Molecular simulation of methane adsorption characteristics on coal macromolecule

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Abstract. In this paper, the molecular model of anthracite named Wender2 was selected to study the adsorption behaviour of single component CH₄ and the competitive adsorption of CH₄/CO₂, CH₄/H₂O and CH₄/N₂. The molecular model of anthracite was established by molecular simulation software (Materials Studio 8.0), and Grand Canonical Monte Carlo (GCMC) simulations were carried out to investigate the single and binary component adsorption. The effects of pressure and temperature on the adsorption position, adsorption energy and adsorption capacity were mainly discussed. The results show that for the single component adsorption, the adsorption capacity of CH₄ increases rapidly with the pressure ascending, and then tends to be stable after the first step. The low temperature is favourable for the adsorption of CH₄, and the high temperature promotes desorption quantity of CH₄ from the coal. Adsorbent molecules are preferentially adsorbed on the edge of coal macromolecules.

The order of adsorption capacity of CH₄/CO₂, CH₄/H₂O and CH₄/N₂ in the binary component is H₂O>CO₂>CH₄>N₂. The change of pressure has little effect on the adsorption capacity of the adsorbent in the competitive adsorption, but it has a great influence on the adsorption capacity of the adsorbent, and there is a positive correlation between them.

1. Introduction

With the acceleration of the industrialization process, CO₂ as a major greenhouse gas (GHG) has led to environmental problems of global warming. Therefore, CO₂ flooding coal seams CH₄ enhanced oil recovery technology (CO₂-ECBM) and CO₂ capture and storage technology (CCS) have become a hot issue at home and abroad today. The adsorption of CH₄ between the adsorbed CH₄ and the CH₄ in the coal seam is improved by the competitive adsorption between the CO₂ and the coalbed methane in the adsorbed state, which improves the recovery rate of the CH₄ in the coal seam and achieves the situation of protecting the environment and developing clean energy [1-2].

Molecular simulation technology is widely used in the study of porous media adsorption, and it can not only carry out molecular microstructure determination, but can get gas molecules isothermal adsorption, adsorption heat and other data. The sorption of MS software (Adsorption isotherms) is a program that predicts the adsorption of single or mixed components in microporous materials and mesoporous materials based on the GCMC (Grand Canonical Monte Carlo) method. In this study, the Monte Carlo simulation method was used to simulate the adsorption of methane molecules in MS under the Sorption module [3-4].

Therefore, this study will be based on the Wender2 model, and the macromolecule structure model of coal is constructed by using Materials Studio, which is close to the actual structure of the model. The interaction between coal and methane molecules is studied to determine the favorable adsorption sites of methane on the surface of coal. It provides a new way to further understand the microcosmic
mechanism of methane gas and coal [5], and develop and utilize coalbed methane to provide theoretical basis.

2. Computational details
In this paper, the adsorption of coal on methane was studied by selecting the Wender2 of anthracite, which is based on the study of the evolution of the macromolecule hydrocarbon generation structure and its mechanism of energy barrier control.

2.1. Coal molecular model
By using the Visualizer module of the MS software, the selected coal structure is drawn. The geometrical structure of coal structure is optimized by molecular mechanics method (MM), and the Forcite module in Materials Studio software is used to simulate the Anneal dynamics model of the anthracite macromolecule model [6]. The global optimization is carried out on the whole potential energy surface and gets a global minimum configuration of energy. The optimal structure is shown in Figure 1.

![Figure 1. Optimum Wender2 macromolecule model.](image)

2.2. Periodic Boundary Condition Construction
Based on the Construction task of Amorphous Cell module in Materials Studio software, periodic boundary conditions were added to the anthracite macromolecule model obtained by annealing the molecular dynamics optimization. According to the principle of energy minimization, the minimum energy configuration is selected in the 10 bituminous coal structure models optimized by molecular mechanics, as shown in Figure 2.

![Figure 2. The lowest energy configuration after Wender2 coal annealing.](image)
3. Results and discussion

3.1. The adsorption of Single component CH₄

3.1.1. Isothermal adsorption  The isothermal adsorption curves of CH₄ in Wender2 at different temperatures are shown in Figure 3. Under the condition of constant pressure, there is a negative correlation between temperature and adsorption capacity. Low temperature is favorable for the adsorption of CH₄. High temperature promotes the desorption of CH₄.

When the pressure is less than the critical pressure (9 MPa), the adsorption capacity of CH₄ increases rapidly with the increase of pressure. When the pressure is higher than the critical pressure, the adsorption capacity of CH₄ gradually increases. There was no significant effect on the adsorption of CH₄.

![Isothermal adsorption curves of CH₄ in Wender2 coal model at different temperatures.](image)

Figure 3. Isothermal adsorption curves of CH₄ in Wender2 coal model at different temperatures.

3.1.2. Adsorption energy The energy of adsorption is used to calculate the interaction between gas molecules and solid surfaces and it is defined as the formula 1.

$$E_{ads} = E_M + E_{gas} - E_{gas-M}$$  \hspace{1cm} (1)

where $E_{ads}$ is the energy of adsorption, $E_M$ the energy of coal molecule model without adsorption of methane, $E_{gas}$ the energy of free gas molecule, $E_{gas-M}$ the total energy absorbed by gas and coal model surface in equilibrium state [2].

It can be seen from Table 1 that the adsorption energy of the benzene ring on the surface of the coal and the physical adsorption of different methane molecules reaches equilibrium. The adsorption energy is different. With the increase of the number of adsorbed methane molecules, the adsorption energy also increases.
Table 1. Adsorption of 1,2,3,4 methane by Wender2 coal molecule model (Kcal/mol).

| The numbers of adsorbed methane | $E_{M+}E_{gas}$ | $E_{gas-M}$ | $E_{ads}$ |
|---------------------------------|-----------------|-------------|-----------|
| 1                               | 169.56          | 162.83      | 6.73      |
| 2                               | 169.56          | 156.92      | 12.64     |
| 3                               | 169.56          | 151.69      | 17.87     |
| 4                               | 169.56          | 146.61      | 22.95     |

3.1.3. Saturated adsorption configuration
When the methane molecules were added to the anthracite Wender2, the energy of the system increased with the increase of the number of methane molecules added, and the energy of the system reached the minimum until the number of methane molecules reached 10[6], as shown in Figure 4.

Figure 4. Saturated adsorption configuration of Wender2 coal.

3.2. The adsorption of binary components CH₄/CO₂, CH₄/N₂, CH₄/H₂O
The isothermal adsorption curve of the adsorption capacity and pressure of each binary component by Wender2 coal is shown in Figure 5.

Figure 5. Isothermal adsorption curves of different binary components of Wender2.
(a) CH₄/N₂, b) CH₄/H₂O, c) CH₄/CO₂
According to the same temperature and pressure, the adsorption capacity of the size of: in the competitive adsorption, coal on the CH\(_4\), CO\(_2\), N\(_2\) and H\(_2\)O adsorption priority order is H\(_2\)O, CO\(_2\), CH\(_4\) and N\(_2\). With the increase of pressure, the adsorption capacity of N\(_2\) and CH\(_4\) did not change obviously, and the adsorption amount of CO\(_2\) increased with the increase of pressure.

4. Conclusions

In this paper, Wender2 was used to study the adsorption behavior of coal on single component CH\(_4\) by using GCMC in MS8.0. The effects of temperature and pressure on the adsorption behaviors of CH\(_4\) and CH\(_4/CO_2\), CH\(_4/H_2O\) and CH\(_4/N_2\) binary components were discussed, and the competitive adsorption behavior was investigated comprehensively.

The adsorption energy increases with the increase of the number of adsorbed methane molecules. Under the same pressure conditions, the temperature is negatively correlated with the adsorption capacity. The high temperature is not conducive to the adsorption of single component CH\(_4\). The low temperature is favorable for the adsorption of single component CH\(_4\). When the pressure is less than 9 MPa, the adsorption capacity of CH\(_4\) increases with the increase of pressure. When the pressure is more than 9 MPa, the adsorption capacity of CH\(_4\) does not increase.

At the same temperature and pressure, the adsorption capacity of CH\(_4\), CO\(_2\), N\(_2\) and H\(_2\)O in the binary component is: N\(_2\) < CH\(_4\) < CO\(_2\) < H\(_2\)O, which indicates that the adsorption order of coal to CH\(_4\), CO\(_2\), N\(_2\) and H\(_2\)O is H\(_2\)O, CH\(_4\) and N\(_2\).