaks were 531.3 eV, 532.35 eV, and 535.41 eV. Therefore, the content ratio between C–O, C=O, and COOH was 0.26:0.23:0.01.

The results of N fitted spectra are shown in Figure 4d. The P_1 peak (Pyridinic nitrogen N-6) located at 399.3 eV was the largest, accounting for 51.86%. The second was the P_2 peak (Pyridinic nitrogen N-5) located at 400.02 eV, accounting for 25.93%. The P_3 peak at 401.65 eV belonged to quaternary nitrogen, accounting for 17.27%. The P_4 peak with the smallest proportion at 404.5 eV belonged to nitrogen oxide, accounting for 4.94%, which was formed by the oxidation of pyridine nitrogen and pyrrole nitrogen in air.

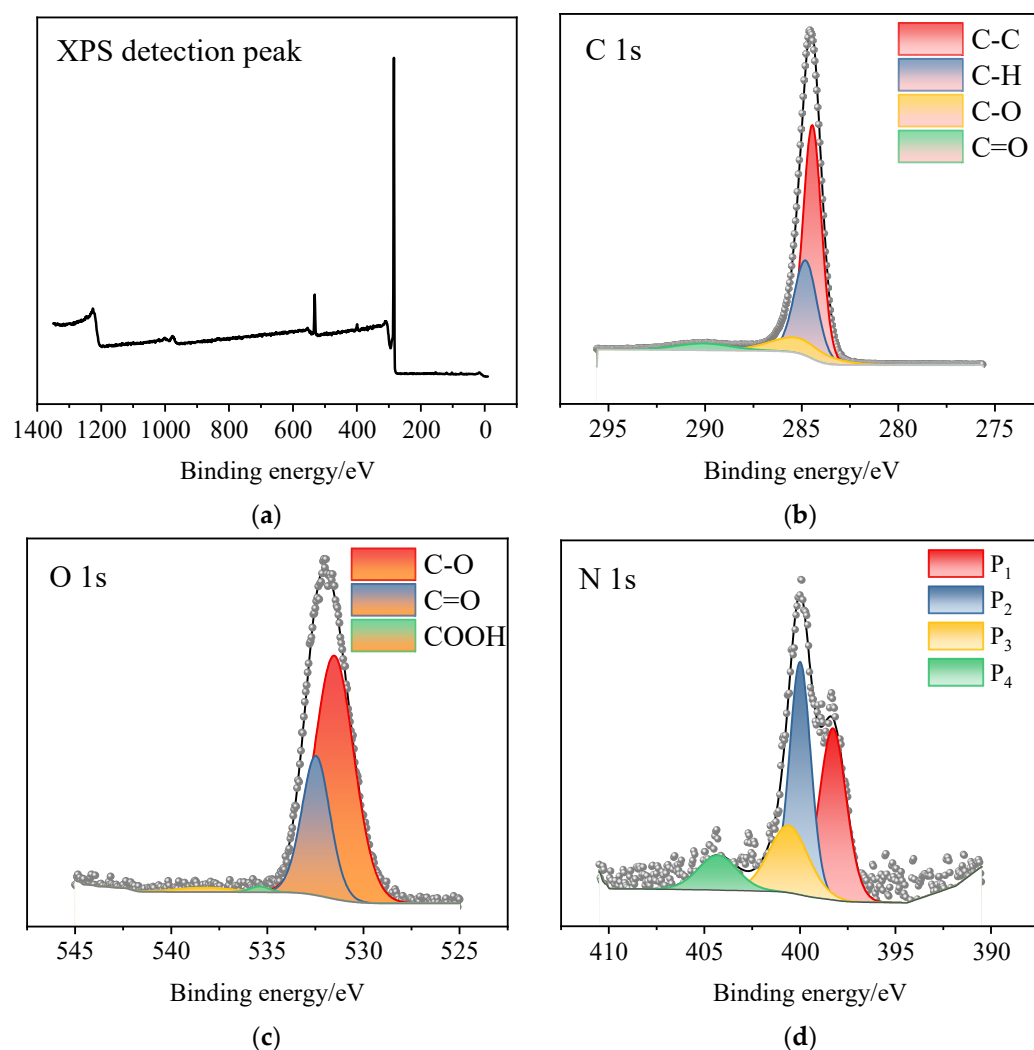


Figure 4. Peaking fitting spectra of gas coal X-ray photoelectron spectroscopy: (a) XPS detection spectrum, (b) C split-peak fitting spectra, (c) O split-peak fitting spectra, (d) N split-peak fitting spectra.

3.5. Construction of the Molecular Structure Model of Gas Coal

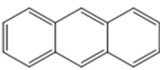
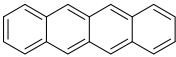
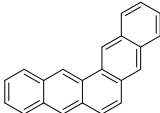
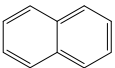
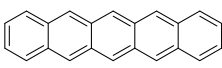
3.5.1. Aromatic Structures

According to Section 2.2, the X_{BP} of gas coal in this study was 0.407, which was close to the X_{BP} values of phenanthrene and anthracene in the literature [21]. According to the conclusion of the molecular structure in the literature [11], the macromolecular structure was dominated by anthracene and phenanthrene, followed by the pyrene and naphthalene rings. The bridging carbon ratio was made close to the calculated value by adjusting the numbers of various aromatic rings. The types and numbers of aromatic structures in the molecular structure are shown in Table 5.

3.5.2. Aliphatic Carbon Structures

The aliphatic carbon in coal mainly exists in the form of branched chain, linked aromatic rings, aliphatic rings, side chains, and bridging carbons [29]. Based on the aromatic carbon ratio, the number of aromatic carbon atoms, and Table 5, the total and aliphatic carbon atoms were calculated to be 181 and 21, respectively. From the abovementioned data, the number of hydrogen atoms in gas coal was calculated to be 150. The proportions of f_{a1}^H , f_{a1}^* , and f_{a1}^0 in gas coal were 6.5%, 4.6%, and 0.9%, respectively. Therefore, the aliphatic carbon atoms in gas coal mostly existed in the forms of methyl, methylene, hypomethyl, and quaternary carbon, and the oxygen-linked lipid carbon was the least abundant.

Table 5. The types and numbers of aromatic structures in gas coal.

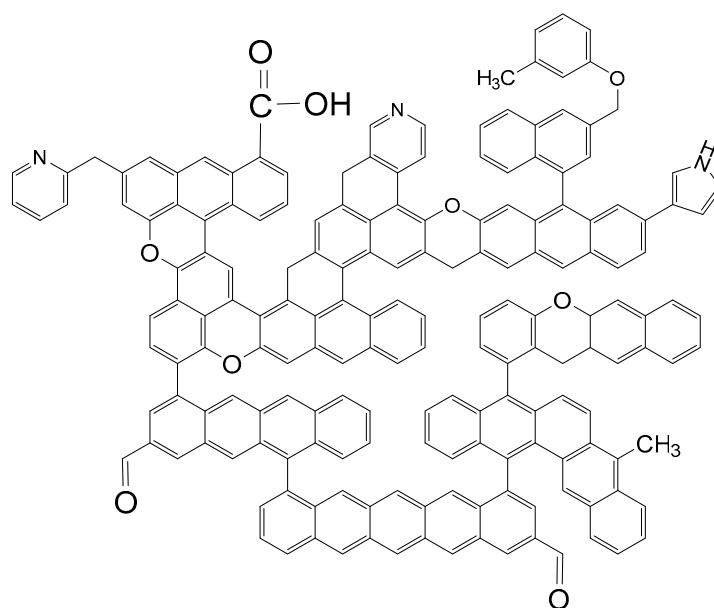
Type	Number	Type	Number
	1		3
	2		1
	2		1
	3		1

3.5.3. Heteroatom Structures

The numbers of oxygen and nitrogen atoms in gas coal were calculated to be 9 and 3, respectively, by the total number of carbon atoms and the atomic ratio. According to XPS analysis, oxygen atoms in gas coal existed in the forms of five ether oxygen bonds, two carbonyl groups, and one carboxyl group. The nitrogen atoms existed in the form of two pyridine nitrogen and one pyrrole nitrogen.

3.5.4. Construction of the Coal Molecular Structure

Based on the number of atoms per element, the molecular formula of gas coal was determined to be $C_{181}H_{150}O_9N_3$. The molecular structure diagram of gas coal was constructed by the Chemdraw software. The MestReNova software was used to calculate the spectrum of the coal molecular structure. Then, the calculated spectrum was compared with the ^{13}C -NMR experimental spectrum, and the comparison chart was further adjusted and optimized according to XRD data. The obtained structural model is shown in Figure 5, and the comparison results of the ^{13}C -NMR spectra are shown in Figure 6.

**Figure 5.** Molecular structure model of gas coal.

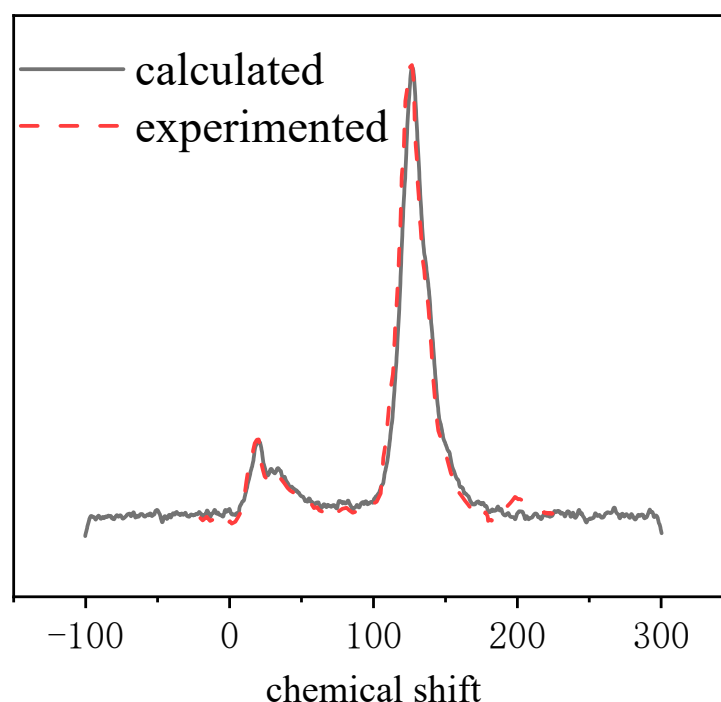


Figure 6. Experimental and calculated ^{13}C -NMR spectra.

According to Figure 6, the calculated spectrum agreed well with the experimental spectrum, which indicated that the molecular model was constructed accurately. However, the largest relative deviation was obtained in the oxygen–carbon region with a chemical shift from 170 ppm to 220 ppm. This finding is mainly due to the side-band effect of the oxygen–carbon region in the experimental process, which led to errors of large intensity and high peak values in the oxygen–carbon region of the experimental spectrum [40]. Therefore, the oxygen–carbon region was further investigated by verifying the rationality of the molecular model through ^{13}C -NMR carbon spectroscopy.

4. Optimization and Validation of the Coal Macromolecule Model

The coal macromolecular structure model was only a collection of analytical results of experimental data, which must be simulated for further analysis and validation. The Materials Studio (MS) software was used to optimize the structure model of coal macromolecules, using molecular mechanics (MM) and molecular dynamics (MD) methods to simulate the structural properties and interactions between molecules. In molecular or periodic system simulations, the Focite module could solve the energy calculation, geometric optimization, and the process of dynamic simulation. The force field was Dreiding, and the parameters of the Dreiding force field were obtained by fitting the quantum chemistry calculation data, and the use of the Dreiding force field reflected the application of quantum chemical theory in molecular simulations.

The information and density of each carbon atom in coal is an important parameter to reflect the molecular structure of coal. The rationality of the model was verified by comparing the agreement between the calculated and experimental carbon spectra, as well as the similarity between the experimental and simulated densities. The refined coal macromolecule model was also reasonably confirmed, because the calculated spectrum was in satisfactory agreement with the experimental spectrum. Therefore, it was not discussed again in this section.

4.1. Optimal Structure

Molecules exist mainly in the lowest energy form in natural situations. Thus, only the lowest energy model represented the optimal state of the molecular structure under

study. The lowest energy could not be guaranteed for the built model during the modeling process. Thus, it was necessary to optimize and find the lowest energy model to ensure that the subsequent results were meaningful [18].

4.1.1. Optimized Method and Parameter Setting

The molecular structure model of gas coal was imported into MS software and automatically hydrogenated to fullness. The lowest energy model was obtained by MM and MD calculations. The module selection and parameter settings were based on the simulation calculation method in the literature [40]. MM and MD calculations were conducted in the Forcite module in MS. The charge distributions were obtained through the charge equilibrium method in the MM calculation. The MM parameters were as follows: the computational method was a smart minimizer, the maximum number of iterations steps was set to 5000 steps considering the computational accuracy and convergence time cost, and the convergence criterion was medium. The Dreiding [41,42] force field was selected, because it was suitable for calculating the structures and various properties of most types of molecules and materials with high accuracy. A fixed-volume, fixed-temperature (NVT) MD simulation was conducted. The MD parameters were as follows: the temperature was 300–600 K, the heating order was 5, the heating rate was 60 K/time. The temperature control program selected Nose [43] to ensure that the distribution of system degrees of freedom was normative, and the time step was 0.1 fs.

4.1.2. Energy-Minimizing Geometrical Configuration and Microcrystalline Structure Parameters

The unoptimized model in Figure 7a was imported into MS for hydrogenation saturation. MM and MD calculations were performed to overcome the molecular structure energy barrier and obtain the minimum energy structure after molecular structural optimization in the Forcite module. The results are shown in Figure 7b. The optimized gas coal molecular model was more compact and had a better stereochemical structure than the models in Figure 7a,b. The optimized molecular energies are shown in Table 6. The calculation and analysis showed that the valence electron energy and the non-bond energy accounted for 39.56% and 60.44% of the total energy, respectively. The total energy of the optimized molecular model was reduced by 91.72%, in which the valence electron energy was reduced by 92.11% and the non-bond energy was reduced by 91.44%. The analyzed results showed that the non-bond energy (hydrogen bond energy, van der Waals energy, and Coulomb energy) plays an important role in the stability of the molecular structure. The van der Waals energy changed the most before and after optimization, which suggests that the π – π interaction between aromatic rings was the main factor in keeping the molecular structure stable. In the valence electron energy (bond stretching energy, bond angle energy, torsion energy, and reversal energy), the descending order was as follows: torsion energy > bond stretching energy > bond angle energy > reversal energy. Therefore, the bond torsion and reversal and the changes in bond angle and length were the basis of the stereoscopic configuration of coal macromolecules. The molecular structure drawn in the Chemdraw software was a planar graph, and the factor of the bond length was ignored. Thus, the bond energy changed the most in the optimized valence energy.

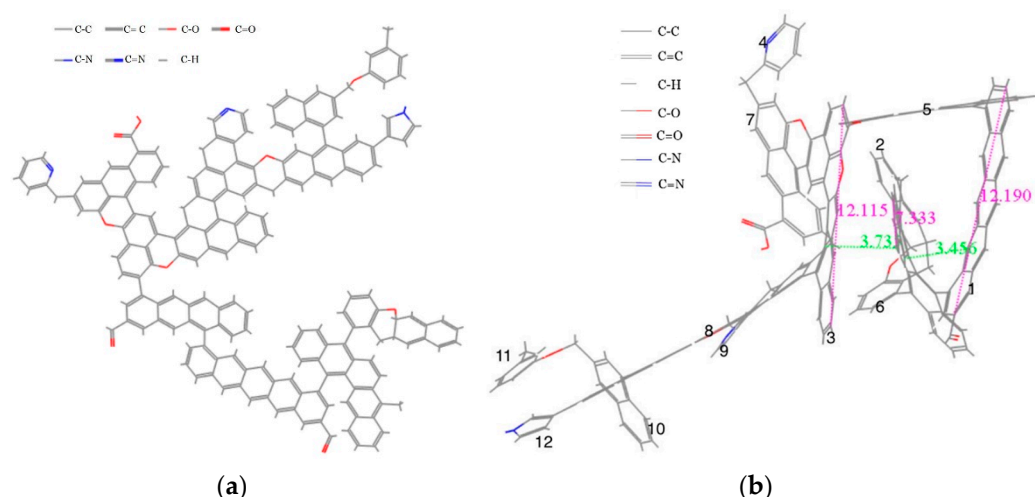


Figure 7. Macromolecular structure model of gas coal before and after optimization: (a) before optimization; (b) after optimization.

Table 6. The energies of the gas-coal macromolecular structure before and after optimization.

E (kcal·mol ^{−1})		Ev (kcal·mol ^{−1})				EN (kcal·mol ^{−1})		
		EB	EA	ET	EI	EH	Evan	EE
Initial	8263.8600	3222.464	38.336	166.689	4.085	0	4850.632	−18.35
Final	684.560	84.553	51.754	131.287	3.120	0	418.828	−4.982

Note: E—total energy; E_V—valence energy; E_B—bond energy; E_A—angle energy; E_T—torsion energy; E_I—inversion energy; E_N—non-bond energy; E_H—hydrogen bond energy; E_{van}—van der Waals energy; E_E—electrostatic energy.

As shown in Figure 7b, a set of approximately parallel combinations (series 1, 2, and 3) appeared between the aromatic lamellar layers in the structural model formed by a single molecule. However, the spacings (d_{002}) of the two aromatic lamellae were not uniform, which were 3.735 and 3.456 nm, respectively. The maximum values of L_a and L_c were 12.190 and 7.191 nm, respectively. The spacing of the aromatic layer was 3.575 nm higher than the measured value, which is due to that the bonds connecting the aromatic layers were twisted and inserted in a set of aromatic lamellae 6 and aliphatic carbon structures after optimization. The π – π interaction between aromatic rings played an important role in structural stability, and two sets of vertical structures (aromatic layers 5, 1, and 3 and aromatic layers 10 and 11) appeared at the edge of the model. The reason is that the coal molecule was in a stable state without force [44]. The microcrystalline structural parameters (d_{002} , L_c , and L_a) of the coal molecular model were slightly different from the experimental values (3.575, 6.62, and 11.77 nm, respectively), which suggests that the short-range order of the high-grade coal structure mainly depends on the directional arrangement of more intermolecular aromatic layers [40].

4.2. Density Simulation

The density of coal is an important physical property, and it was used to verify the reasonability of the model by comparing the value of the constructed model with the experimental value. The Amorphous Cell module in MS software was utilized to add periodic boundary conditions to the model shown in Figure 7b for MM and MD. The constructs of a series of structural models were obtained, and the minimum energy model was selected. The parameters of the density simulation were as follows: the calculation used periodic boundary conditions, the Dreiding force field was used to simulate the field force, and the charge was calculated by the charge balance method (QEq). The number of molecules was 1, the initial density value was 0.7 g/cm³, the final density value was

1.4 g/cm³, and the interval was 0.05 g/cm³ [45]. The geometric configuration with the minimum energy was selected as shown in Figure 8. The relationship between the density and the potential energy of the structural model is shown in Figure 9.

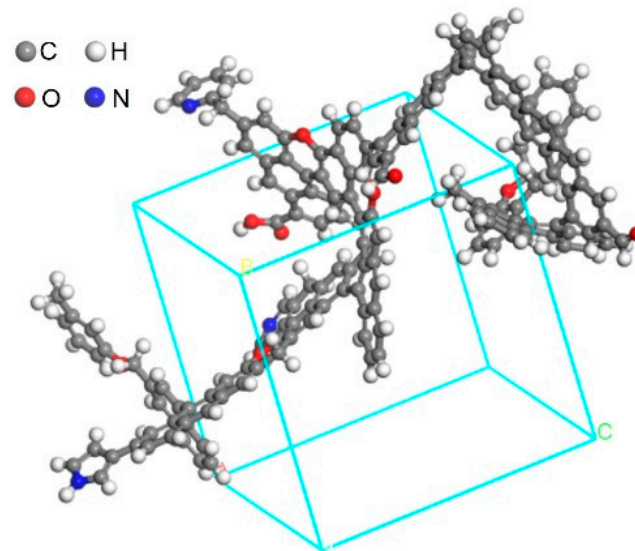


Figure 8. Structure of gas coal with a density of 1.0 g/cm³.

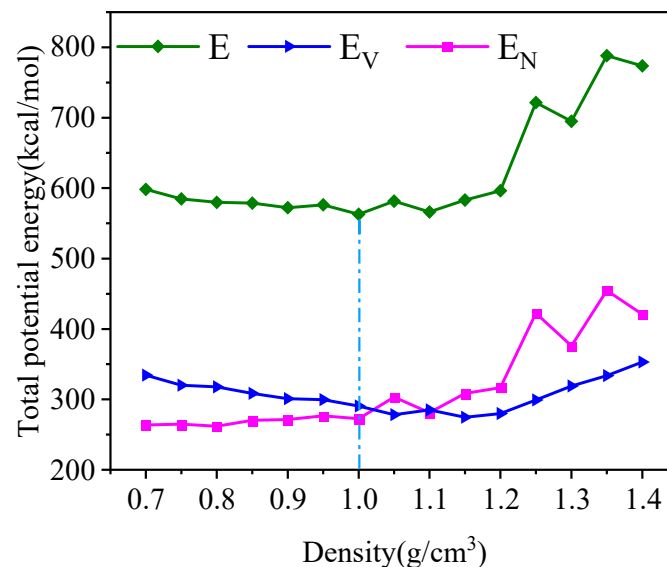


Figure 9. Relationships between the structural model density and potential energy.

As shown in Figure 9, the total potential energy of the molecular structure decreased gradually first and then increased rapidly with the rise in density. When the density was 1.0 g/cm³, the total potential energy of the molecular structure model was the minimum and the value was 562.944 KJ/mol. At this time, 1.0 g/cm³ was the simulated density of the model, and the parameters of coal molecular crystal cells were $a = b = c = 1.6003$ nm. Its structural energy is shown in Table 7. When the density was less than 1.0 g/cm³, E_V played a dominant role at this stage. When the density was greater than 1.0 g/cm³, the dominant was E_N . The density calculated by simulation was smaller than the experimental density of gas coal (1.2564 g/cm³). The reason is that excluding the influence of trace elements and small molecular substances in coal during the density test is difficult under actual conditions [46,47]. Thus, the calculated density was considered reasonable.

Table 7. Energy of the coal sample from Huainan.

Density (g/cm ³)	E (kcal/mol)	EV			EN			
		EB	EA [32]	ET	EI	EH	Evan	EE
1.0	562.944	87.167	52.554	128.714	4.002	0	326.40	−27.967

Comparing Tables 6 and 7 showed that the torsion energy had the largest change among the valence electron energies after periodic boundary conditions were added. The reason is that the energy minimization only was achieved by twisting appropriately when the gas coal molecules under periodic boundary conditions interacted with the surrounding molecules. After periodic boundary conditions were added, the most obvious change in non-bond energy was observed for the van der Waals energy. The major contributor is that the aromatic layers located in parallel were distorted and deformed in the process of the gas coal molecular structure. Thus, they became more compact, which ultimately destroyed π – π interactions between the aromatic layers in the molecule.

5. Conclusions

In this study, proximate analysis, ultimate analysis, ¹³C-NMR, XPS, and XRD were performed on Huainan gas coal to quantify its structure. The macromolecular structure model of coal was constructed and optimized based on the quantitative analysis results. The model was verified and optimized by NMR carbon spectroscopy and MS software to obtain the correct molecular model. The following conclusions were drawn.

The results showed that X_{BP} was 0.407. The aromatic structures were mostly anthracene and phenanthrene, followed by naphthalene and benzene rings. The molecule model contained five ether–oxygen bonds, two carbonyl groups, one carboxyl group, two pyridine nitrogen, and one pyrrole nitrogen. Its molecular formula was determined to be $C_{181}H_{150}O_9N_3$.

The minimum energy value of the optimized molecules was 684.560 KJ/mol. The van der Waals energy was the main component of non-bond energy, which was the main factor to stabilize the coal molecular structure and change the energy. The changes including the bond length, angle, torsion, and inversion were the basis of coal molecules with stereoscopic configuration. The intermolecular aromatic lamellae were arranged in an approximately parallel manner by the π – π interaction. The short-range order of the high-grade coal structure was determined by the directional arrangement of the intermolecular aromatic lamellae.

The coal molecular crystal unit was constructed by adding periodic boundary conditions to the optimized structure, and it was used for the density simulation. The result showed that the simulative density of the coal molecular crystal unit was 1.0 g/cm³ when the total energy reached the lowest value of 562.944 kcal/mol, which was close to the real density measured by the experiment. At the same time, the predicted carbon spectrum obtained by the MestReNova software agreed well with the experimental spectrum, which suggests that the construction of the gas coal macromolecular model is reasonable and effective.

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