Research Article

Molecular Simulation on Adsorption Difference of Water and Methane on Long-Flame Coal

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The adsorption difference of water and methane by long-flame coal is compared and analyzed by molecular simulation. The results show that when the single-component isothermal adsorption pressure is less than 15 MPa, the adsorption capacity of CH_4 and H_2O increases gradually with the increase of the adsorption pressure, and the average adsorption amount of H_2O is much higher than that of CH_4; after more than 15 MPa, the average adsorption amount of CH_4 and H_2O is saturated. When the two-component isothermal adsorption pressure is less than 0.7595 MPa, the long-flame coal molecule can adsorb both CH_4 and H_2O; after more than 0.7595 MPa, the average adsorption amount of H_2O is much larger than that of CH_4 indicating that H_2O is in a dominant position in the competitive adsorption with CH_4.

1. Introduction

The energy status of "rich coal, poor oil, and little gas" in China determines that coal is the main energy source in China [1]. In the process of coal production, it is a difficult problem to improve the efficiency of gas extraction, and the key to improving the efficiency of gas extraction is to increase the permeability of the coal seam [2]. Through previous research, hydraulic measures are generally used to improve the permeability of the coal seam in engineering practice and to reduce the difficulty of gas extraction and gas accidents. Coal seam water infusion is an effective measure to increase coal seam permeability, and analyzing the influence effect of moisture injection on coal adsorption gas is the focus of research. China's long-flame coal resources are very rich, accounting for more than 40% of total coal reserves [3]. The proportion of long-flame coal mining and consumption in coal supply is increasing, and the application of hydraulic measures will be more and more widely used; the adsorption difference of long-flame coal on water and methane is important for efficient and safe exploitation of long-flame coal.

In the field of experimental research and engineering practice, scholars at home and abroad have conducted a lot of studies on the effect of water on methane adsorption by coal. Xu et al. [4] proved that hydraulic punching can improve coal seam permeability and can promote coal seam gas extraction by numerical simulation and field test. Song et al. [5] put forward the integrated technology of drilling, hydraulic jet fracturing, and hydraulic punching, which proved that hydraulic jet fracturing can improve the permeability of hard coal seam. Yue et al. [6] proved that water can be adsorbed on the surface of coal particles and replace part of the gas on the surface of coal particles by analyzing the influence of water movement on gas desorption capacity during spontaneous absorption height experiments. According to Arif et al. [7] and Zheng et al. [8] by analyzing the

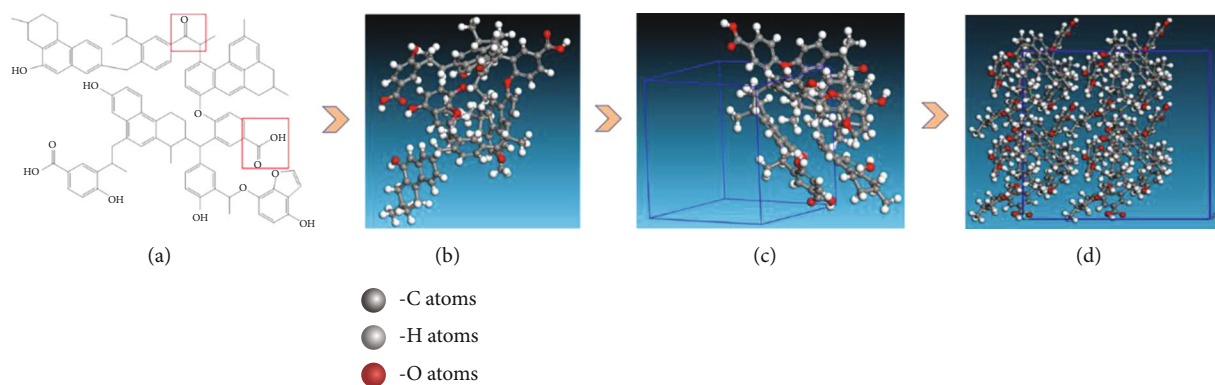(a)   (b)   (c)   (d)

● -C atoms
● -H atoms
● -O atoms

FIGURE 1: Coal molecular model: (a) long-flame coal macromolecular structure, (b) long-flame coal molecule lowest energy structure model, (c) long-flame coal molecule lowest energy structure model with the periodic boundary condition, and (d) supercell expansion of long-flame coal molecule with periodic boundary conditions.

TABLE 1: Detailed parameters of the molecular model.

Element formula (%)	Molecular weight	Element content (%)		
		C	H	O
$C_{97}H_{92}O_{13}$	1464	79.51	6.28	14.21

effect of the presence of water molecules on the adsorption behavior of CH_4, it was concluded that compared with nonpolar CH_4 molecules, polar water molecules occupied the adsorption position in coal. Ma et al. [9] proved that water in low-rank coal can inhibit the adsorption of CH_4 and CO_2. Yue et al. [10] carried out the influence experiment of self-absorption water to gas desorption and discovered the natural invasion of water which promoted the desorption of adsorbed gas.

According to Chen and Cheng [11], using the high-pressure adsorption-water injection-desorption test device, the displacement desorption amount, pressure relief desorption amount, and total gas desorption amount of coal under different adsorption equilibrium pressure and moisture condicies are measured and calculated; it revealed that the injected water can displace the gas adsorbed by the coal body, and the higher the moisture content is, the greater the displacement desorption amount is. The above research has revealed that water has some effect on the adsorption of methane in coal from engineering practice and laboratory tests, but there is a lack of in-depth analysis on micromechanism.

With the rapid development of computer materials, molecular simulation has been widely used to study the micromechanism of water molecules on the methane adsorption of coal. Clarkson and Bustin [12] demonstrated that moisture will reduce the adsorption capacity of coal. Li et al. [13] proved that water can replace the adsorbed methane. Xia et al. [14] confirmed that water can promote the desorption of methane by studying the effect of oxygen functional groups in coal on the water absorption of methane. Zhu et al. [15, 16] constructed coal molecules with sulfur-containing groups and established methane adsorption isotherm curves under different moisture content conditions. It was proved that the existence of moisture would lead to a sharp decline in methane adsorption capacity. You et al. [17, 18] used the oxygen functional group modified graphite surface model to run the MD

simulation and found that water molecules tend to adsorb the carboxyl group and the adsorption between water and coal is spontaneous. Meng et al. [19] adopted the method of combining methane desorption experiments and molecular simulation to study the influence of water molecules on methane desorption characteristics of coal, and the results showed that the interaction between coal molecules and H_2O molecules is stronger. Gao et al. [20] and Hao et al. [21, 22] showed that the surface of the coal matrix has a stronger affinity for H_2O than CH_4. Chen et al. [23] studied the adsorption amount of methane under different water moisture by molecular simulation and proved that with the increase of the number of water molecules, the water molecules can replace the methane position which has been adsorbed on the long-flame coal molecules. Studies were proving that moisture content has a great influence on low-rank coal, and with the increase of moisture content, the adsorption capacity of coal molecules to methane gas decreases [24–28]. The above studies have explored the micromechanism of the effect of water on coal adsorbing methane, but there are few reports about the effect of water on coal adsorbing methane.

To explore the micromechanism of long-flame coal adsorption methane and moisture on coal-absorbing methane, this article selects the long-flame coal molecule in Shendong Mining Area as a research object [29]. Since the amount of adsorption and the number of coal-based molecules is a linear relationship, so a long-flame coal molecule is used as the basic structural unit. By studying and analyzing the molecular adsorption models of methane-long-flame coal and water-long-flame coal binary systems, the saturated adsorption amounts of methane molecules and water molecules are obtained, and the binary system of methane-long-flame coal and water-long-flame coal and the ternary system of water-methane-long-flame coal are constructed and analyzed, and based on the average adsorption amount and adsorption heat of water molecules and methane molecules,

TABLE 2: Energy changes of the long-flame coal molecule before and after adsorption of different numbers of CH_4.

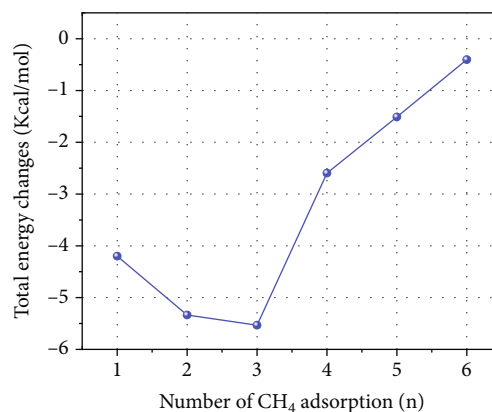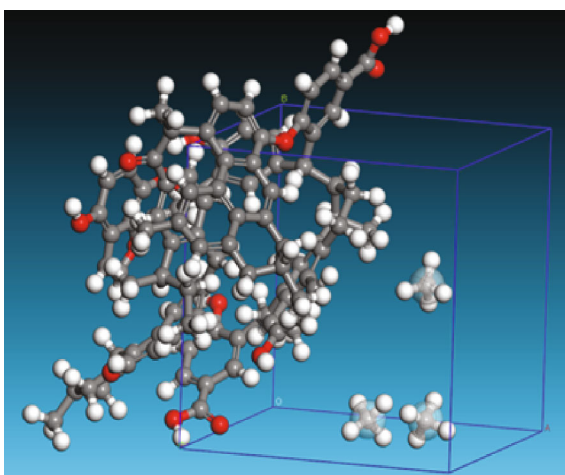| Number of CH_4	Total energy difference (kcal/mol)	Valence electron energy difference (kcal/mol)				Nonbonding energy difference (kcal/mol)		
		Bond	Angle	Torsion	Inversion	H-bond	van der Waals	Electrostatic
1	-4.200	0	0	0	0	0	-4.299	0.099
2	-5.533	0	0	0	0	0	-6.242	0.709
3	-5.335	0	0	0	0	0	-2.667	-2.668
4	-2.596	0	0	0	0	0	-1.517	-1.079
5	-1.510	0	0	0	0	0	-0.851	-0.659
6	-0.403	0	0	0	0	0	-0.312	-0.091

FIGURE 2: Saturated molecular structure model and total system energy of the long-flame coal molecule-absorbing methane molecules.

the adsorption difference of water molecules and methane molecules by long-flame coal molecule is analyzed under the constant temperature of 30°C and adsorption pressure of 0.01-15 MPa, and the effects of long-flame coal on the adsorption difference of water molecules and methane molecules are obtained.

2. Model Construction and Parameter Selection

2.1. Coal Macromolecular Structure Model. In this paper, the macromolecular structure of long-flame coal in the Shendong Mining Area is taken as the molecular model, as shown in Figure 1(a), and the detailed parameters of this molecule are shown in Table 1. Using the Forcite module in materials studio for molecular dynamics simulation, when optimizing energy, select the task item energy. The force field is Dreiding, quality is medium, and charge is set to "Charge Using QEq" to balance the interaction between electrons. van der Waals and electrostatic power use the atom-based algorithm [30]. When optimizing geometry optimization, the quality options select customized, and the smart algorithm is used to fully eliminate the adverse interaction between atoms. During the annealing process, the temperature control method selects nose, the temperature is set to 303.15 K, the canonical ensemble is NVT ($T = 303.15$ K), and the step is 1 fs, which makes the system reach the full equilibrium state, as shown in Figure 1(b).

The periodic boundary condition is constructed for the long-flame coal molecular model optimized by annealing; using the construction item of amorphous cell plate, the long-flame coal molecule with periodic boundary condition is piled up in cubic crystals that a 3D structure model with the density of 1.25 g/cm^3 was obtained. By using NVT ($T = 303.15$ K) ensemble annealing and the nose temperature control method, the model of the lowest energy structure of long-flame coal molecule under the periodic boundary condition is obtained [31], and the result is shown in Figure 1(c), and the supercell expansion of long-flame coal molecule with periodic boundary conditions is shown in Figure 1(d).

2.2. Construction of Adsorption Model

2.2.1. Adsorbate Model and Adsorption Simulation. The molecular structure models of methane molecule and water molecule are drawn in Materials Studio software, the molecular dynamics simulation is performed by the Forcite module, the parameters setting is the same as that of the abovementioned long-flame coal molecule, and the lowest energy structure models of methane molecule and water molecule are obtained. Adsorption simulation of adsorbate by long-flame coal adopts Sorption module and uses locate task to build adsorption model, the temperature is set to 303.15 K, and this adopts the random sampling method (Metropolis) can ensure the computational efficiency of the model and obtain the

TABLE 3: Energy changes of the long-flame coal molecule before and after adsorption of different numbers of H_2O.

| Number of H_2O	Total energy difference (kcal/mol)	Valence electron energy difference (kcal/mol)				Nonbonding energy difference (kcal/mol)		
		Bond	Angle	Torsion	Inversion	H-bond	van der Waals	Electrostatic
1	-2.961	0	0	0	0	-2.892	2.957	-3.025
2	-7.675	0	0	0	0	-6.721	5.016	-5.971
3	-8.233	0	0	0	0	-7.223	4.402	-5.413
4	-9.766	0	0	0	0	-9.166	8.439	-9.039
5	-17.717	0	0	0	0	-14.913	8.589	-11.394
6	-13.009	0	0	0	0	-12.911	6.921	-7.018
7	-24.966	0	0	0	0	-20.405	13.445	-18.005
8	-29.811	0	0	0	0	-25.172	13.783	-18.422
9	-36.427	0	0	0	0	-31.018	14.410	-19.819
10	-38.580	0	0	0	0	-29.870	14.358	-23.068
11	-40.664	0	0	0	0	-32.199	18.802	-27.266
12	-52.794	0	0	0	0	-39.826	11.731	-24.699
13	-49.361	0	0	0	0	-37.960	21.300	-32.702
14	-48.987	0	0	0	0	-34.597	14.280	-28.670
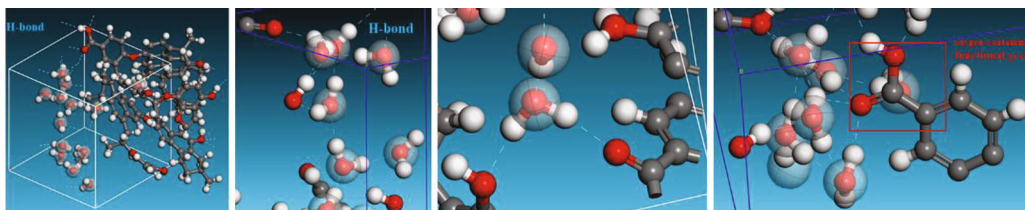
FIGURE 3: H-bonds in the binary system of water-long-flame coal. Blue dashed lines represent H-bond.

important sampling points corresponding to the system. The maximum number of loading steps and the maximum number of production steps are all set to 100000, the temperature cycle is set to 5 times, and the molecular structure model of CH_4 and H_2O adsorbed by long-flame coal was obtained.

2.2.2. Isothermal Adsorption Model.
Different pressures have different effects on the adsorption characteristics of CH_4 and H_2O in the structure of long-flame coal. To study the adsorption capacity of long-flame coal to CH_4 and H_2O, the lowest energy structure model of long-flame coal molecule under periodic boundary conditions (Figure 1(c)) is imported into the adsorption isotherm task in the Sorption module by using Materials Studio software, and single-component isothermal adsorption of methane molecules and water molecules is carried out, respectively, to obtain the adsorption amount and adsorption heat of methane and water. The adsorption temperature is 303.15 K, and the adsorption pressure range is from 0.01 to 15 MPa. The parameter settings of the two-component isothermal adsorption are the same as those of the single-component isothermal adsorption. The mixed isothermal adsorption of water molecules and methane molecules is carried out at a ratio of 1 : 1. The adsorption amount and adsorption heat of methane and water under the two-component isothermal adsorption are simulated.

2.3. Linearization of Langmuir Adsorption Model.
Under the same coverage rate, a uniform surface, and constant temperature, Langmuir Sorption isotherm is an ideal equation for single-layer adsorption, which can be a good description of chemical adsorption or gas-solid adsorption which has particularly strong physical adsorption. It is assumed that the adsorption surface is uniform, there is no interaction between the adsorption molecules, and the adsorption is monolayer localization adsorption. The calculation method is shown in Equation (1).

$$V = \frac{V_m bP}{1 + bP}, \tag{1}$$

where P is the gas adsorption equilibrium pressure, MPa; V is the adsorption amount of equilibrium pressure P under the constant condition, cm^3/g; V_m is the saturated adsorption amount of coal, cm^3/g; b is the gas adsorption constant, and b represents the strength or weakness of gas adsorption capacity on the solid surface.

The data of average adsorption amount can be obtained by isothermal adsorption simulation of single-component and two-component. By Langmuir function fitting, we can obtain R^2. R^2 measures the overall fit degree of the regression equation. The higher the R^2 is, the higher the correlation is. The
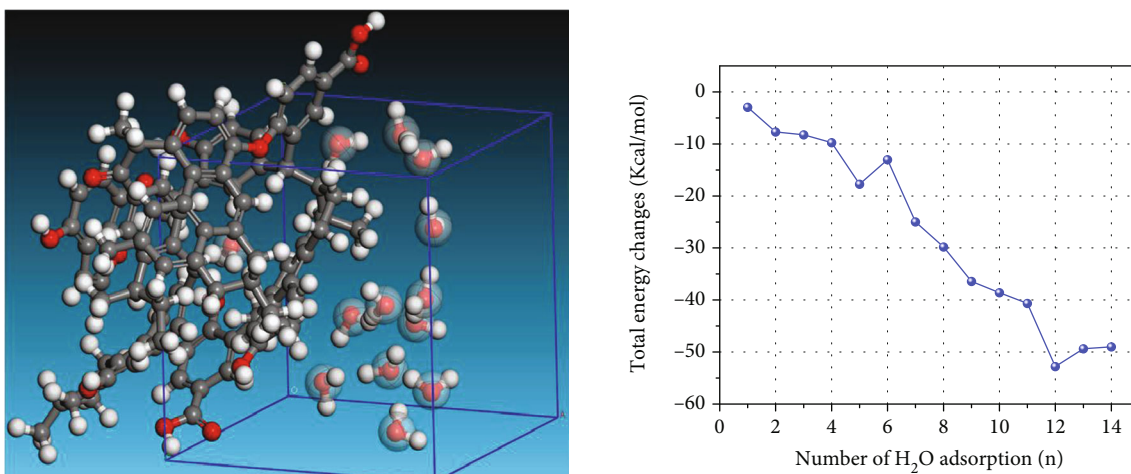
FIGURE 4: Saturated molecular structure model and total system energy of the long-flame coal molecule-absorbing water molecules.

TABLE 4: Single-component isothermal adsorption data of the long-flame coal molecule to methane molecules and water molecules.

Pressure (MPa)	Average adsorption amount of CH_4 (mmol/g)	Average adsorption amount of H_2O (mmol/g)	Pressure (MPa)	Average adsorption amount of CH_4 (mmol/g)	Average adsorption amount of H_2O (mmol/g)
0.01	0.003	0.454	8.255	0.711	5.874
0.760	0.217	2.801	9.004	0.744	5.978
1.509	0.341	3.680	9.754	0.763	5.981
2.259	0.385	4.118	10.503	0.779	5.999
3.008	0.506	4.760	11.253	0.816	5.951
3.758	0.553	5.050	12.002	0.779	5.997
4.507	0.647	5.407	12.752	0.756	5.958
5.257	0.592	5.499	13.501	0.843	6.023
6.006	0.681	5.661	14.251	0.826	5.99
6.756	0.665	5.825	15.000	0.818	5.97
7.505	0.734	5.890			

correlation between adsorbates and adsorbents can be judged by the fitting degree between adsorption amount and Langmuir adsorption isotherms.

3. Result Analysis

3.1. Analysis of Saturated Adsorption Data

3.1.1. Saturated Adsorption Data of Methane Molecules. During the simulation process, recorded each component's energy corresponding to long-flame coal adsorbed with different amounts of methane molecules before and after, and calculated that the change of energy differences in each component before and after adsorption, the total energy difference is the sum of valence energy and the nonbond energy, and as shown in Table 2, the positive value indicates that the energy after adsorption increases, and the negative value indicates that the energy after adsorption is reduced.

It can be seen from Table 2 that in the process of the long-flame coal molecule adsorbing methane molecules, only nonbonding energy can play a role, which indicates that

the adsorption of long-flame coal molecule to methane molecules belongs to physical adsorption. Physical adsorption is a process of giving off heat, the bigger the absolute value of interaction energy is, the more energy is given off, and the more stable the structure is after adsorption [32, 33]. In the nonbonding energy, the process of adsorbing methane molecules only involves van der Waals energy and electrostatic energy, and van der Waals energy accounts for 76.23% of the total energy difference, which indicates that van der Waals energy can occupy the absolute dominant.

Based on the simulation results, the saturated adsorption molecular configuration of the long-flame coal molecule adsorbing methane molecules is exported, and the system energy diagrams of methane molecules adsorbed by long-flame coal molecule are drawn, as shown in Figure 2.

From the analysis of Figure 2, it can be concluded that with the increase of the number of methane molecules, the total energy difference of the system first decreases as the number of methane molecules increases and increases rapidly when the number of adsorbed methane molecules is 3. The main reason is that the long-flame coal molecule-absorbing
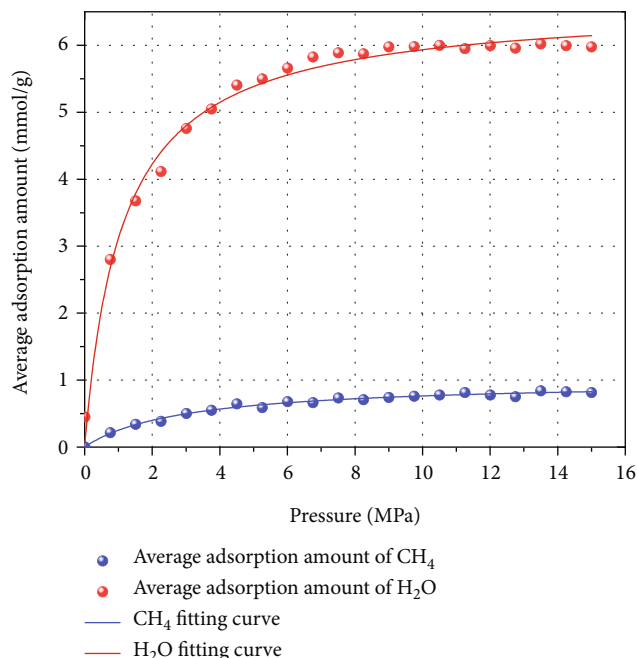
FIGURE 5: Single-component isothermal adsorption curve at 303.15 K.

methane molecule is an exothermic process. The greater the energy difference, the interaction between long-flame coal molecule and methane molecules is. When the minimum value is reached, the long-flame coal molecule adsorbing methane molecules can reach saturation. Therefore, when the number of long-flame coal adsorption methane molecules is less than 3, the adsorption of long-flame coal molecule on methane molecules has not reached saturated, and the total energy difference between the entire systems has been decreased. When the number of methane molecules adsorbed by long-flame coal exceeds 3, the adsorption of methane molecules by long-flame coal molecule reaches saturation state, and at this time, the long-flame coal molecule starts to repel methane molecules, the ability of long-flame coal to adsorb methane molecules decreases, and the total energy difference of the system starts to rise. It can be concluded that the saturated adsorption amount of long-flame coal molecule is the molecular number of adsorbates corresponding to the lowest total energy point of the system, and its saturated adsorption amount is 3 molecules/(u.c) (u.c is the abbreviation of unit cell).

3.1.2. Saturated Adsorption Data of Water Molecules.
The energy difference of long-flame coal before and after adsorbing different amounts of water molecules is shown in Table 3.

In Table 3, we can conclude that in the process of long-flame coal molecule adsorbing water molecules, there are only H-bond, van der Waals, and electrostatic energy. By calculation, the average values of H-bond, van der Waals, and electrostatic are -21.776 kcal/mol, 11.317 kcal/mol, and -16.751 kcal/mol, respectively, indicating that H-bond energy is dominant in the process of long-flame coal molecule adsorbing water molecules, and electrostatic and van der Waals are second.

TABLE 5: Fitting data of different adsorbates with Langmuir under single-component.

Adsorbate	Isothermal adsorption equation	Correlation coefficient $R^2(\%)$	Langmuir's volume V_L (mmol/g)
CH_4	$Y = 0.31P/(1 + 0.33P)$	$R^2{}_1 = 98.56$	0.31
H_2O	$Y = 5.89P/(1 + 0.0.89P)$	$R^2{}_2 = 98.77$	5.89

H-bond refers to all H-bonds in the water long-flame coal binary system, including H-bonds contained in long-flame coal molecules and water molecules, H-bonds between coal molecule and water molecules, and H-bonds between water molecules and water molecules, as shown in Figure 3. Oxygen-containing functional groups provide adsorption sites for water molecules. Water molecules that form H-bonds with long-flame coal molecule continue to form H-bonds with other water molecules. Other water molecules form H-bonds with multiple water molecules. As the adsorption is physical adsorption and H-bonds participate in adsorption, the aggregation of water molecules leads to desorption and bond breaking of water molecules [34]. The broken hydrogen atoms form OH with oxygen atoms in coal molecule, and oxygen atoms insert into oxygen vacancies in coal molecules. Therefore, not only the adsorption of H_2O on the surface of uncoordinated O-atoms contributes to the adsorption of energy but also the hydrogen bond contributes to the absorption of energy, which results in that the adsorption capacity of long-flame coal molecule on water molecules is greater than that of methane [35, 36].

From Figure 4, it shows that when the number of water molecules adsorbed by long-flame coal is 12, the total energy reaches the lowest point, so the saturated adsorption amount of water molecules adsorbed by long-flame coal is 12 molecules/(u.c).

3.2. Effect of Adsorption Equilibrium Pressure

3.2.1. Isothermal Adsorption Results of Single-Component Adsorption.
The single-component isothermal adsorption of methane molecules and water molecules at 303.15 K is simulated by Materials Studio, and its data are shown in Table 4.

The simulated data are fitted by the Langmuir adsorption model and plotted as shown in Figure 5. The fitting information of different adsorbates is obtained by fitting, as shown in Table 5.

As can be seen from Figure 5, with the increase of pressure, the average adsorption amount of long-flame coal to methane molecules and water molecules increases sharply (0.01–0.76 MPa), increases slowly (0.76–15 MPa), and then flattens after 15 MPa. The results show that when the temperature is constant, the increase of adsorption pressure is beneficial to the adsorption of CH_4 molecules and H_2O molecules by long-flame coal. At 0.01–0.76 MPa, the long-flame coal molecule adsorbs water molecules or methane molecules, which is affected by the interfacial tension of pores, and increases the adsorption pressure, and the methane molecules and water
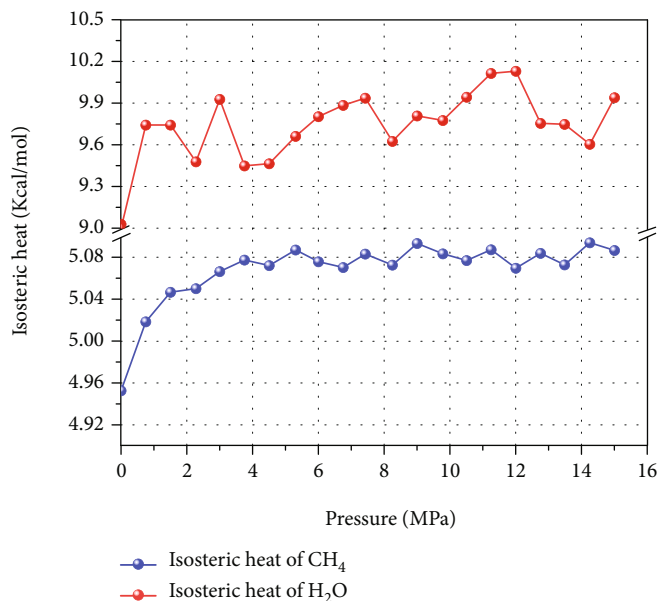
FIGURE 6: Isothermal adsorption heat curves of single-component at 303.15 K.

TABLE 6: Two-component isothermal adsorption data of the long-flame coal molecule to CH_4/H_2O.

Pressure (MPa)	Average adsorption amount of CH_4 (mmol/g)	Average adsorption amount of H_2O (mmol/g)	Pressure (MPa)	Average adsorption amount of CH_4 (mmol/g)	Average adsorption amount of H_2O (mmol/g)
0.01	0.003	0.424	8.255	0.183	5.558
0.760	0.137	2.997	9.004	0.277	5.808
1.509	0.163	3.813	9.754	0.207	5.636
2.259	0.197	4.163	10.503	0.267	6.036
3.008	0.131	4.818	11.253	0.240	6.154
3.758	0.181	4.574	12.002	0.312	5.974
4.507	0.152	5.119	12.752	0.248	6.307
5.257	0.227	5.363	13.501	0.229	6.241
6.006	0.177	5.463	14.251	0.268	6.406
6.756	0.213	5.379	15.000	0.299	6.386
7.505	0.248	5.297			

TABLE 7: Fitting data of different adsorbates with Langmuir under two-component.

Adsorbate	Isothermal adsorption equation	Correlation coefficient R^2 (%)	Langmuir's volume V_L (mmol/g)
CH_4	$Y = 0.13P/(1 + 0.04P)$	$R^2_3 = 77.12$	0.13
H_2O	$Y = 5.13P/(1 + 0.55P)$	$R^2_4 = 98.75$	5.13

molecules can overcome the surface tension and certain capillary force into the long-flame coal molecule [37]; therefore, the average adsorption amount of water molecules and methane molecules increased sharply. At 0.76–15 MPa, with the increase of adsorption equilibrium pressure, the average adsorption amount of long-flame coal molecule to methane molecules and water molecules increases slowly, and the max-

imum value can reach 0.843 mmol/g and 6.023 mmol/g; at this time, the value of the average adsorption amount of methane molecules and water molecules tends to the saturated adsorption amount gradually. When the adsorption pressure is more than 15 MPa, the average adsorption amount of long-flame coal to methane molecules and water molecules tends to be stable, reaching the state of adsorption saturation.

In the process of single-component adsorption simulation, the adsorption heat under each pressure is recorded, and the average value of adsorption heat under three groups of the same pressure is plotted, as shown in Figure 6.

As can be seen from Table 5, under the same conditions, $R^2_1 > R^2_2$, the results show that the adsorption amount of long-flame coal molecule to water molecules and methane molecules increases in a Langmuir curve with the increase of adsorption equilibrium pressure, and the fitting degree of the average adsorption amount of the long-flame coal
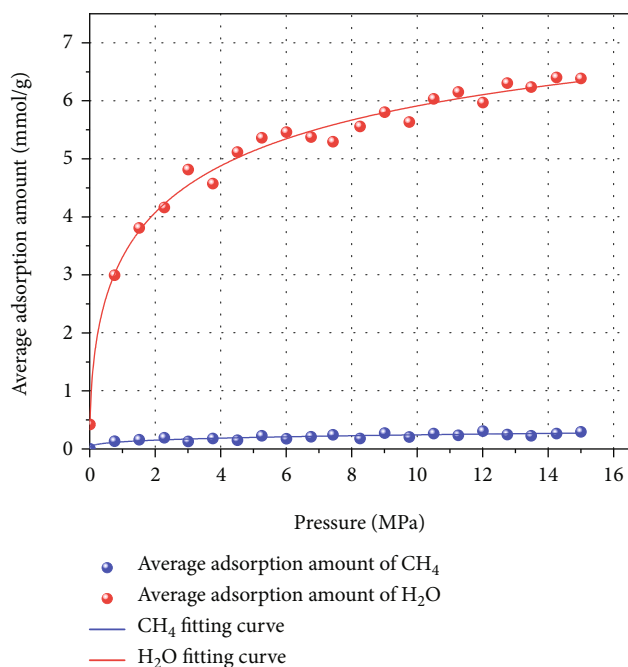
FIGURE 7: Two-component isothermal adsorption curve at 303.15 K.

TABLE 8: Adsorption amount of methane and water at 0.01–0.76 MPa for two-component adsorption.

Pressure (MPa)	Average adsorption amount of CH_4 (mmol/g)	Average adsorption amount of H_2O (mmol/g)
0.085	0.018	0.7
0.16	0.032	1.117
0.235	0.052	1.428
0.31	0.093	1.456
0.385	0.126	1.629
0.46	0.153	1.777
0.535	0.168	1.892
0.61	0.194	2.099
0.685	0.203	2.15

molecule to water molecules is higher than that of the methane molecules; the heat of adsorption is an index to measure the capacity of adsorption, and the greater the heat of adsorption, the stronger the capacity of adsorption, combined with Figure 6; under the same adsorption pressure and temperature, the average value of adsorption heat of long-flame coal molecule to water molecules is 9.749 kcal/mol, and the average adsorption heat of methane molecule is 5.068 kcal/mol, and it can be concluded that long-flame coal molecule adsorbs water molecules more easily, which is consistent with the previous research [38].

3.2.2. Isothermal Adsorption Results of Two-Component Adsorption. The two-component adsorption data of the long-flame coal molecule-absorbing CH_4/H_2O at 303.15 K is obtained by Materials Studio simulation, as shown in Table 6.

The simulated adsorption data is fitted into a graph, as shown in Figure 6, and the fitting curves of different adsorbates are shown in Table 7.

Figure 7 shows that the average adsorption amount of methane molecules and water molecules increases rapidly (0.01–0.76 MPa), and the average adsorption amount of water molecules increases slowly at (0.76–15 MPa) and tends to level off after more than 15 MPa; but the average adsorption amount of methane molecules tends to smooth after 0.76 MPa. It can be concluded that when the adsorption pressure is less than 0.76 MPa, the long-flame coal molecule has strong adsorption of methane molecules and water molecules, and when the adsorption pressure is higher than 0.76 MPa, the average adsorption amount of the long-flame coal molecule to water molecules still increases with the increase of the adsorption pressure, indicating that the adsorption of long-flame coal molecule to water molecules is still strong, but the average adsorption amount of methane molecules has tended to be flat, indicating that the adsorption of long-flame coal molecule to methane molecules is weak.

The above data can determine that the competitive adsorption is in the range of 0.01–0.76 MPa. In order to ensure that the data is not accidental and prove the accuracy of the opinion, a more detailed simulation analysis is conducted for the range of 0.01–0.76 MPa, and the data obtained are shown in Table 8.

The results show that the range of 0.01–0.76 MPa is the turning point of competitive adsorption of water and methane, and the average adsorption amount of water is 13.724 times that of methane. In this process, methane and water molecules will undergo competitive adsorption.

The adsorption heat curves of the two-component are plotted as shown in Figure 8.

As can be seen from Table 7, $R^2_4 > R^2_3$, which indicates that the simulated adsorption data of water molecules agree with Langmuir model relatively well, but the adsorption data of methane molecules agree poorly. According to the data of adsorption heat in Figure 8, when the long-flame coal molecule adsorbs the mixture of water molecules and methane molecules, the average adsorption heat of water molecules is 9.77 kcal/mol and that of methane molecules is 9.269 kcal/mol; that is, the adsorption heat of water molecules is slightly larger than that of methane molecules.

4. Discussion

Hydraulic measures are often used in engineering practice to increase the permeability of coal seams. Hydraulic measures can promote gas desorption in coal and reduce the difficulty of gas extraction in coal seams, so it is very important to study the adsorption difference between methane and water on coal for exploring the hydraulic measures to promote extraction.

According to the research of the paper, with the increase of the adsorption equilibrium pressure, the average adsorption amount of the long-flame coal molecule to methane
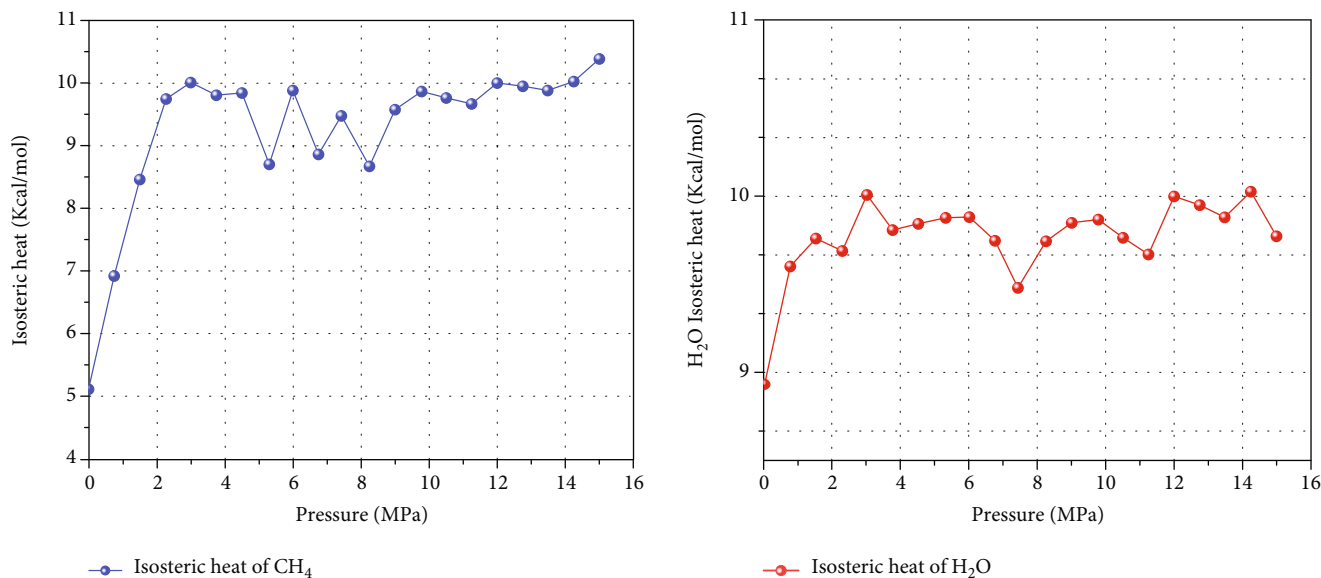
FIGURE 8: Isothermal adsorption heat curves of two-component at 303.15 K.

molecules and water molecules increases greatly, but the increased amplitude decreases with the increase of the adsorption equilibrium pressure, and it is revealed that there is a critical adsorption equilibrium pressure. When the gas pressure environment exceeds the critical pressure, it will have little effect on the adsorption. With the increase of the adsorption pressure, the increase of the average adsorption amount of water molecules gradually decreases, which also shows that there is a limit of additional moisture in terms of affecting coal adsorption gas; after exceeding the limit of additional moisture, the increase of additional moisture will have little impact on coal adsorption of gas. Therefore, the critical pressure and the limited moisture should be taken into consideration when the coal seam is injected with water to increase permeability.

From the adsorption data obtained by simulation, compared with the saturated adsorption amount of methane molecules, the saturated adsorption amount of water molecules is 4.33 times that of methane molecules, and the adsorption heat of water molecules is 1.9236 times than that of methane molecules; the bigger the adsorption heat is, the stronger the adsorption capacity is; previous studies found that after the long-flame coal molecular structure with methane molecules adsorbing water molecules, the interaction between coal molecule and methane molecules weakens, and this proves that the adsorption capacity of long-flame coal molecule to water molecules is greater than to methane molecules. In the mixed adsorption experiment of long-flame coal molecule to methane molecules and water molecules, the average adsorption amount of long-flame coal molecule to water molecules is much larger than that of methane molecules, and the average adsorption amount of water molecules is 24.7507 times that of methane molecules by calculating the average value of the average adsorption amount under multiple same pressures; it can be seen that in the competitive adsorption of long-flame coal molecule to methane molecules and water molecules, water molecules are in an advantage.

5. Conclusion

(1) The saturated adsorption amount of long-flame coal molecule adsorbing methane molecules and water molecules is 3 molecules/(u.c) and 12 molecules/(u.c), respectively; in the process of long-flame coal molecule adsorbing methane molecules, whether in the adsorption stage or exclusion stage, van der Waals energy is the main energy, which belongs to typical physical adsorption, while in the process of long-flame coal molecule adsorbing water molecules, H-bond energy is dominant, and van der Waals and electrostatic are second

(2) In single-component isothermal adsorption of water molecules and methane molecules by long-flame coal, when the adsorption pressure is less than 15 MPa, with the increase of the adsorption pressure, the average adsorption amount of the long-flame coal molecule to methane molecules and water molecules increases gradually, and the average adsorption amount of water molecules is much larger than that of methane molecules. When the adsorption pressure is more than 15 MPa, the average adsorption amounts of methane molecules and water molecules are saturated

(3) In mixed isothermal adsorption of water molecules and methane molecules by long-flame coal, when the adsorption pressure is less than 0.7595 MPa, long-flame coal molecule has adsorption to methane molecules and water molecules. When the adsorption pressure is more than 0.7595 MPa, the average adsorption amount of water molecules is much larger than that of methane molecules (the conclusion is drawn under the condition that the absolute

adsorption amount is considered in this work); with the increase of the adsorption pressure, the average adsorption amount of methane molecules tends to be flat, and the average adsorption amount of water molecules is still increasing

(4) Under the same conditions, whether single-component adsorption or two-component adsorption, the fitting degree between the adsorption of water molecules by long-flame coal molecule and Langmuir adsorption model, the average adsorption amount, and the adsorption heat of water molecules are greater than those of methane molecules; the results show that in the competitive adsorption of the long-flame coal molecule to methane molecules/water molecules, water molecules are in a dominant position

Data Availability

The figures and tables data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflict of interest.

Acknowledgments

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