

Article

Study on the Wetting Mechanisms of Different Coal Ranks Based on Molecular Dynamics

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Abstract: The exploration of coal wettability is not only of paramount significance in the mitigation of coal dust and the development of coalbed methane, but it also provides crucial technical support for realizing the geological storage of CO₂ within the ‘dual-carbon’ background. Molecular simulation serves as an effective means by which to investigate coal wettability at the microscopic level. This study employed a molecular dynamics simulation to investigate the wettability of coal across 13 distinct coal ranks. Through the analysis of trajectory files, and the incorporation of experimental data during the modeling process, the mechanisms governing the evolution of wettability were revealed. The results demonstrated that the contact angle on the surface of coal increases with the elevation of coal rank. The molecule relative concentration analysis revealed that, with increasing coal rank, the overlap range between water droplets and the coal slab decreases, the height increases, and the diffusion degree of water molecules decreases, which are outcomes consistent with the results of the contact angle measurement. The contact angle was strongly correlated with the number of hydrogen bonds and secondarily correlated with the numbers of carbonyls, hydroxyls, and ether oxygens. The formation of hydrogen bonds was notably correlated with the number of hydroxyls, followed by that of ether oxygens, while its correlations with carbonyls and carboxyls were comparatively weaker. The contact angle exhibited positive correlations with vitrinite reflectance and carbon content, while showing negative correlations with oxygen content, H/C, and O/C. Additionally, it demonstrated positive associations with total sp² carbon (f_a), aromatic carbon (f'_a), and non-protonated aromatic carbon (f_a^N), and negative associations with aliphatic carbon (f_{al}) and methylene carbon (f_{al}^H). Understanding the variations in wettability among different coal ranks can provide a foundational model and theoretical basis for further exploration of the complex interactions among coal, gas, and water across various coal ranks.

Keywords: coal rank; coal; wettability; molecular dynamics simulation

Citation: Zhang, C.; Zhang, S.; Tang, S.; Zhang, S.; Li, J. Study on the Wetting Mechanisms of Different Coal Ranks Based on Molecular Dynamics. *Processes* **2024**, *12*, 455. <https://doi.org/10.3390/pr12030455>

Academic Editor: Raymond Cecil Everson

Received: 5 January 2024

Revised: 13 February 2024

Accepted: 21 February 2024

Published: 23 February 2024



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1. Introduction

The wettability of coal has been extensively studied by numerous researchers [1–4]. In the context of coal mine disaster prevention and control, the wettability of coal stands out as a critical factor in the efficient reduction of dust and the implementation of water injection to prevent gas outbursts [5–9]. Regarding coalbed methane development, carbon dioxide sequestration, and the enhancement of the coalbed methane recovery ratio, coal wettability emerges as a critical determinant for safeguarding coal reservoirs, augmenting seepage, and modifying reservoir characteristics to optimize the rates of gas and water transport [10–13]. Therefore, conducting research on the wettability of coal reservoirs and exploring the complex mechanisms of coal–gas–water interactions are crucial, not only for improving the effectiveness of coal dust control and guiding coalbed methane production, but also for providing theoretical guidance for the clean transformation of the coal industry under the ‘Dual Carbon’ background and the achievement of CO₂ geological sequestration.

Many scholars have investigated the relationships between wettability and the physicochemical properties of coal through physical experiments. Wang [14] utilized contact methods and sedimentation experiments to investigate the characteristics of coal pores and the influences of functional groups on the contact angle. The results indicated that the presence of a greater number of oxygen-containing functional groups indicates better wettability. Li [6,15] and Zhang et al. [16] selected coal samples with different degrees of metamorphism, and, through the analysis of physicochemical properties, they demonstrated significant correlations between wettability and the parameters of coal particle size, moisture, ash, inorganic minerals, oxygen content, and oxygen-containing functional groups. Xu et al. [8] employed scanning electron microscopy and infrared spectroscopy to analyze two coal samples exhibiting different degrees of metamorphism. They concluded that coal wettability is closely associated with coal structure. Yan et al. [17] characterized the coal quality of middle- and low-rank coal samples and found that hydroxyl functional groups significantly influenced coal wettability. Zhou et al. [18,19] analyzed the NMR parameters of six coal samples and found that the carbon skeleton parameters contributed to wettability differences among coals of different ranks. However, these studies experimentally revealed the relationship between coal structure and wettability for a limited number of coal samples with different degrees of metamorphism. The measurement of experimental contact angles does not offer molecular-level insights into the interaction of water molecules with the coal surface. Therefore, a microscopic explanation and a comprehensive summary of the relationships among coal samples of different ranks are still lacking.

Wettability studies on coal have long focused on the influences of experimental aspects, such as coal composition and surface chemical structure. With the continuous development of computer technology, molecular simulation is increasingly applied to study the micro-mechanism of coal surface wettability. This approach has gradually become an important method in the field of coal flotation [20–23]. Zhao [24] revealed the significant effects of carbon and oxygen elements in coal on the wettability of coal dust. This was achieved by constructing bituminous coals from three groups of coal seams in the Pingdingshan mining area, and then combining them with molecular simulation. Li [25] used Wiser molecules to construct coal surfaces with various oxygen-containing functional groups. Through molecular dynamics simulation analysis, it was concluded that hydroxyl groups exhibited stronger hydration ability than other oxygen-containing groups. Meng et al. [26] analyzed the wettability of three coal samples with different degrees of metamorphism through molecular simulation. From a microscopic perspective, they elucidated the mechanism by which different surfactants influence the wettability of coal surfaces through considerations of adsorption positions, adsorption spacing, and anti-adsorption phenomena. Xia et al. [27] modified the surface of graphene with different oxygen-containing functional groups. They revealed the molecular-level mechanism behind the interaction between polar and nonpolar molecules during the flotation of coal. Yao et al. [4] used a molecular dynamics approach to simulate the wetting behaviors of two coal molecule surfaces with different oxygen-containing functional groups under different temperature and pressure conditions. This approach revealed the microscopic mechanism behind the changing water wettability pattern caused by the injection of CO₂ into the coal seam. In general, the current use of molecular simulation methods to study wettability is limited in the choice of coal macromolecule models. Most studies directly use the classical coal molecule models from many years ago, or they utilize graphene surfaces modified with oxygen-containing functional groups. Some opt for the use of one or two modeled coal molecules to conduct simulation experiments by changing the number of oxygen-containing functional groups on the surface. However, with improvements in experimental testing tools, the modeling of coal macromolecules from different coal ranks and coal qualities has enabled macromolecular studies on the wettability of full-rank coal samples. Conducting molecular simulation studies on wettability with all-rank coal samples can effectively overcome the limitations associated with coal macromolecule selection. This approach enhances the completeness

and precision in studying the evolution of wettability and its influencing factors across the entire spectrum of coal ranks and types.

In this study, we used 13 coal molecular models, representing various degrees of evolution, to create a coal macromolecule series encompassing lignite and anthracite. Simulations were conducted to explore the wettability of coal molecules across different ranks. The resulting trajectory files were scrutinized to analyze energy changes, the number of hydrogen bonds, the distribution of relative water molecule concentrations, the dynamic characteristics of water molecules, and the relationship between wettability and coal structure during the coal surface wetting process. This microscopic investigation aimed to analyze the influence of water on coal surface wetting and gain insights into the wettability characteristics across different coal ranks. In-depth analysis of water's wetting effects on coal surfaces, understanding the wettability characteristics of coal surfaces at different ranks, and investigating the microscopic mechanisms of coal wettability evolution. This study provides theoretical guidance for the subsequent development of clean coal industrialization and CO₂-ECBM technology.

2. Coal Molecular Model

In this study, 13 coal samples were used for simulations, with vitrinite reflectance ranging from 0.46% to 3.21%. A coal metamorphic sequence including low ($R_o < 0.65\%$), medium ($0.65\% < R_o < 2.0\%$), and high ($R_o > 2.0\%$) ranks was formed, with R_o values used to delineate the metamorphic grades of coal samples. Six coal samples were obtained by our research group from the Hequ (HQ), Xiaoyi (XY), Dianping (DP), Gaoyang (GY), Yangquan (YQ), and Zhaozhuang (ZZ) coal mines. Additionally, the remaining seven samples originated from the Wumuchang (WMC) [28], Shendong (SD) [29], Yanzhou (YZ) [30], Majiliang (MJL) [31], Liulin (LL) [32], Duerping (DEP) [33], and Chengzhuang (CZ) [34] coal mines. Vitrinite reflectance, proximate analysis, and ultimate analysis results for each coal sample are presented in Table 1. The spatial distribution of the samples is illustrated in Figure 1.

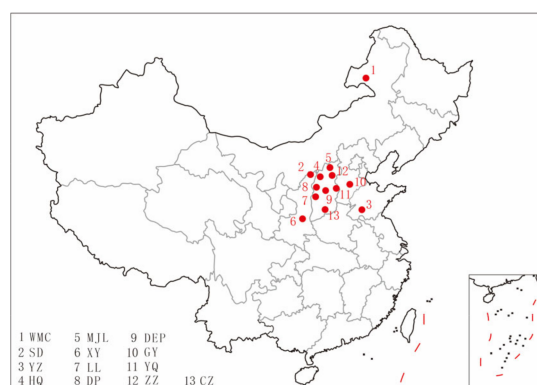


Figure 1. Coal sample collection point diagram.

It can be seen from Table 1 that, with increasing vitrinite reflectance, the coal structure also changes. The content of C increased, the content of O decreased, the contents of S and N were low, so the changes were not obvious; the O/C and H/C also decreased. The above results show that each coal sample forms a coal metamorphic sequence that conforms to the overall coal metamorphic law.

The modeling methods employed for each coal sample were consistent, ensuring comparable results. In addition to determining the elemental contents of coal molecules through ultimate analysis, nuclear magnetic resonance spectroscopy (¹³C-NMR) was utilized to extract carbon skeleton information. Fourier transform infrared spectroscopy (FTIR) provided the effective structural parameters of both aromatic and aliphatic hydrocarbons, while X-ray photoelectron spectroscopy (XPS) was employed to ascertain the existence forms and contents of oxygen, nitrogen, and sulfur. Finally, the molecular formula of each coal rank

was determined through fitting and correction. Samples were classified into distinct coal grades based on their R_o values.: $C_{122}H_{104}N_2O_{18}$ (WMC, lignite), $C_{194}H_{144}N_2O_{31}$ (SD, long-flame coal), $C_{222}H_{185}N_3O_{17}S_5$ (YZ, long-flame coal), $C_{214}H_{189}N_3O_{34}S$ (HQ, long-flame coal), $C_{222}H_{168}O_{22}N_2$ (MJL, gas coal), $C_{235}H_{207}N_3O_6S_2$ (XY, fat coal), $C_{170}H_{158}N_2O_9$ (LL, coking coal), $C_{207}H_{170}O_3N_2S$ (DP, coking coal), $C_{244}H_{188}N_2O_7S$ (DRP, lean coal), $C_{199}H_{139}O_3N_3S_2$ (GY, lean coal), $C_{189}H_{147}O_3N_3S$ (YQ, meager coal), $C_{204}H_{157}O_5N_3$ (ZZ, anthracite), and $C_{199}H_{146}N_2O_9$ (CZ, anthracite).

Table 1. Information on coal samples.

Number	Coal Sample	R_o (%)	Coal Rank	Proximate Analysis (%)			Ultimate Analysis (%)					Atomic Ratio		Density (g/cm ³)	Angle (°)
				M_{ad}	A_{ad}	V_{daf}	C	H	O	N	S	H/C	O/C		
1	WMC [25]	0.46	lignite	5.14	16.15	33.15	77.79	4.47	16.02	1.29	0.43	0.69	0.15	1.39	29.26
2	SD [26]	0.51	long-flame coal	9.77	1.77	41.17	77.93	4.71	16.18	4.71	0.18	0.73	0.16	1.17	26.77
3	YZ [27]	0.62	long-flame coal	1.92	14.32	46.23	80.17	5.61	8.12	1.43	4.68	0.84	0.08	1.17	44.55
4	HQ	0.67	long-flame coal	2.96	36.66	28.47	75.69	5.35	16.55	1.68	0.73	0.85	0.16	1.30	40.36
5	MJL [28]	0.74	gas coal	1.70	20.30	38.18	81.69	5.09	11.14	1.35	0.73	0.85	0.16	1.30	40.36
6	XY	1.27	fat coal	0.73	5.63	28.15	83.54	4.93	2.63	1.43	1.80	0.71	0.02	1.30	40.36
7	LL [29]	1.38	coking coal	4.68	3.39	28.94	79.30	5.73	8.92	1.36	0.69	0.87	0.08	1.22	43.71
8	DP	1.50	coking coal	0.60	4.17	18.80	90.38	4.76	2.09	1.48	1.30	0.63	0.02	1.35	58.90
9	DEP [30]	1.74	lean coal	0.62	8.61	17.04	90.13	4.56	3.32	1.44	0.55	0.61	0.03	1.35	56.00
10	GY	1.96	lean coal	0.56	6.89	17.22	84.18	4.30	1.40	1.26	1.93	0.61	0.01	1.30	64.41
11	YQ	2.04	meager coal	1.50	3.18	8.28	89.25	3.44	1.49	1.48	1.11	0.46	0.01	1.35	64.07
12	ZZ	2.21	anthracite	0.86	10.61	10.84	91.31	3.58	3.12	1.62	0.37	0.47	0.03	1.35	66.90
13	CZ [31]	3.21	anthracite	0.74	14.76	11.30	89.22	3.51	5.61	1.10	0.56	0.47	0.05	1.48	57.52

Note: R_o means maximum vitrinite reflectance; M_{ad} and A_{ad} represent the air–dry–base moisture content and ash yield, respectively; V_{daf} is the volatile matter mass fraction of the sample in the dry ash-free basis.

3. Molecular Simulation Section

3.1. Coal Molecular Simulation

The coal molecules of each coal rank underwent geometric optimization using the Geometry Optimization function in the Forcite module of the Materials Studio 9.0 software (This experiment was completed in HUASUAN Technology). Subsequently, the Anneal function was employed for structural relaxation to achieve the lowest energy configuration (Figure 2).

3.2. Molecular Dynamics Simulation of Coal–Water Interaction

The wettability test for coal typically occurs on a flat surface of coal. Thus, prior to conducting the water wetting simulation, establishing plate models of coal molecular slices is imperative. Given the irregularities of the coal surface, constructing a flat surface is essential for an accurate wettability simulation. This process can be directly accomplished using the Amorphous Cell module of the Materials Studio software. By inputting the density values corresponding to coal molecules of each rank (refer to Table 1), a rectangular thin plate model can be constructed for each coal sample. For the sake of comparison, the dimensions of the model were uniformly established as $90 \times 65 \text{ \AA}$, with a thickness of $17 \text{ \AA}$, a size sufficient for spreading water droplets, thereby meeting the requirements for wetting simulations. Owing to varying molecular densities across different coal ranks, the number of coal molecules differs among the constructed plate models. Nonetheless, this discrepancy in molecule count is minor, typically around 25 molecules. The constructed coal plate underwent geometric optimization and annealing, using the Forcite function to derive the optimal configuration for each coal molecule (Figure 3b), both before and after optimization. The enhanced uniformity of the pores in the coal plate model was evident, aligning more closely with the actual coal plate structure. At the same time, employing the same module, a spherical water droplet was constructed with a density of 1 g/cm^3 , containing a total of 500 water molecules and a radius of $15 \text{ \AA}$ (Figure 3d).

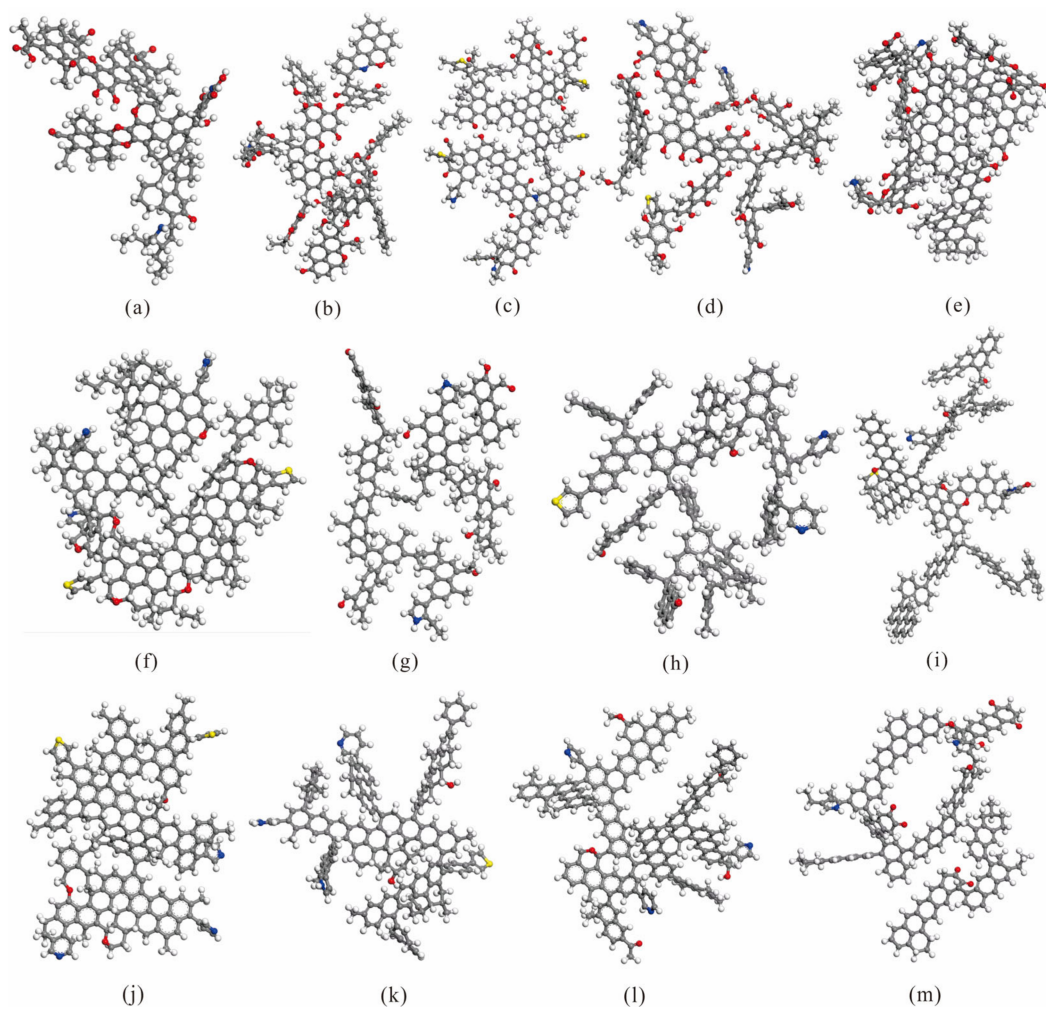


Figure 2. Molecular models of different coal samples. (a) WMC; (b) SD; (c) YZ; (d) HQ; (e) MJL; (f) XY; (g) LL; (h) DP; (i) DEP; (j) GY; (k) YQ; (l) ZZ; (m) CZ.

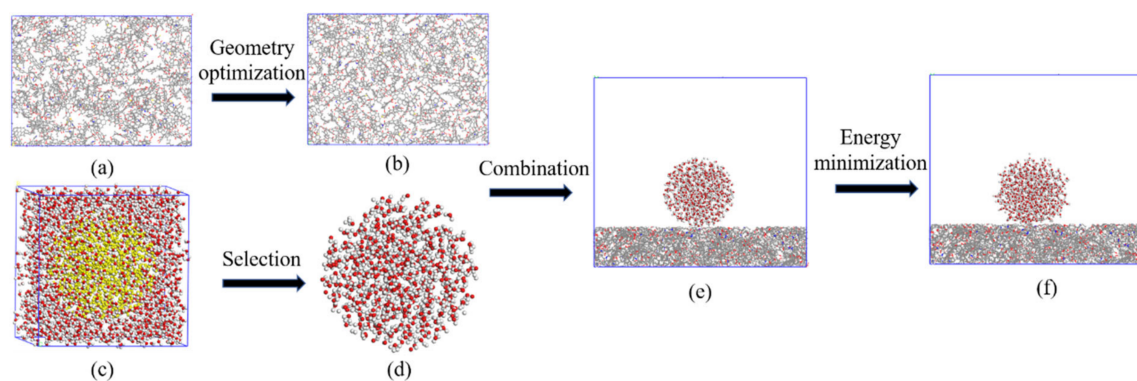


Figure 3. The construction of the wetting simulation model. (a) Initial plate model of coal molecules; (b) plate model of coal after geometry optimization; (c) established water molecule unit cell; (d) water droplet model selected from the water molecule unit cell; (e) water droplet added onto the coal surface; (f) model after energy minimization.

Utilizing the Layers function of the Build module, a 63 Å vacuum layer was added into the coal plate crystal to mitigate the influences of periodic boundaries. It is generally accepted that the first layer of atoms exposed to air is considered to be the coal surface (<3 Å). The water droplets, once constructed, were applied to the surfaces of the coal plate

models, and the overall structures underwent preliminary optimization and relaxation. After optimization, the water droplets exhibited slight dispersion (Figure 3f). This phenomenon arises from the introduction of water molecules into the coal system, rendering it thermodynamically unstable. Driven by the interaction forces within the coal–water system, the water droplets disperse, gravitating towards the surface of the coal molecules [35]. To conduct a molecular dynamics simulation of the overall structure, the Dynamic task item in the Forcite module was chosen. Due to the relatively large number of molecules in the system, the number of molecules in the coal slab model is no less than 20, representing a medium-sized coal dust–water molecular system. The NVT ensemble was selected for the simulation. [36]. Additionally, the temperature control method employed was Nosé, the force field chosen was COMPASSII, and the electrostatic force and van der Waals force were determined using the PPPM and Atom-based methods, respectively. The simulation utilized a time step of 1 fs with a total step size of 800 ps. Following the simulation, the contact wetting angle of the droplets was measured for each coal rank.

4. Results and Discussion

4.1. Simulation Results and Energy Changes

At present, the majority of scholars commonly employ the contact angle value θ at the solid–liquid interface to determine the wetting properties of coal. When θ is less than 90° , it is considered partial wetting or adhesive wetting, whereas, when θ is greater than 90° , it is considered non-wetting. Following the MD simulation, the ultimate configuration of the coal–water system was acquired. As illustrated in Figure 4, water droplets spread across the surfaces of coal at different coal ranks, with a more pronounced spreading observed in low-rank coal. As the coal rank increases, the extent of spreading gradually decreases. The average values of the contact angles on the XZ and YZ planes of the coal–water system were taken as the final contact angles. The measurement results are shown in Table 1. It is evident from the measurements that, with increasing coal rank, the contact angle of the coal plate surface tends to increase.

The energy changes in the coal–water system model across different coal ranks were analyzed (Figure 5). Based on the investigations by scholar Feng [35], the energy changes in the entire system can be broadly categorized into three stages: the energy stabilization stage, the adsorption stage, and the interaction stage. In the energy stabilization stage (0–200 ps), the system's energy achieves initial equilibrium. During this phase, the water droplet transitions from a spherical to a rapidly spreading state, resulting in a significant reduction in energy. In the adsorption stage (200–600 ps), the system's energy attains a second equilibrium stage. The energy variation in each coal rank system is observed to be modest compared to that in the first stage, with a limited range of change. This phenomenon arises from the adsorption of water molecules on the coal surface, forming hydrogen bonds with functional groups and leading to a slight decrease in energy. In the interaction stage (600–800 ps), the system reaches a third equilibrium stage. Notably, the energy fluctuations in low-rank coal are substantial, due to its well-developed large pores. Certain water molecules are capable of penetrating the pores of coal and adsorbing near oxygen-containing functional groups. The aqueous solution itself exhibits a polar coupling effect with certain water molecules, resulting in further heat release and a subsequent decrease in energy. In contrast, the reduced oxygen-containing functional groups and macropores in medium–high-rank coal result in minimal changes in energy, limiting the movement of water molecules.

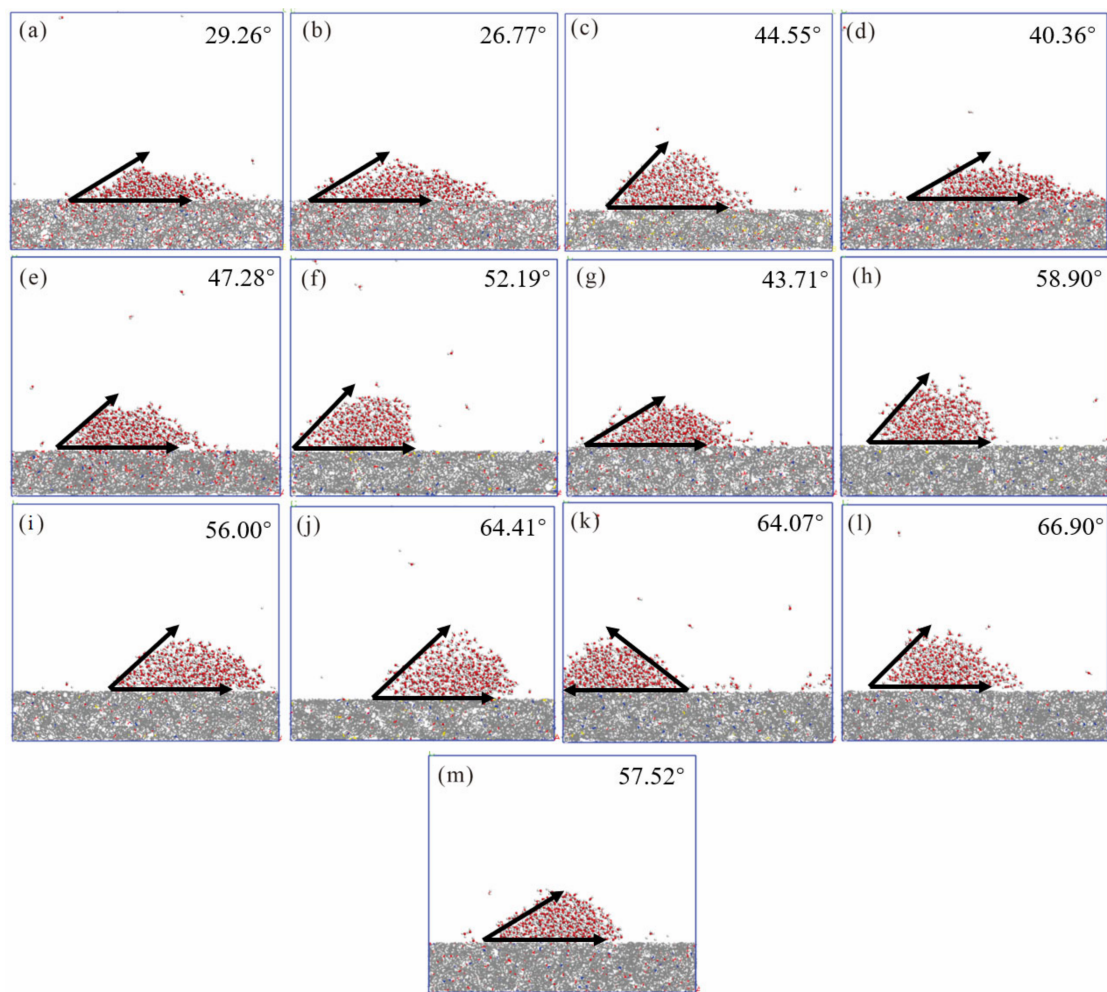


Figure 4. Surface wetting angle of different coal samples. (a) WMC; (b) SD; (c) YZ; (d) HQ; (e) MJL; (f) XY; (g) LL; (h) DP; (i) DEP; (j) GY; (k) YQ; (l) ZZ; (m) CZ.

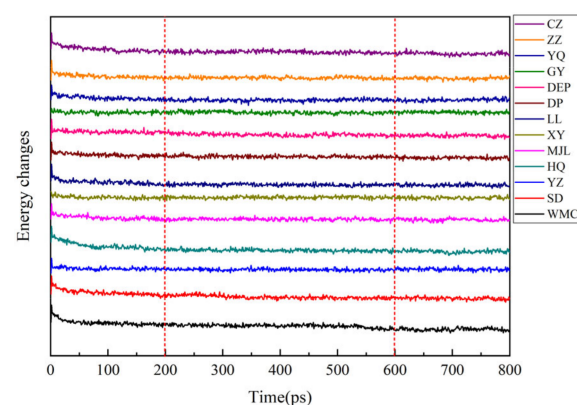


Figure 5. Energy changes in coal–water system with different coal samples.

4.2. Hydrogen Bonds

The formation of hydrogen bonds (HBs) between oxygen-containing functional groups and water molecules on the coal surface is one of the consequences of the strong hydrophilicity of the coal surface [37]. Counting the number of hydrogen bonds provides further information about the structure of the coal surface in relation to the water layer. The hydrogen bond geometric standard was used to calculate the hydrogen bond; specifically, the distance between the donor and acceptor is less than 0.25 nm, and the angle formed by

the donor-hydrogen-acceptor is greater than 135° . The statistics of the number of hydrogen bonds between the surface of each coal rank and water molecules are presented in Table 2.

Table 2. Statistics on the number of hydrogen bonds (HBs) and oxygen-containing functional groups in different coal samples.

Number	Coal Sample	HBs	Oxygen-Containing Functional Groups				
			-C=O	-COOH	-OH	-C-O-C-	-CHO
1	WMC [25]	94	3	2	7	4	0
2	SD [26]	82	9	0	9	13	0
3	YZ [27]	29	8	6	3	0	0
4	HQ	85	2	2	28	2	0
5	MJL [28]	54	4	3	9	3	0
6	XY	10	0	0	1	5	0
7	LL [29]	34	5	0	4	0	0
8	DP	4	0	0	2	0	1
9	DEP [30]	12	1	0	1	5	0
10	GY	6	1	0	1	1	0
11	YQ	22	1	0	2	0	0
12	ZZ	11	1	0	1	3	0
13	CZ [31]	15	7	0	1	1	0

Table 2 reveals that the number of hydrogen bonds decreases sharply as the coal rank increases. The number of hydrogen bonds is closely related to the number of oxygen-containing functional groups. The statistics of the number of oxygen-containing functional groups in each coal sample reveal that lower-order coals contain higher amounts of carbonyl, carboxyl, hydroxyl, and ether oxygens. This phenomenon is the direct cause of the smaller wetting angle and higher number of hydrogen bonds observed in the low- and medium-rank coals. Correlation analysis of the contact angle, number of hydrogen bonds, and number of oxygen-containing functional groups (Table 3) indicates a robust correlation between the contact angle and the number of hydrogen bonds on the surfaces of coals of varying ranks. There is also a high correlation with the presence of carbonyl, hydroxyl, and ether oxygen groups. This is not only due to their ease of forming hydrogen bonds, but also because these functional groups are present in relatively larger quantities across various coal samples. The formation of hydrogen bonds exhibits a strong correlation with the number of hydroxyl groups, followed by that of ether oxygen groups, while the correlations with the numbers of carbonyl and carboxyl groups are not strong.

Table 3. Correlation between contact angle and number of hydrogen bonds (HBs) with oxygen-containing functional groups for different coal ranks.

Correlation	Angle	HBs	-C=O	-COOH	-OH	-C-O-C-	-CHO
Angle	1						
HBs	−0.87909	1					
-C=O	−0.57683	0.398672	1				
-COOH	−0.36544	0.331269	0.41051	1			
-OH	−0.52507	0.742642	0.097232	0.28167	1		
-C-O-C-	−0.54787	0.454336	0.31011	−0.20406	0.145618	1	
-CHO	0.20335	−0.28858	−0.3118	−0.16457	−0.13333	−0.23895	1

There are two forms of hydrogen bonds formed by water molecules, the O_W-H_C type and the H_W-O_C type. Figure 6 further shows the hydrogen bonds formed on each oxygen-containing functional group. It can be observed that the hydroxyl group can form two types of hydrogen bonds involving oxygen and hydrogen atoms, and these hydrogen bonds exhibit shorter bond lengths, indicating strong hydrogen bonding. Low-rank coals contain more hydroxyl groups, explaining the strong correlation between the numbers

of hydrogen bonds and hydroxyl groups. Hydroxyl groups are less abundant in the Xiaoyi coal sample, resulting in a smaller number of hydrogen bonds on the surface of Xiaoyi coal. Only H_W-O_C hydrogen bonds can be formed between a carbonyl group and a water molecule, resulting in a smaller contribution to the formation of hydrogen bonds. Carboxylic groups, on the other hand, have a higher tendency to form hydrogen bonds with water molecules, and both types of hydrogen bonds can be formed, involving both two oxygen atoms and one hydrogen atom. The number of hydrogen bonds formed between the carboxyl group and the water molecule is higher. On a carboxyl group, at least three hydrogen bonds can form. This is also the mechanism behind the sequence of different coal surface wettability derived by Yao [4] and other scholars, where carboxyl > hydroxyl > other oxygen-containing functional groups. However, the number of carboxyl groups in the 13 coal samples selected for this study is not substantial. Consequently, its contribution to the formation of hydrogen bonds is limited. An O_W-H_C hydrogen bond can be formed on the ether oxygen group, and the number of ether oxygen groups is second only to the number of hydroxyl groups in each coal sample. Therefore, the contribution of ether oxygen groups to the formation of hydrogen bonds is greater than those of carbonyl and carboxyl groups. Although the aldehyde group can form both types of hydrogen bonds with the same hydroxyl group, the number of aldehyde groups is very small, existing only in the Dianping coal sample. Consequently, its contribution to hydrogen bonding is minimal.

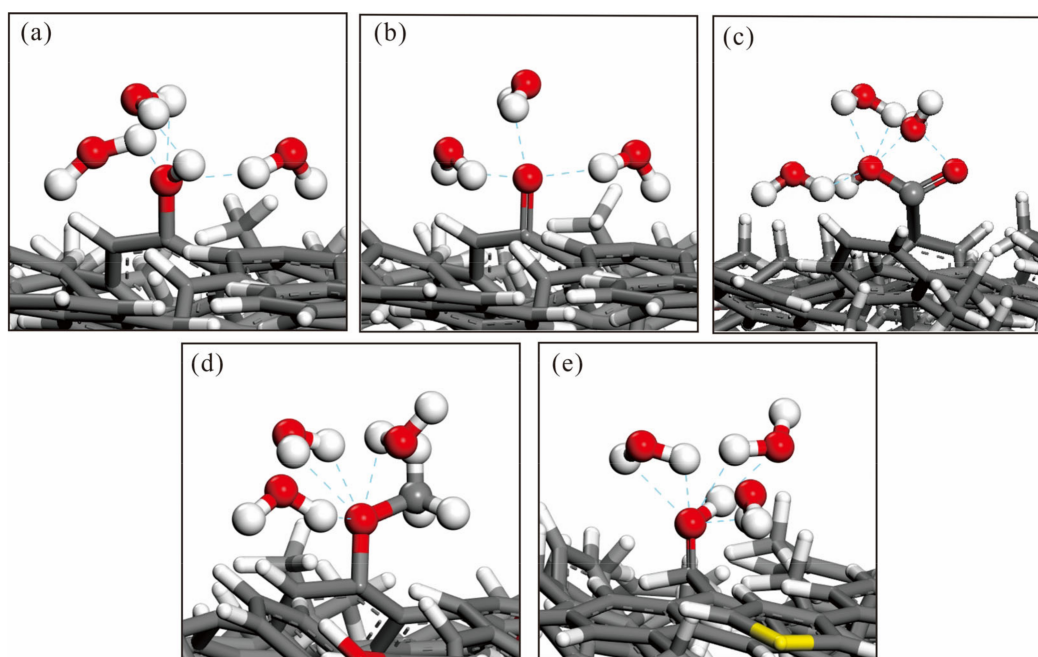


Figure 6. Schematic diagram of hydrogen bonding formation by oxygen-containing functional groups. (a) Hydroxyl; (b) carbonyl; (c) carboxyl; (d) ether oxygen group; (e) aldehyde group.

4.3. Relative Concentration Analysis

The relative concentration analysis reveals the distribution of substances in a certain direction, and the peak of the relative concentration distribution curve indicates the position with concentrated molecules, groups, or atoms [38]. MS software was used to analyze the relative concentration distribution of water molecules on the surfaces of coal molecules along the Z-axis and X-axis. This analysis aimed to uncover the impact of the aqueous solution on coal molecule surfaces and elucidate the adsorption behavior of water molecules on these surfaces. Figure 7 illustrates the distribution of the relative concentration of water molecules along the Z-axis and X-axis. The width of the Z-axis curve corresponds to the height of the water droplet in the coal–water system model, and the height of the curve indicates the concentration of water molecules at that specific position. As depicted in

Figure 7a, the relative concentration of water on the surfaces of coals of different ranks is not zero within the height of 17 Å, indicating that some water molecules penetrate the pores in the coal plate models of different coal ranks. This suggests that wetting not only occurs on the surface of the coal seam, but also that it is associated with the interior of the coal seam. A small number of water molecules can permeate the surface of the coal seam and adsorb near the oxygen-containing functional groups in the coal molecules. However, the relative concentration of water molecules in the pores varies among different coal ranks. The relative concentrations of water molecules in the pores of low and medium-rank coals is higher than that in high-rank coals. This is attributed to the large pores of low and medium-rank coals, leading to a significant overlap between the relative concentration distribution of water molecules and coal molecules and signifying pronounced wettability. Consequently, low- and medium-rank coals exhibit higher susceptibility to wetting.

In the Z-axis relative concentration distribution curve, each coal sample exhibits an extreme value of water molecules on its surface, corresponding to the point where water molecules are most concentrated along the Z-axis. The range of the extreme value of the relative concentration of water molecules decreases, from 9.583 to 6.211, as the coal rank increases, and the overall trend of water molecules decreases with rising coal rank. The initial position of water molecule concentration ranges from 4.75 to 12.25 Å, and the end position ranges from 33.75 to 55.25 Å. This suggests that, as the overlap range between water droplets and the coal plate (within 17 Å) diminishes, the height of water droplets increases, and the wettability worsens.

The width of the X-axis curve in Figure 7b denotes the width and position of the contact surface between the water droplet and the coal surface, while the height of the curve represents the concentration of water molecules at the corresponding position. As seen from the graph, with increasing coal rank, the extreme value of water molecules ranges from 2.359 to 3.756, and the overall change is not substantial. The width of the water droplet varies, within the range of 68.5 to 43.0 Å, indicating that, as the coal rank increases, the contact surface between water droplets and the coal surface diminishes, leading to a lower degree of water molecule diffusion and, consequently, reduced wettability.

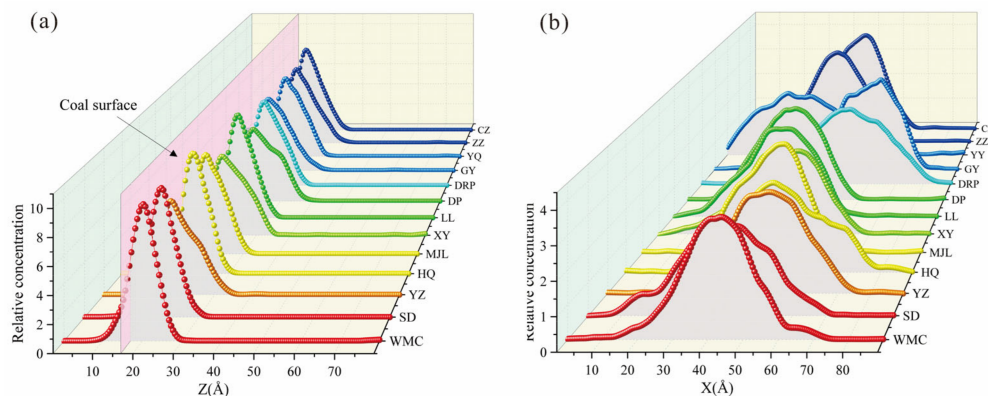


Figure 7. The relative concentration distribution of water molecules along the coordinate axis. (a) Z-axis; (b) X-axis.

4.4. Dynamic Characteristics of Water Molecules

The diffusion behavior of water molecules on the surface of the coal plate can be elucidated by analyzing the dynamic characteristics of water molecules. The calculation formulas for the mean square displacement (MSD) and diffusion coefficient (D) of water molecules on the coal surface are as follows:

$$\text{MSD} = \frac{1}{N} \sum_{i=1}^N [r_i(t) - r_i(0)]^2 \quad (1)$$

where N represents the number of diffusing molecules, and $r_i(t)$ and $r_i(0)$ denote the position vectors of the molecules at time t and $t = 0$, respectively. It is usually assumed that the mobility of water molecules is influenced by the degree of coalization.

The formula for calculating the diffusion coefficient obtained from the Einstein equation is as follows:

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^N [r_i(t) - r_i(0)]^2 \quad (2)$$

By combining Equations (1) and (2), the relationship between MSD and the diffusion coefficient can be expressed as follows:

$$D = \lim_{t \rightarrow \infty} \left(\frac{\text{MSD}}{6t} \right) = \frac{1}{6} K_{\text{MSD}} \quad (3)$$

Figure 8 presents the MSD curves of water molecules in the wetting systems of coal samples at different ranks. As observed in the figure, with increasing coal metamorphism, the MSD curves of water molecules can be roughly divided into three stages, corresponding to the three following stages, mentioned earlier, in the energy curve division: the energy stabilization stage (0–200 ps), the adsorption stage (200–600 ps), and the interaction stage (600–800 ps). In the energy stabilization stage, the curve slope rises rapidly, due to the spreading of water droplets in the coal molecular system, resulting in the fast movement of water molecules to achieve energy balance. During the adsorption stage, as water droplets have already dispersed in the first stage, water molecules further enter the pores of the coal matrix, adsorbing near oxygen-containing functional groups. In comparison to the first stage, the movement speed of water molecules decreases, leading to a shallower curve slope. In the interaction stage, owing to the abundance of oxygen-containing functional groups in low- and medium-rank coals, as well as the formation of hydrogen bonds with water molecules, the migration rate of water molecules is restricted in these coals. Consequently, the slopes of the curves for low- and medium-rank coals are lower than that of high-rank coal in this stage. High-rank coal, with fewer oxygen-containing functional groups, exhibits greater hydrophobicity, resulting in a stronger “release” capability for water and an increased curve slope.

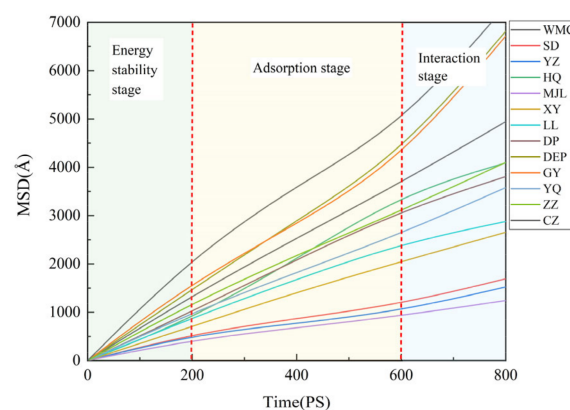


Figure 8. MSD curves of water molecules on the surfaces of different coal samples.

The diffusion coefficients were calculated by fitting the Mean Square Displacement (MSD) curves of water molecules in each coal sample. The diffusion coefficients ranged from 2.955 to 14.477 ($10^{-9} \text{ m}^2/\text{s}$), as depicted in Figure 9, which illustrates their relationships with coal rank. It is evident that, with increasing coal rank, the overall trend of diffusion coefficients shows an upward trajectory, aligning with the patterns observed in the metamorphic evolution of coal.

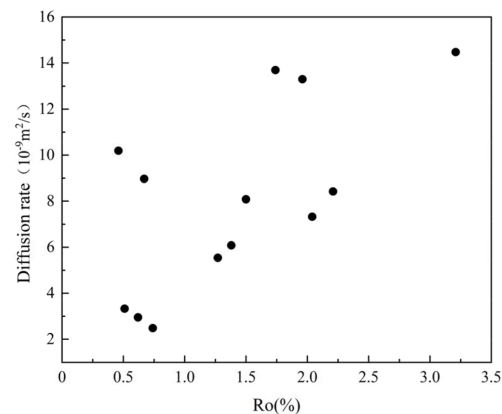


Figure 9. Diffusion rate of water molecules on the surfaces of different coal ranks.

4.5. The Effects of Structural Parameters on Wettability

4.5.1. Analysis of Coal Quality Elements

As the degree of coal evolution increases, the contact angle of coal also increases. This is attributed to the reduction in oxygen-containing functional groups and the augmentation of hydrophobic components, leading to a decrease in wettability [18]. The results of the ultimate analysis tests for the coal samples of different coal ranks (Table 1) were compiled, and the relationships between these results and the contact angle were analyzed. Figure 10 reveals that the contact angle of the coal surface increases with the rise in vitrinite reflectance, exhibiting a positive correlation with vitrinite reflectance. The increase in vitrinite reflectance indicates a higher degree of coal metamorphism, transitioning from hydrophilic to hydrophobic behavior. The contact angle enlarges with rising carbon content, showing a positive correlation with carbon content. The predominant form of carbon is hydrophobic, and the increase in carbon content implies an augmented degree of aromatic ring condensation and shortened alkyl side chains, contributing to increased coalification and hydrophobicity, resulting in an enlarged contact angle. Conversely, the contact angle diminishes with increasing oxygen content, displaying a negative correlation with oxygen content. Oxygen primarily exists in the form of oxygen-containing functional groups, such as carboxyl and hydroxyl groups, which possess strong polarity and affinity for water, contributing significantly to wetting. From a microscopic functional group perspective, a decrease in oxygen content indicates the gradual removal of hydrophilic oxygen-containing functional groups during coal metamorphism, leading to a deterioration in coal wetting properties. This aligns with the earlier discussion on hydrogen bonds.

Additionally, wetting behavior is negatively correlated with the H/C and the O/C. The H/C serves as one of the parameters reflecting the coal structure. As the coal structure contains more cyclic structures, indicative of higher degrees of coalification, the H/C decreases, resulting in an increase in hydrophobicity. Higher oxygen content enhances hydrophilicity, while higher carbon content increases hydrophobicity. Consequently, a larger O/C signifies a greater hydrophilicity in coal.

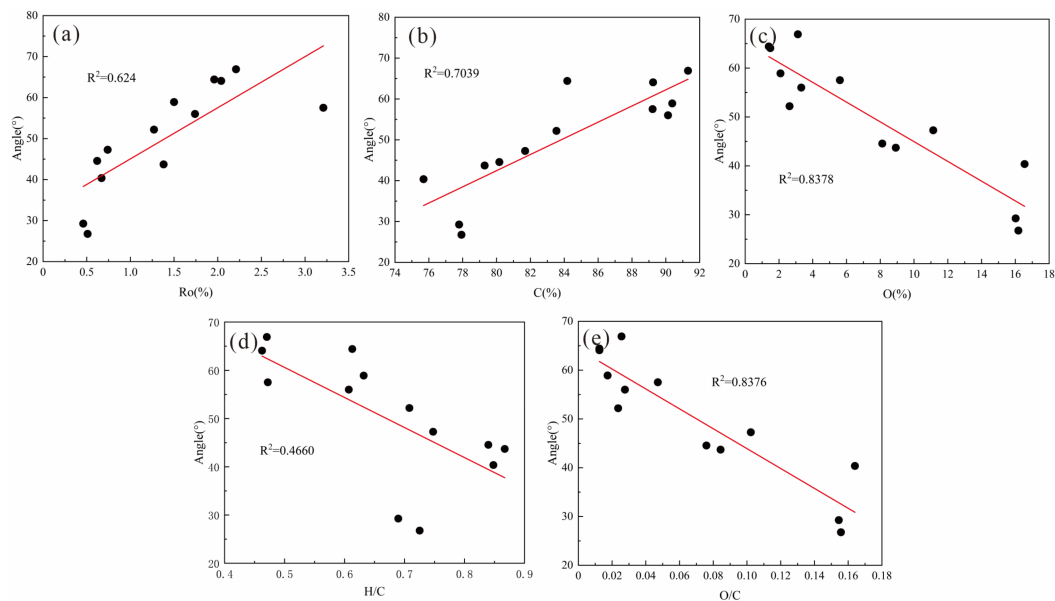


Figure 10. Analysis of coal quality elements of contact angle. (a) Vitrinite reflectivity; (b) carbon content; (c) oxygen content; (d) H/C; (e) O/C.

4.5.2. Analysis of ^{13}C -NMR Parameters

The ^{13}C -NMR parameters for each coal sample from different coal ranks (Table 4) were counted, and the wetting mechanisms of the coal surfaces of different coal ranks were further analyzed from the molecular structures of coal samples. The ^{13}C -NMR parameters of coal mainly consist of aromatic carbon and aliphatic carbon [8,39]. The relationships between the ^{13}C -NMR parameters and the contact angle of each coal rank were analyzed.

Table 4. Structural parameters of different coal samples of different ranks.

Number	Coal Sample	^{13}C -NMR Parameters (%)												X_{BP}
		f_a	f_a^C	f_a^I	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^*	f_{al}^H	f_{al}^O	
1	WMC	66.00	9.00	63.27	18.00	39.00	11.00	16.00	12.00	30.55	9.00	24.00	0	0.13
2	SD	71.00	6.00	65.00	42.00	23.00	3.00	11.00	9.00	29.00	5.00	22.00	3.00	0.16
3	YZ	74.00	1.00	64.00	45.00	19.00	8.00	5.00	6.00	26.00	11.00	12.00	3.00	0.10
4	HQ	72.78	1.40	71.37	45.63	25.75	5.09	10.63	10.02	27.22	19.92	5.83	1.47	0.16
5	MJL	74.24	5.10	69.14	45.68	23.46	6.08	4.06	13.32	25.76	10.05	12.64	3.07	0.24
6	XY	60.13	0	60.13	42.00	18.12	0	7.88	10.25	39.87	20.15	10.36	9.36	0.21
7	LL	71.99	1.55	70.44	46.88	23.56	2.78	5.42	15.36	28.01	17.41	10.60	0	0.28
8	DP	81.77	0.86	80.92	59.98	20.94	2.82	2.02	16.10	18.23	10.26	7.16	0.81	0.25
9	DEP	79.81	3.93	75.88	48.98	26.90	1.88	6.33	18.69	20.19	6.93	9.60	3.66	0.33
10	GY	72.41	9.98	62.42	44.25	18.17	1.46	0	12.89	27.59	6.39	7.95	13.25	0.26
11	YQ	82.08	13.36	68.82	38.65	30.17	0	0	16.31	17.92	3.33	1.58	13.01	0.30
12	ZZ	84.47	2.42	82.05	45.49	36.56	0	13.14	23.42	15.53	11.26	1.94	2.33	0.40
13	CZ	86.59	10.18	84.43	54.47	21.94	0.97	0.65	20.32	13.41	5.03	7.93	0.45	0.36

Note: f_a total sp^2 carbon; f_a^C : carbonyl or carboxyl group; f_a^I : aromatic carbon; f_a^H : protonated aromatic carbon; f_a^N : non-protonated aromatic carbon; f_a^P : aromatic carbon-bonded hydroxyl or ether oxygen; f_a^S : alkylated aromatic carbon; f_a^B : aromatic bridgehead carbon; f_{al} : total sp^3 hybridized carbon; f_{al}^* : CH_3 ; f_{al}^H : CH or CH_2 ; and f_{al}^O : aliphatic carbon-bonded oxygen.

The structure of aromatic carbon in coal is closely related to its maturity. The aromatic carbon content of each coal rank accounts for more than 60% of the total carbon content. The total sp^2 carbon (f_a) contains carbonyl carbon (f_a^C) and aromatic carbon (f_a^I). The aromatic carbon is composed of protonated aromatic carbon (f_a^H) and non-protonated aromatic carbon (f_a^N). The non-protonated aromatic carbon contains aromatic carbon-bonded hydroxyl or ether oxygen (f_a^P), alkylated aromatic carbon (f_a^S), and aromatic bridgehead carbon (f_a^B).

Aromatic carbon (f'_a) serves as a primary component of aromatic structure, also known as aromaticity, which has a direct correlation with the evolutionary degree of coal. As depicted in Figure 11a, it is evident that, with the increasing degree of coalification, the aromaticity (f'_a) of coal significantly increases, while the content of carbonyl carbon (f_a^C) is minimal. Protonated aromatic carbon (f_a^H) and non-protonated aromatic carbon (f_a^N) reflect the contents of protonated carbon and heteroatom carbon in aromatic rings. As shown in Figure 11b, with the increasing degree of coalification, the content of protonated aromatic carbon rises. Although the variation trend of non-protonated aromatic carbon (f_a^N) is not as pronounced, as illustrated in Figure 11c, an overall increasing trend can still be observed. Alkylate aromatic carbon (f_a^S), as depicted in Figure 11d, decreases with the increasing degree of coalification. Aromatic bridgehead carbon (f_a^B), as shown in Figure 11e, exhibits a linear increase with rising coal rank, indicating a continuous enlargement of aromaticity and aromatic condensed rings during coal evolution, leading to an increase in the aromatic ring size. Aromatic carbon-bonded hydroxyl or ether oxygen (f_a^P) represents the distribution of oxygen-containing functional groups in coal. As shown in Figure 11f, it is evident that, with the increasing degree of coalification, the content of aromatic carbon-bonded hydroxyl or ether oxygen (f_a^P) decreases, indicating the detachment of oxygen-containing functional groups.

The aliphatic carbon (f_{al}) of coal is connected to the aromatic unit in the form of side chains, and contains methyl carbon (f_{al}^*), methylene carbon (f_{al}^H), and oxygen-bonded aliphatic carbon (f_{al}^O). The variation in aliphatic structure among coal samples of different ranks is depicted in Figure 12. Methyl carbon (f_{al}^*) increases rapidly before the vitrinite reflectance reaches 0.7%, whereas methylene carbon (f_{al}^H) exhibits a contrasting rapid decrease (Figure 12a,b). This phenomenon arises from the aromatic condensed rings starting to shed aliphatic functional groups and side chains before the first transition point, resulting in a decrease in the methyl–methylene ratio. Subsequently, methyl carbon (f_{al}^*) decreases rapidly, due to further aliphatic ring closure reactions, leading to a rapid reduction in aliphatic compounds and their subsequent conversion into aromatic compounds. Methylene carbon (f_{al}^H) is associated with the breaking and condensation of long-chain aliphatic carbons into aromatic rings, showing an overall decreasing trend. The oxygenated aliphatic carbon (f_{al}^O) in aliphatic side chains represents the distribution of carbon atoms attached to oxygen. It can be observed that, apart from a few coal samples, the content of oxygen-bonded aliphatic carbon (f_{al}^O) is relatively low in higher coal ranks.

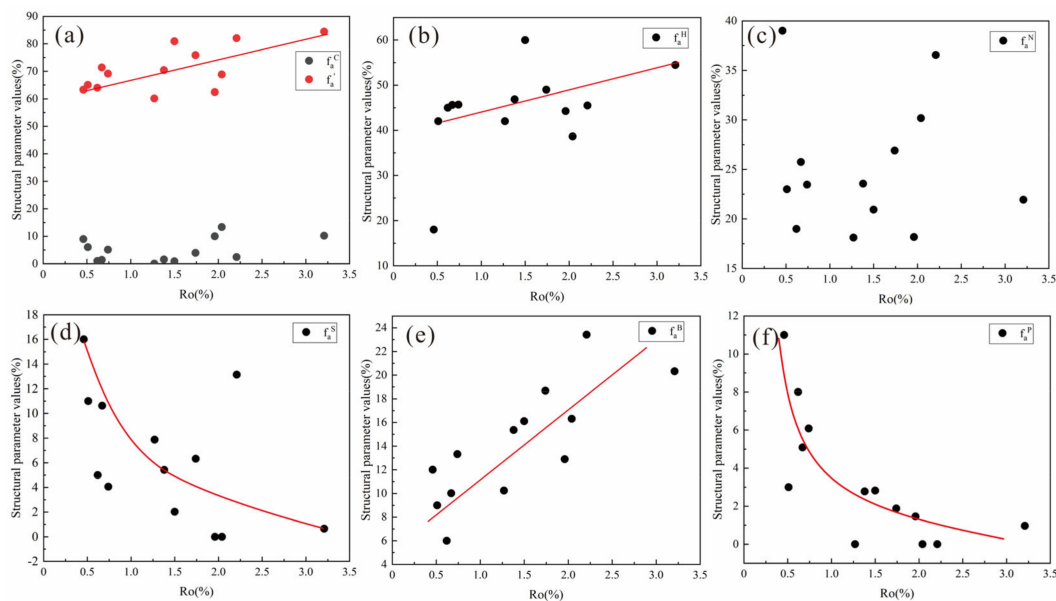


Figure 11. The changes in aromatic carbon structural parameters among coal samples of different ranks. (a) f'_a , f_a^C ; (b) f_a^H ; (c) f_a^N ; (d) f_a^S ; (e) f_a^B ; (f) f_a^P .

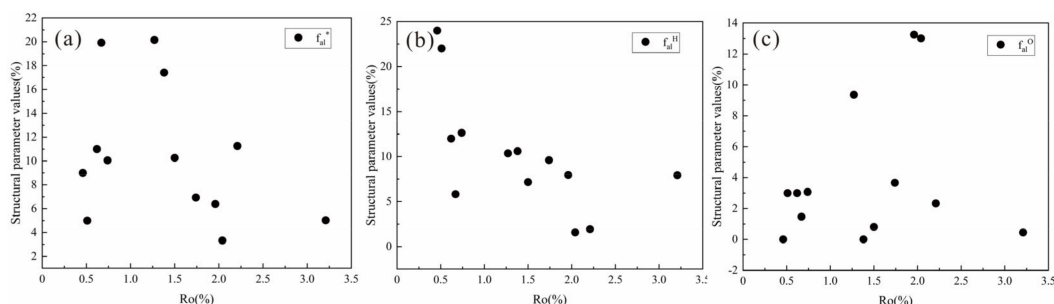


Figure 12. The variation in aliphatic carbon structural parameters among coal samples of different ranks. (a) f_{al}^* ; (b) f_{al}^H ; (c) f_{al}^O .

Combining the ^{13}C -NMR parameters of each coal rank with their corresponding wetting angles, it can be seen from Figure 13 that wettability becomes worse with the increase in total sp^2 carbon (f_a), in which aromatic carbon (f'_a) shows an obvious upward trend as a whole. The increase in aromatic carbon content with rising coal rank, attributed to the detachment of oxygen-containing functional groups, organic matter condensation, and the subsequent increase in aromatic carbon, leads to elevated carbon content and enhanced hydrophobicity, which are results consistent with the previously discussed relationship between contact angle and carbon content. Furthermore, there is a correlation with non-protonated aromatic carbon (f_a^N).

In contrast, aliphatic carbon (f_{al}) and methylene carbon (f_{al}^H) exhibit overall downward trends, forming negative correlations with the contact angle. The relationships between other parameters and wetting behavior are less apparent. With increasing aromatic carbon content, the aliphatic carbon content inevitably decreases. Aliphatic carbon exists in the form of aliphatic side chains, playing a role in connecting aromatic structural units. As coal rank increases, aromatic condensed rings begin to shed aliphatic functional groups and side chains, leading to a reduction in methylene carbon. Consequently, wetting behavior deteriorates.

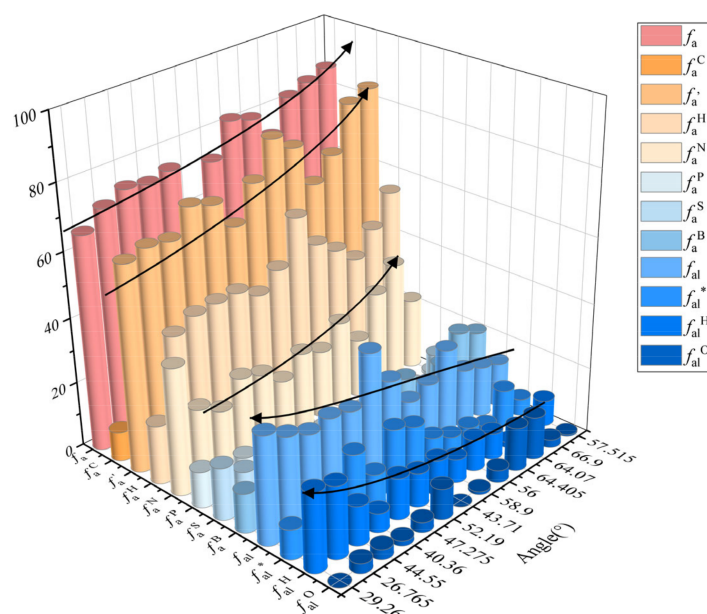


Figure 13. Analysis of ^{13}C -NMR parameters of contact angle.

5. Conclusions

In this paper, the wettability of coal molecules from 13 different coal samples of different ranks was simulated, analyzed, and compared, and the following conclusions were obtained.

The contact angle of different coal–water systems correlates positively with rising coal rank, generally conforming to the trend of coal metamorphic evolution. Meanwhile, upon analyzing the energy fluctuations in the statistical system within the trajectory file, the energy change curve reveals the three following distinct stages: the energy stabilization stage, the adsorption stage, and the interaction stage.

The correlation analysis between the contact angle and the numbers of hydrogen bonds and oxygen-containing functional groups reveals a significant positive correlation with the number of hydrogen bonds and a favorable correlation with the numbers of carbonyl, hydroxyl, and ether oxygen groups. The formation of hydrogen bonds is significantly correlated with the number of hydroxyl groups, followed by ether oxygen groups, and it is not strongly correlated with carbonyl and carboxyl groups.

From the relative concentration distribution of water along the Z-axis and X-axis in different coal rank wetting systems, water molecules permeate the pores of low and medium-rank coals. With increasing coal rank, the overlap range of water droplets and the coal plate reduces, the height of the water droplet increases, the contact area between the water droplet and the coal surface decreases, and the diffusion degree of water molecules decreases, indicating a decline in wettability.

The Mean Square Displacement curve of water corresponds to the energy change curve, with water molecules moving at a faster rate during the energy stabilization stage, which is attributed to droplet spreading. In the adsorption stage, water molecules penetrate the pores and adsorb near oxygen-containing functional groups, leading to a reduced movement rate within each coal rank system. In the interaction stage, the oxygen-containing functional groups of low-rank and medium-rank coals establish hydrogen bonds with water molecules, resulting in lower slopes of the curves for water molecules in low and medium-rank coals compared to high-rank coals.

By analyzing the elemental parameters of coal molecules of different coal ranks, it is evident that the contact angle exhibits positive correlations with vitrinite reflectance and carbon content, and negative correlations with oxygen content, H/C, and O/C. The ^{13}C -NMR parameters of coal samples of different ranks were analyzed, revealing positive correlations between the wetting angle and total sp^2 carbon (f_a), aromatic carbon (f'_a), and non-protonated aromatic carbon (f_a^N), and negative correlations with aliphatic carbon (f_{al}) and methylene carbon (f_{al}^H).

Author Contributions: C.Z.: investigation, conceptualization, methodology, software, writing—original draft preparation, data, and validation. S.Z. (Songhang Zhang): conceptualization, methodology, data, validation, resources, writing—review and editing, supervision, project administration, and funding acquisition. S.T.: supervision and writing—review and editing. S.Z. (Shouren Zhang): supervision. J.L.: investigation. All authors have read and agreed to the published version of the manuscript.

Funding: This project was financially supported by the Key Project of the National Natural Science Foundation of China (grant no. 41872178).

Data Availability Statement: The research data of this article can be obtained from the author “Chen Zhang” through reasonable request.

Conflicts of Interest: Author Shouren Zhang was employed by the company China United Coalbed Methane Corporation Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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