



## Molecular simulation of competitive adsorption of CO<sub>2</sub>/N<sub>2</sub>/O<sub>2</sub> gas in bituminous coal

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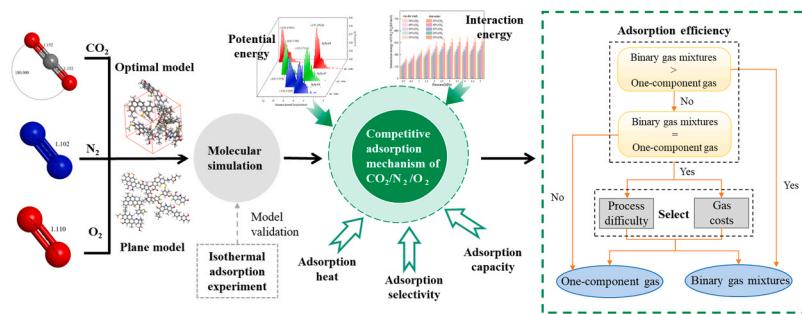
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### GRAPHICAL ABSTRACT



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### ABSTRACT

The main cause of coal spontaneous combustion is the oxidation and temperature rise of coal. Injecting composite inert gas for fire prevention and extinguishing is one of the important methods to prevent coal spontaneous combustion. A large number of studies have macroscopically investigated the fire prevention and extinguishing effects of CO<sub>2</sub>/N<sub>2</sub> and their synergistic actions. However, there is currently a lack of research at the molecular level on the competitive adsorption mechanism between mixed inert gases (CO<sub>2</sub>, N<sub>2</sub>) and O<sub>2</sub> molecules in coal. Therefore, this study conducted adsorption experiments using Qian Yingzhi (QYZ) bituminous coal and compared them with the simulation data of the Wiser coal model to verify the reliability of the Wiser model. Subsequently, employing grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) methods, the competitive adsorption behavior of different proportions of binary mixed component gases (CO<sub>2</sub>/O<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>) at a temperature of 303.15 K was investigated from five perspectives: adsorption capacity, adsorption selectivity coefficient, potential energy distribution, competitive adsorption heat, and interaction energy. The results indicate that among the competitive component gases, CO<sub>2</sub> exhibits the strongest adsorption effect on the entire system, which is closely correlated with the distribution range of adsorption energy sites. The adsorption heat and adsorption amount of CO<sub>2</sub> consistently exhibit a negative correlation, whereas the relationship between the adsorption heat of N<sub>2</sub> and O<sub>2</sub> and the adsorption amount shows a positive correlation. Their adsorption capacities depend on the pressure and the proportion of the two gases. Based on the isothermal adsorption curve of CO<sub>2</sub>/N<sub>2</sub>, it is recommended that the gas pressure during actual inert gas injection be less than 2.5 MPa. Under this

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pressure, the competitive adsorption effect is no longer significant, providing a certain theoretical basis for high-pressure injection. Moreover, the preliminary determination of the optimal injection ratio range is from 4:6–3:7. Furthermore, a systematic logical framework for selecting underground inert gas composition is proposed, and an underground mobile inert gas infusion process is adopted. The actual gas composition for infusion is determined based on cost factors in practical engineering. The research results can provide guidance for the selection of gas injection parameters for mixed inert gas fire prevention and extinguishing in goaf.

## 1. Introduction

Spontaneous combustion of coal is one of the five major hazards affecting mine safety and production, which can lead to serious waste of resources and environmental pollution, and even endanger the safety of workers' lives [1]. Carbon dioxide is the main product of coal self-ignition, carried along with oxygen and nitrogen in the ventilation airflow. However, carbon dioxide and nitrogen are also the main extinguishing agents, possessing advantages such as inerting, oxygen isolation, cooling, explosion prevention, and large diffusion range [2]. The main reason for coal self-ignition is the oxidative heating of coal, and the involvement of these gases can affect the oxidative characteristics of coal. Injecting composite inert gases to a large extent prevents or delays the oxidation of residual coal in goaf, including N<sub>2</sub>, CO<sub>2</sub>, and a certain proportion of synergistic three-gas injection modes. However, due to the different physical properties of CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>, when they coexist in the same goaf, they will compete for adsorption into the coal [3–5]. This competitive adsorption is crucial for elucidating the mechanism of coal self-ignition prevention and control, and thus becomes the subject of this study.

A significant amount of research has focused on the prevention and suppression of coal spontaneous combustion using inert gas. This is primarily achieved through the design and construction of coal spontaneous combustion experimental systems to conduct macroscopic experiments on inert gas suppression of coal spontaneous combustion [6]. Wu et al. [7] utilized a coal spontaneous combustion oxidation program temperature-rise and coal open flame combustion experimental apparatus, independently developed, to investigate the effectiveness of CO<sub>2</sub> and N<sub>2</sub> throughout the entire process of coal combustion prevention. Chu et al. [8] employed a coal low-temperature oxidation kinetics testing system to study the cooling and spontaneous combustion inhibition effects of high-temperature coal bodies in a closed fire zone during gas injection fire suppression processes. Si et al. [9] conducted research on the distribution laws of temperature and adsorption fields within porous media during intermittent CO<sub>2</sub> injection processes using independently developed adsorption devices and diffusion-permeation experimental platforms, proposing a quadrilateral for coal spontaneous combustion prevention. It should be noted that coal, formed over geological periods through prolonged biological, chemical, and physical processes, possesses various pore structures, fissures, and structural characteristics within its interior. Consequently, coal exhibits a complex internal surface structure. Considering the aforementioned points, it is necessary to investigate adsorption principles at the molecular scale. [10–12]

Currently, molecular simulation techniques are primarily employed in studies such as gas injection for gas displacement and carbon dioxide sequestration, providing theoretical support for the prevention and control of gas disasters and energy utilization in goaf [13]. From a thermodynamic perspective, Li et al. [14] investigated the adsorption behavior of CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub> in coal, finding a positive correlation between adsorption energy and adsorption heat, with adsorption potential being influenced by adsorption enthalpy, adsorption quantity, and adsorption entropy. Du et al. [15] studied the adsorption behavior of CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub> mixtures on montmorillonite using molecular simulation methods, and found that lowering the temperature can enhance selectivity. Additionally, injecting gas at lower temperatures is more conducive to triggering the desorption behavior of the adsorbed

gases. It is evident that various gases exhibit competitive adsorption behavior on the surface of coal rocks due to differences in adsorption quantity, adsorption potential, and interaction forces under the same environment. Duan et al. [16] and Niu et al. [17] studied the competitive adsorption characteristics of CH<sub>4</sub>/CO<sub>2</sub> in shale, which indicates that CO<sub>2</sub> exhibited more pronounced preferential adsorption behavior compared to CH<sub>4</sub>. Liu et al. [18] performed dynamic adsorption experiments on different coal and shale samples, investigating the process and mechanism of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> competitive adsorption. Research on the competitive adsorption between binary gas components is mainly aimed at coalbed methane extraction, where high-pressure CO<sub>2</sub> (or N<sub>2</sub>) is injected into coal seams to replace CH<sub>4</sub>. There is relatively less research on their competitive adsorption with oxygen, despite oxygen being crucial in analyzing the physical adsorption process in coal spontaneous combustion.

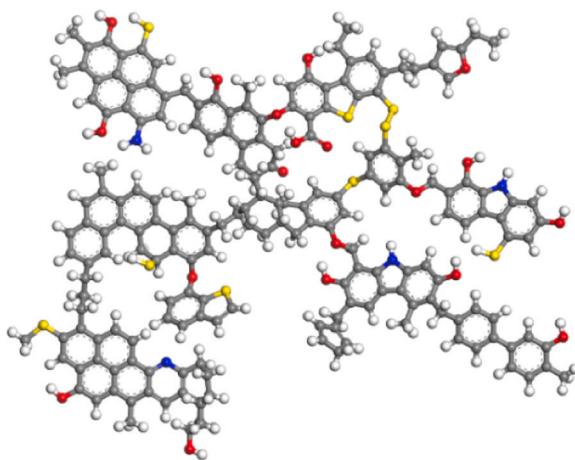
To reveal the fire prevention mechanism in goaf, Ding et al. [19] conducted a study on the adsorption behavior of O<sub>2</sub> by oxygen-containing coal, using Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) methods, with CO<sub>2</sub>/N<sub>2</sub> as the competing gases. The results indicate that CO<sub>2</sub> exhibits a stronger inhibition effect on coal spontaneous combustion compared to N<sub>2</sub>. Wu et al. [20] determined the competitive ability of inert gases and oxygen in coal through calculations of interaction energy and isosteric heat of adsorption, ranking them as CO<sub>2</sub> > O<sub>2</sub> > N<sub>2</sub>. The adsorption capacity of gases in coal is also influenced by their composition and content [21]. However, there is currently a lack of research at the molecular level on the competitive adsorption mechanisms of binary mixed gases composed of different proportions of CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> in coal. Therefore, the GCMC and MD methods are used to investigate the competitive adsorption behavior of different proportions of binary mixed gases (CO<sub>2</sub>/O<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>) at a temperature of 303.15 K. The study aims to analyze the competitive rules among different gas components on adsorption quantity, adsorption selectivity coefficients, potential energy distribution, competitive adsorption heat, and interaction energy. The research findings can provide theoretical parameters and guidance for the selection of gas mixtures for fire prevention and extinguishing in goaf.

## 2. Methodology

### 2.1. Model construction

The coal structure model proposed by American scholar W.H. Wiser in 1970 is considered to be a relatively comprehensive and reasonable model [22], suitable for young bituminous coal (carbon content 82%–83%). The preliminary established Wiser bituminous coal model molecular structure is illustrated in Fig. 1, with a molecular formula of C<sub>192</sub>H<sub>166</sub>N<sub>4</sub>O<sub>19</sub>S<sub>9</sub>. After hydrogen saturation optimization, geometric optimization, annealing, and dynamic optimization, the lowest energy configuration of the molecule is ultimately obtained. The parameter settings are listed in Table 1.

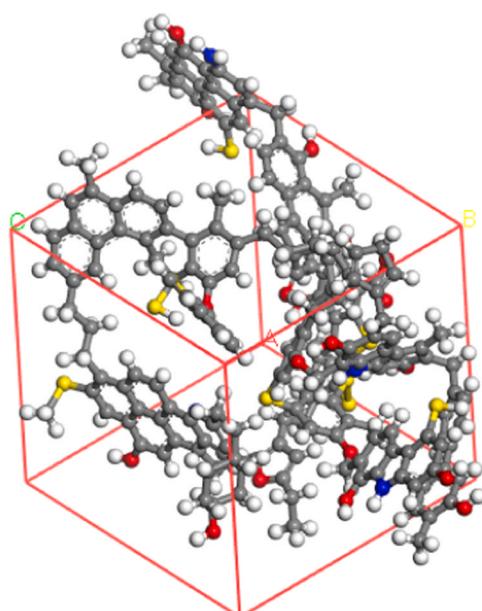
To introduce periodic boundary conditions, the model density was adjusted incrementally by 0.05 g/cm<sup>3</sup> in each step, while observing the trend of potential energy variation. The optimal cell size for the model molecule was determined to be 1.2 g/cm<sup>3</sup>, which closely resembles the density of actual bituminous coal. The optimal bituminous coal molecule is depicted in Fig. 2, with edge lengths A=B=C=16.3 Å and



**Fig. 1.** Two-dimensional plane Wiser model.

**Table 1**  
Parameter settings [23–26].

Module	Geometric Optimization Parameters	Module	Annealing Optimization Parameters
Task	Geometry optimization	Task	Anneal
Quality Algorithm	Customized Smart	Quality Anneal cycles	Medium 10
Energy	0.001 kcal/mol	Initial temperature	300 K
Force	0.1 kcal/mol	Ensemble	NVT Canonical Ensemble
Max iterations	50000	Max iterations	1000000
Forcefield Charge	Dreiding Charge using QEq	Thermostat Initial velocities	Nose Random



**Fig. 2.** Optimal coal molecule.

interfacial angles  $\alpha=\beta=\gamma=90^\circ$ .

In the Material Studio software, molecular models of CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> were constructed individually. Energy optimization was performed on the models of small gas molecules to obtain the lowest energy conformations, as depicted in Fig. 3. The CO<sub>2</sub> molecule adopts a linear three-atom molecular structure, while N<sub>2</sub> and O<sub>2</sub> exhibit non-polar diatomic molecular models. The bond length of the CO<sub>2</sub> molecule is 1.152 Å with a standard bond angle of 180°, while the bond lengths of N<sub>2</sub> and O<sub>2</sub> are 1.102 Å and 1.110 Å, respectively.

## 2.2. 2.2 Simulation parameters and calculations

The coal molecule models with the lowest energy under periodic boundary conditions were imported into the Fixed pressure task of the Sorption module. Simultaneously, the adsorbate molecules of the mixed gas were introduced, with the pressure set according to the partial pressures converted from the gas mixture ratios. The Metropolis method was selected as the Method, with a Medium precision level chosen for quality. The temperature was set to 303.15 K. Equilibration steps were set to 1000,000, and the number of production steps was set to 1000,000.

In binary competitive adsorption, the adsorption capacity provides a qualitative assessment of the relative adsorption strengths of two gases. However, the most intuitive parameter for evaluating the magnitude of adsorption capacity is the adsorption selectivity. The adsorption selectivity of adsorbate A with respect to adsorbate B, denoted as  $S_{A/B}$ , is defined [27] as Eq. (1). In a gas adsorption system, if  $S_{A/B} > 1$ , adsorbate A is more readily adsorbed than adsorbate B in this system.

$$S_{A/B} = \frac{x_A/x_B}{y_A/y_B} \quad (1)$$

where  $x_A$  and  $x_B$  represent the molar concentrations of adsorbate A and adsorbate B in the adsorbed phase;  $y_A$  and  $y_B$  represent the molar concentrations of adsorbate A and adsorbate B in the free phase.

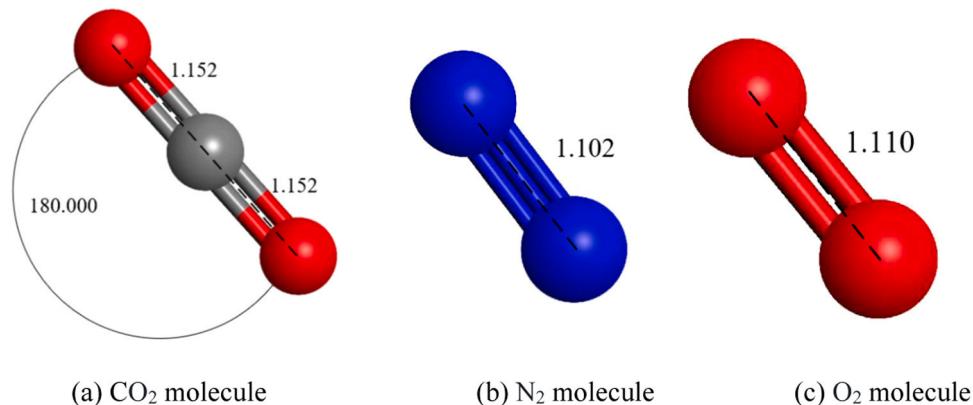
## 2.3 Model validation

The coal samples used in this experiment were taken from the western pillar of the QYZ Coal Mine and belong to bituminous coal. The coal samples were crushed into powder and particles below 6 mm using a jaw crusher, and then sieved using standard sieves to obtain particles with a diameter of 0.1–0.2 mm, which were subsequently dried in a drying oven for use in adsorption experiments. Isothermal adsorption experiments of bituminous coal samples were conducted using a homemade adsorption apparatus based on the volumetric method, with CO<sub>2</sub> selected as the adsorption gas. The specific adsorption apparatus is shown in Fig. 4, and the instrument model can be found in our previously published article [28]. The adsorption capacity is calculated using Eq. (2).

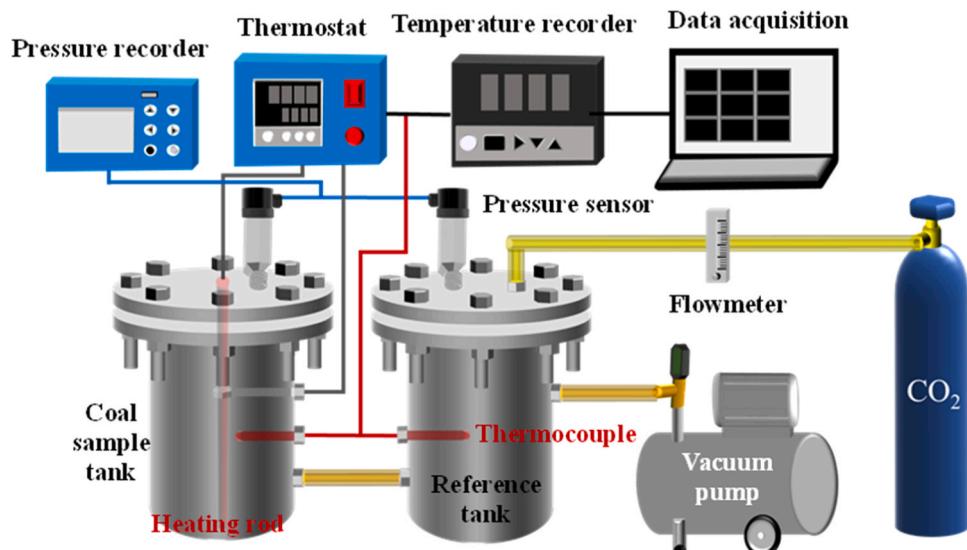
$$n = 1000 \frac{\varphi_i P_i V_i - \varphi_j P_j V_j}{GRT} \quad (2)$$

where  $\varphi_i$  represents the volume fraction of the target gas, %;  $P_i$  represents the total pressure of the gas in the coal sample canister before adsorption, MPa;  $V_j$  represents the volume of the target gas component in the coal sample canister after adsorption equilibrium, cm<sup>3</sup>;  $\varphi_j$  represents the volume fraction of the target gas component in the coal sample canister after adsorption equilibrium, %;  $P_j$  represents the total pressure of the gas in the coal sample canister after adsorption equilibrium, MPa;  $V_i$  represents the volume of the target gas component in the coal sample canister before adsorption, cm<sup>3</sup>;  $n$  represents the amount of the target gas component substance in the coal sample canister before adsorption, mmol/g;  $T$  represents the system temperature, K;  $G$  represents the mass of the coal sample, g;  $R$  represents the molar gas constant, J/(mol·K).

The experimental results of CO<sub>2</sub> adsorption on QYZ bituminous coal



**Fig. 3.** Adsorbate molecule.



**Fig. 4.** Adsorption apparatus.

samples are compared with the simulated data from the Wiser bituminous coal model to validate the reliability of the Wiser model. The variation curve of the adsorption capacity of QYZ coal samples with pressure at 303.15 K conditions is shown in Fig. 5. According to the growth trend of the isothermal adsorption curve, the coal adsorption gas process is roughly divided into three stages: rapidly increase, slowly increase, and gently increase. The relative growth rate is calculated according to Eq. (3).

$$g = \frac{C_i - C_j}{C_i} \times 100\% \quad (3)$$

where  $g$  represents the relative growth rate, %;  $C_i$  represents the total value of CO<sub>2</sub> adsorption capacity, mmol/g;  $C_j$  represents the base value of CO<sub>2</sub> adsorption capacity, mmol/g.

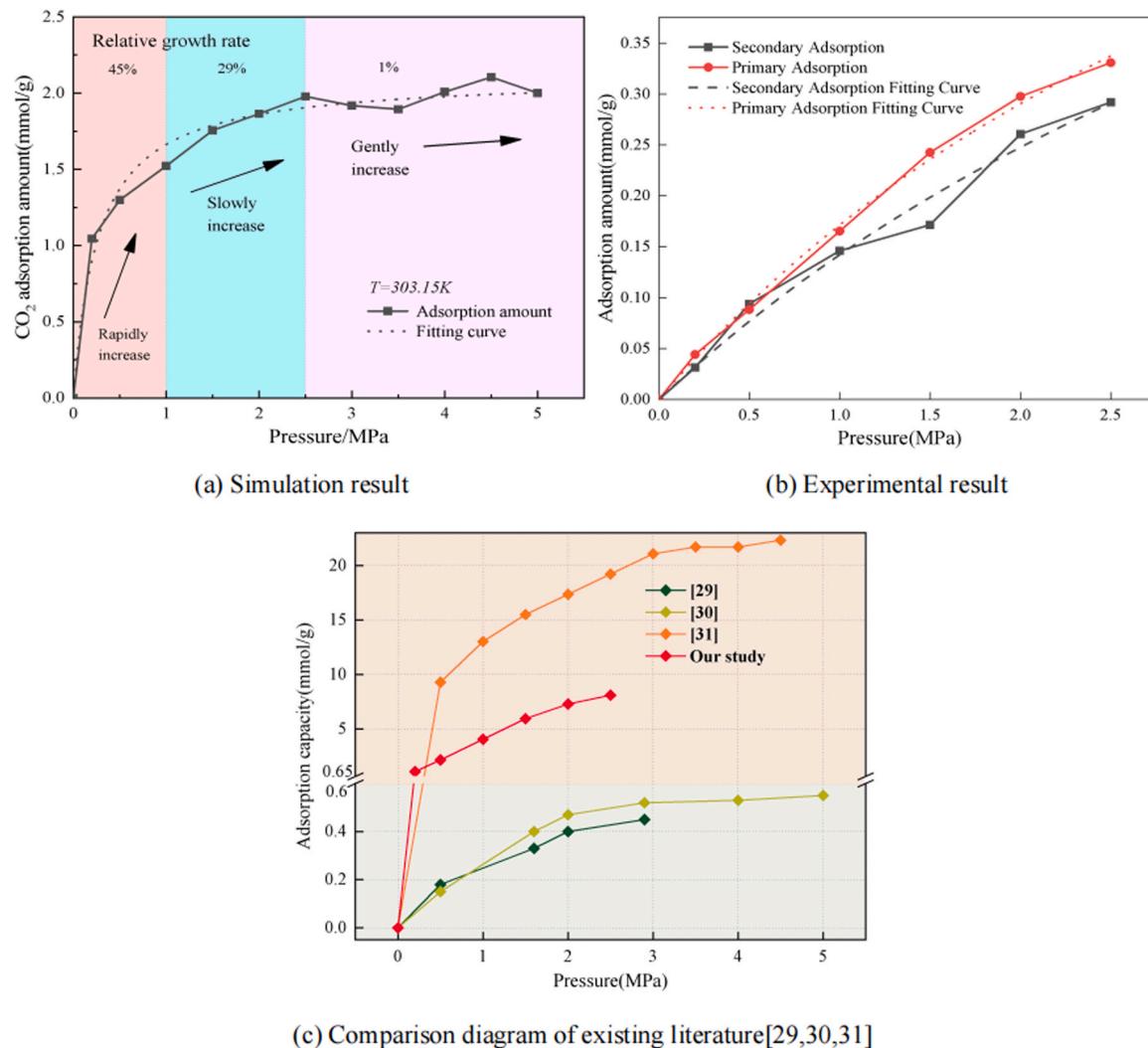
From Fig. 5(a), it can be observed that the adsorption capacity increases with increasing pressure, reaching saturation at 2.5 MPa. As shown in Fig. 5(b), the adsorption capacities of both primary and secondary adsorption coal samples increase with pressure. The adsorption capacity of the primary adsorption coal sample is greater than that of the secondary adsorption coal sample. This is because secondary adsorption is based on primary adsorption, and after the first adsorption is completed, most of the adsorption sites on the coal surface are occupied by carbon dioxide. Therefore, the desorption amount is less after adsorption equilibrium, resulting in the saturation adsorption value of

the second adsorption at the same pressure being lower than that of the first experiment. Due to the difference in scale between macroscopic adsorption experiments and microscopic adsorption molecular simulation calculation models, there are differences in the comparison of adsorption capacities, but the trend of curve changes is basically consistent. When the pressure increases from 2 MPa to 2.5 MPa, the adsorption capacity increases by 0.03 mmol/g and tends to saturation, which is consistent with the pressure at which saturation adsorption is reached in molecular simulation under the same environmental conditions. From Fig. 5(c), it can be seen that this study compared with the research of scholars from different regions and found that the main growth trend remains stable between 0 and 2.5 MPa and gradually stabilizes after 2.5–3 MPa. Through verification, this study is basically consistent with the research results of scholars, indicating that molecular simulation of coal can be used for qualitative analysis of adsorption laws of bituminous coal samples, and it is reliable to a certain extent.

### 3. Results and discussion

### 3.1. Analysis of adsorption capacity of binary mixture gases

The competitive adsorption characteristics of three types of adsorbate molecules were simulated using grand canonical Monte Carlo and molecular dynamics methods. A coal seam temperature of 303.15 K and pressures ranging from 0 to 5 MPa were selected. The competitive



**Fig. 5.** QYZ Variation of Adsorption Capacity of Coal Sample with Pressure. (a) Simulation result (b) Experimental result. (c) Comparison diagram of existing literature [29–31].

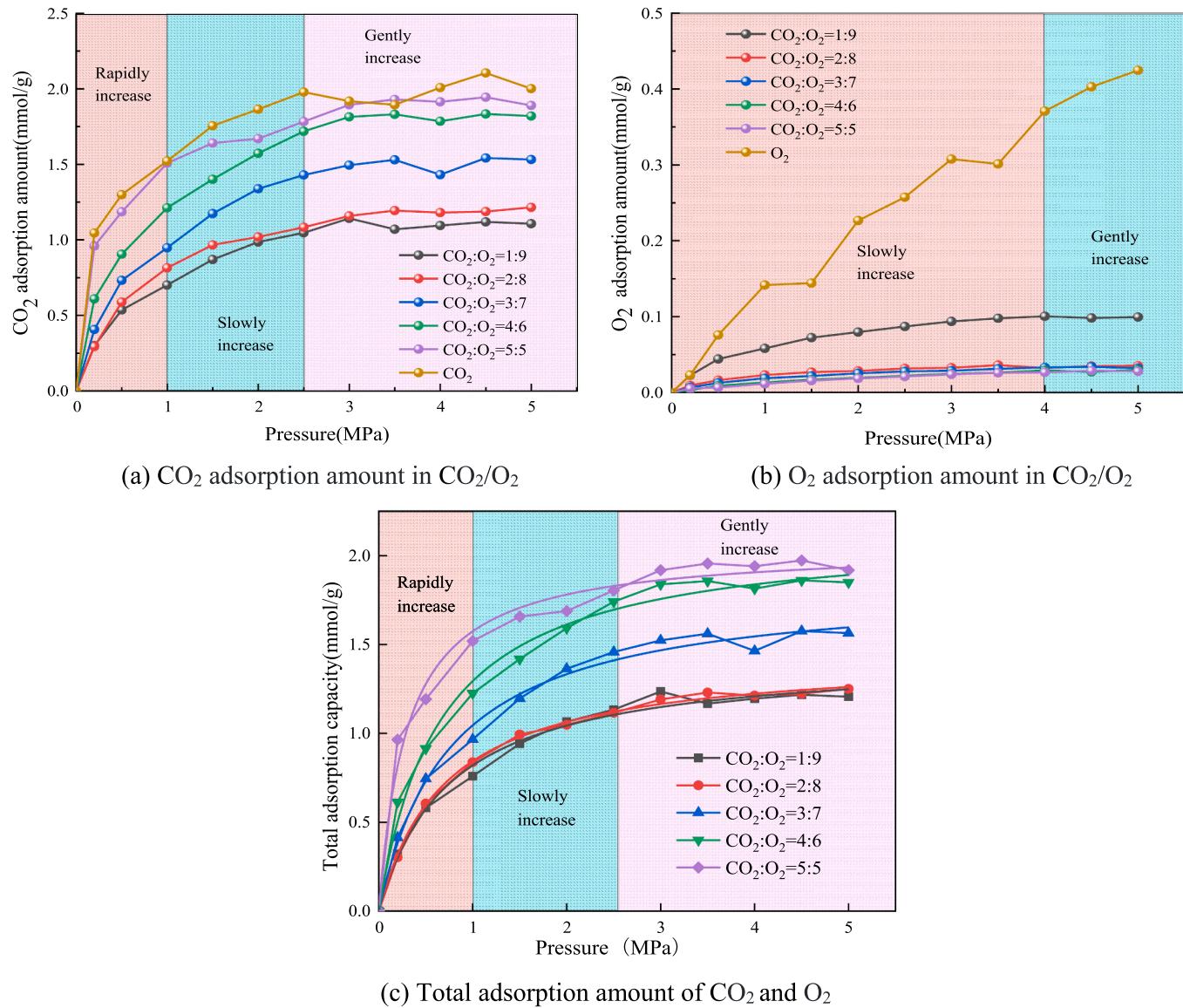
adsorption behavior of binary mixtures ( $\text{CO}_2/\text{O}_2$ ,  $\text{O}_2/\text{N}_2$ ,  $\text{CO}_2/\text{N}_2$ ) with competitive adsorption ratios of 1:9, 2:8, 3:7, 4:6, and 5:5 was simulated on the wiser large molecule model. The adsorption isotherms are shown in Fig. 6.

From Fig. 6, it can be observed that the range of adsorption variation for  $\text{CO}_2$  under single-component conditions is 0–2.001 mmol/g. As the content of  $\text{CO}_2$  in the  $\text{CO}_2/\text{O}_2$  mixture increases continuously, the isothermal adsorption curve for the  $\text{CO}_2$  component gradually approaches that of the single-component case. When the  $\text{CO}_2$  content increases to 50%, the isothermal lines for the mixed gas adsorption component of  $\text{CO}_2$  are essentially equivalent to those for the single component, with a variation range of 0–1.94 mmol/g. Under the same conditions, the adsorption variation range for  $\text{O}_2$  as a single component is 0–0.424 mmol/g. It sharply decreases to 0–0.0994 mmol/g when the  $\text{CO}_2$  content reaches 10%, and further decreases to 0–0.035 mmol/g when the content is at 20%. Subsequently, as the content continues to increase, the rate of decrease in the range of  $\text{O}_2$  adsorption capacity variation slows down. Compared with the adsorption capacity of the single component, the pressure required for  $\text{O}_2$  to reach adsorption equilibrium also decreases, reaching saturation earlier. It can be seen that  $\text{CO}_2$  has an absolute adsorption advantage in competitive adsorption with  $\text{O}_2$ . The adsorption sites on the coal molecule surface are primarily occupied by  $\text{CO}_2$ , but influenced by the  $\text{O}_2$  content, not all adsorption sites for  $\text{CO}_2$  will be occupied by  $\text{CO}_2$ . Only when the

concentrations of  $\text{CO}_2$  and  $\text{O}_2$  are equal, are the adsorption sites on the molecular surface basically entirely occupied by  $\text{CO}_2$ , with a minimal portion occupied by  $\text{O}_2$ .

From Fig. 7, it can be observed that as the concentration of  $\text{O}_2$  in the  $\text{N}_2/\text{O}_2$  mixture increases, the adsorption capacity of  $\text{O}_2$  also gradually increases. When the concentrations of  $\text{O}_2$  and  $\text{N}_2$  are equal, the adsorption capacity changes are 0–0.2663 mmol/g for  $\text{N}_2$  and 0–0.1342 mmol/g for  $\text{O}_2$ , indicating that under competitive adsorption at the same concentration, the adsorption capacity of  $\text{O}_2$  is lower than that of  $\text{N}_2$ . Under the same conditions (303.15 K, 0–5 MPa), the adsorption capacities of the two gases as single components are nitrogen 0–0.433 mmol/g and oxygen 0–0.424 mmol/g, respectively, with a very small difference. This indicates that the interaction between  $\text{N}_2$  and  $\text{O}_2$  in competitive adsorption is significant. Although there is a certain difference in the ability of the two gas molecules to occupy adsorption sites on the coal molecule surface, the difference is not large, and  $\text{N}_2$  has a competitive adsorption advantage.

From Fig. 8, it is evident that  $\text{N}_2$ , in competitive adsorption with  $\text{CO}_2$ , is also surpassed by  $\text{CO}_2$  with a larger difference in adsorption capacity. Research conducted by Wu et al. found that the adsorption capacity of DX coal gas is  $\text{CO}_2 > \text{N}_2$ . Additionally, simulations by Cheng et al. [32] revealed a similar trend between  $\text{CO}_2$  and  $\text{N}_2$  in lignite. Scholars such as Gao et al. [33] explained that the adsorption trends of  $\text{CO}_2$  and  $\text{N}_2$  in various coal samples remain consistent, indicating that the coal type has



**Fig. 6.** Adsorption capacity in different proportions of  $\text{CO}_2/\text{O}_2$  binary mixed systems.

little influence, and the dominant factor is the intrinsic properties of coal. In summary,  $\text{CO}_2$  overwhelmingly surpasses  $\text{N}_2$  and  $\text{O}_2$ , indicating that  $\text{N}_2$  has a stronger competitive adsorption ability than  $\text{O}_2$ . The overall competitive adsorption capacity ranking is  $\text{CO}_2 > \text{N}_2 > \text{O}_2$ . Lou et al. [34] combined with coal low-temperature oxidation program heating experiments and thermogravimetry, concluding that the sequence of the three gases is  $\text{CO}_2 > \text{N}_2 > \text{O}_2$ . Therefore, it is concluded that the inhibitory effect of  $\text{CO}_2$  on coal spontaneous combustion is always more significant than that of  $\text{N}_2$ .

Differing slightly from  $\text{O}_2$ , as the  $\text{CO}_2$  content in the  $\text{CO}_2/\text{N}_2$  mixed gas increases and the adsorption isotherms of the mixed components approach the single-component  $\text{CO}_2$  adsorption isotherm, the variation in  $\text{CO}_2$  adsorption capacity remains nearly constant when the concentration of  $\text{CO}_2/\text{N}_2$  in the mixed gas is between 4:6 and 3:7. Due to the significant influence of  $\text{CO}_2$  competitive adsorption, at a temperature of 303.15 K and pressures ranging from 0 to 5 MPa, the range of variation in  $\text{N}_2$  adsorption capacity under single-component conditions is from 0 to 0.4338 mmol/g. This range sharply decreases to 0–0.0895 mmol/g when the  $\text{CO}_2$  content reaches 10% and further drops to 0–0.03324 mmol/g at 20%  $\text{CO}_2$  content before slowly decreasing with increasing  $\text{CO}_2$  concentration. It can be observed that compared to the

competition between  $\text{O}_2$  and  $\text{CO}_2$  for adsorption, the adsorption capacity of  $\text{N}_2$  is slightly lower than that of  $\text{O}_2$ . This indicates that the influence of  $\text{N}_2$  on  $\text{CO}_2$  is less significant than that of  $\text{O}_2$  on  $\text{CO}_2$ , suggesting that  $\text{N}_2$  has a lower interference with the adsorption of  $\text{CO}_2$  on coal and exhibits lesser interaction with  $\text{CO}_2$ . This also demonstrates that the changes before and after adsorption of coal molecules with mixed gases stem not only from the interaction between coal and gas molecules but also from the interaction among different adsorbate molecules.

From Fig. 8, it can be observed that the optimal injection pressure is 2.5 MPa. At this pressure, the adsorption capacities of both  $\text{CO}_2$  and  $\text{N}_2$  have reached their maximum values, and the competitive effect is quite significant. Further increasing the pressure would yield diminishing returns, indicating lower cost-effectiveness. This finding provides a theoretical basis for high-pressure injection in practical engineering applications. Subsequent research in this paper reveals that as the partial pressure of  $\text{CO}_2$  gradually increases, the competitive adsorption effect becomes less pronounced. The optimal injection ratio of  $\text{CO}_2$  to  $\text{N}_2$  falls within the range of 4:6–3:7. This information can be further combined with factors such as process complexity and gas costs in practical engineering to determine the actual composition of injected gases.

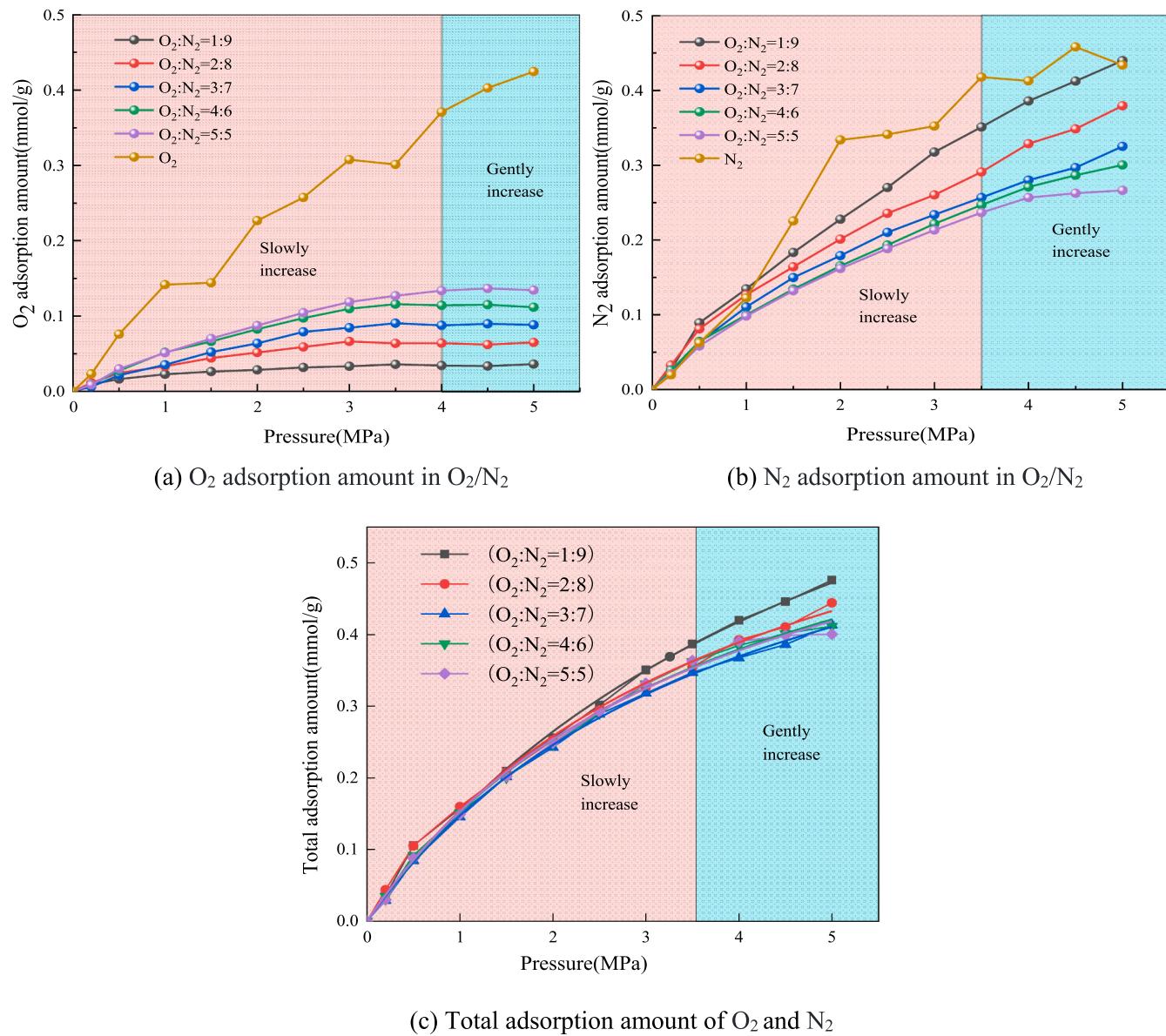


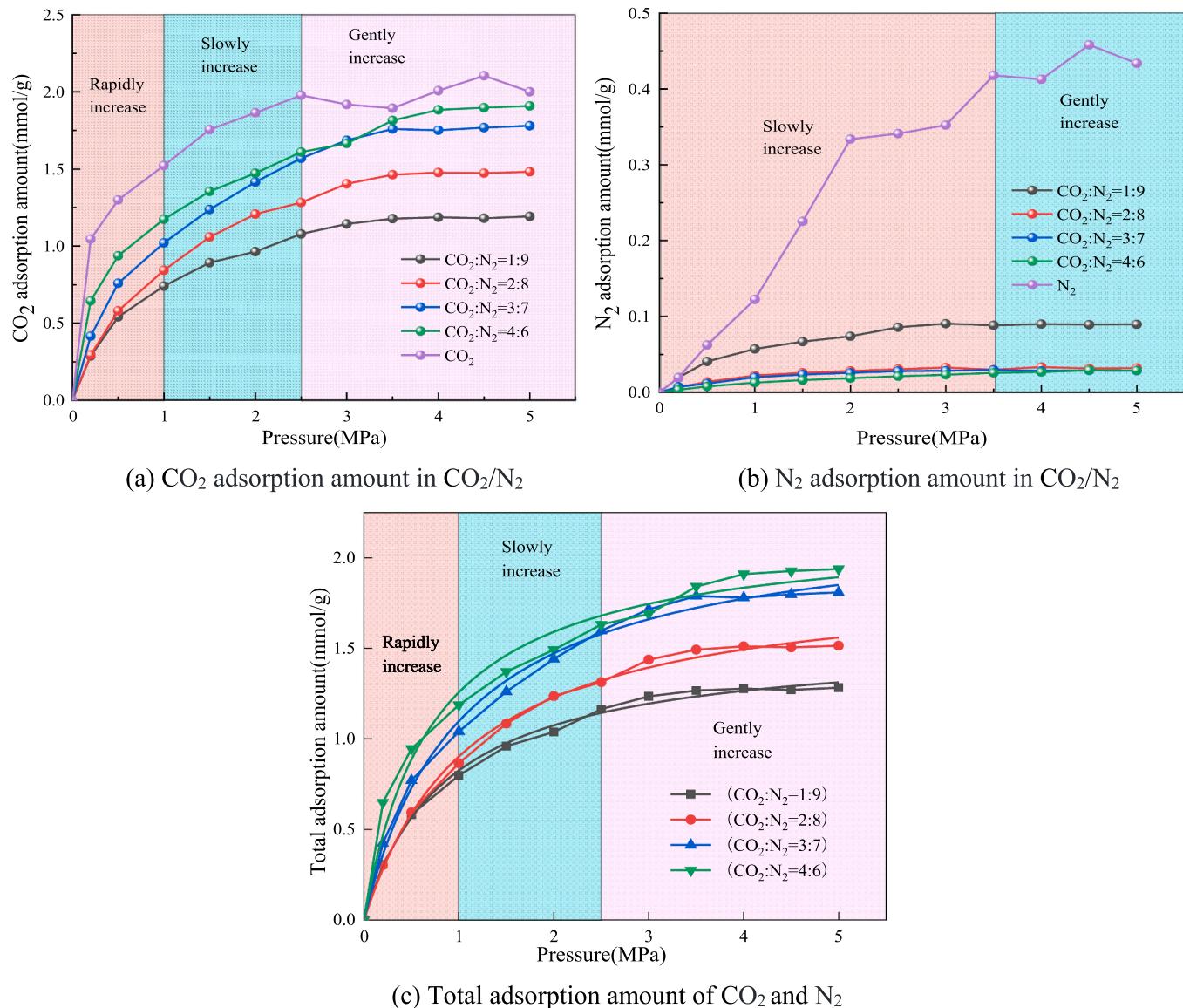
Fig. 7. Adsorption capacity in different proportions of O<sub>2</sub>/N<sub>2</sub> binary mixed systems.

### 3.2. Analysis of adsorption selectivity of binary mixture gases

The adsorption selectivity between the three gases pairwise is illustrated in Fig. 9. The range of adsorption selectivity of CO<sub>2</sub> in competitive adsorption with O<sub>2</sub> and N<sub>2</sub> is 67.96–286.05 and 99.55–302.7, respectively, far exceeding 1. This indicates the absolute advantage of CO<sub>2</sub> in competitive adsorption and the decline in adsorption selectivity with increasing pressure, ultimately leveling off. This is because as the pressure increases, the gas components gradually reach saturation, resulting in minimal changes in adsorption capacity. Interestingly, compared to O<sub>2</sub>, CO<sub>2</sub> exhibits higher adsorption selectivity towards N<sub>2</sub> under the same conditions, indicating that N<sub>2</sub> has a relatively lower impact on CO<sub>2</sub> compared to O<sub>2</sub> in competition. In the competition with O<sub>2</sub>, the average highest adsorption selectivity of CO<sub>2</sub> is reached when the concentration reaches 20%, but it is lower at low pressure (below 0.5 MPa) than at concentrations of 40% and 50%. The same pattern is also evident in the competition with N<sub>2</sub>, where the highest adsorption selectivity of CO<sub>2</sub> is achieved at 40% concentration under low pressure, but the highest selectivity is observed at a concentration of 20% at high pressure. Therefore, under low-pressure conditions, higher CO<sub>2</sub>

concentrations result in higher adsorption selectivity towards N<sub>2</sub> and O<sub>2</sub>, while there exists a lower concentration ratio under high-pressure conditions.

The adsorption selectivity of O<sub>2</sub> to N<sub>2</sub> follows a similar pattern to the variation of CO<sub>2</sub> with pressure at lower concentrations, but becomes relatively stable when the concentration exceeds 30%, regardless of pressure changes. It is noteworthy that when the concentration is below 20% (the normal oxygen concentration in air is 21.2–21.7%) and the pressure is below 2.5 MPa, the adsorption selectivity of O<sub>2</sub> to N<sub>2</sub> is greater than 1, indicating that coal molecules in this concentration and pressure range would preferentially adsorb O<sub>2</sub>. Therefore, the adsorption capacities of N<sub>2</sub> and O<sub>2</sub> are influenced by pressure and proportion. At pressures <1 MPa and O<sub>2</sub> concentration proportions below 20%, the adsorption capacity of O<sub>2</sub> exceeds that of N<sub>2</sub>, possibly because the molecular kinetic diameter of oxygen is smaller than that of nitrogen, making it easier for oxygen to enter the pores of coal for adsorption under low pressure conditions. However, when the proportions of the two gases are equal, the adsorption capacity of N<sub>2</sub> is stronger than that of O<sub>2</sub>. This differs from the findings of scholars like Wang Yuheng et al., who believed that the adsorption capacity of coal for O<sub>2</sub> > N<sub>2</sub>, but



**Fig. 8.** Adsorption capacity in different proportions of  $\text{CO}_2/\text{N}_2$  binary mixed systems.

overlooked the limited conditions under which  $\text{O}_2$  and  $\text{N}_2$  adsorption capacities vary. Therefore, regarding the adsorption of nitrogen and oxygen by coal molecules, a higher nitrogen content does not necessarily weaken the adsorption of  $\text{O}_2$ . It is uncertain whether an increase in  $\text{N}_2$  concentration can prevent coal oxidation. The primary role of  $\text{N}_2$  lies more in occupying space and reducing temperature.

### 3.3. Analysis of potential energy distribution of binary gas mixtures

The energy distribution of competitive adsorption between pairs of three gases is depicted in Fig. 10. For comparative analysis, the energy distributions of  $\text{CO}_2$  competing with  $\text{N}_2$  and  $\text{O}_2$  at concentrations of 10%, 30%, and 40% are juxtaposed. Beginning with the competition between  $\text{CO}_2$  and  $\text{N}_2$ , it is observed that under the influence of  $\text{N}_2$ , the energy distribution range of  $\text{CO}_2$  gradually shifts towards the energy zero point with increasing  $\text{N}_2$  content, albeit remaining significantly lower in numerical value compared to  $\text{CO}_2$ . This observation aligns with the findings of Wang [35], who also noted the pronounced competitive advantage of  $\text{CO}_2$  in binary gas systems, with the peak energy decreasing from 68.35 kJ/mol to 35.65 kJ/mol. Additionally, Jin et al. [36] simulated the competitive adsorption behavior of gases on coal surfaces and

concluded that with an increase in the total injection amount of multiple gases, the competitive advantage of  $\text{CO}_2$  against  $\text{N}_2$  and  $\text{O}_2$  diminishes. The absolute value of  $\text{CO}_2$ 's energy position gradually decreases, while that of  $\text{N}_2$  increases with concentration. As for  $\text{O}_2$ , its energy distribution exhibits a relatively higher absolute value compared to  $\text{N}_2$ . Under similar conditions, the energy of  $\text{CO}_2$  is at a lower absolute value relative to  $\text{N}_2$ , indicating that  $\text{O}_2$  has a stronger impact on  $\text{CO}_2$  than  $\text{N}_2$ , effectively reducing the adsorption energy of  $\text{CO}_2$  molecules on coal surfaces, consistent with the principles of adsorption selectivity. Hence, it can be inferred that the higher competitive adsorption selectivity of  $\text{CO}_2/\text{N}_2$  compared to  $\text{CO}_2/\text{O}_2$  is attributed to  $\text{CO}_2$  possessing more and higher energy distribution points during competition with  $\text{N}_2$ .

The energy distributions of  $\text{O}_2/\text{N}_2$  mixed compositions with  $\text{O}_2$  concentrations of 10%, 30%, and 50% are compared. Consistent with the adsorption selectivity principle, when  $\text{O}_2$  concentration is low, the absolute value of  $\text{O}_2$ 's adsorption energy distribution is greater than that of  $\text{N}_2$ , measured at 12.05 kJ/mol and 4.55 kJ/mol respectively. However, as the concentration increases, the energy distribution range of  $\text{N}_2$  surpasses that of  $\text{O}_2$ , directly indicating that the distribution range of adsorption energy points is a direct factor influencing the adsorption capacity.

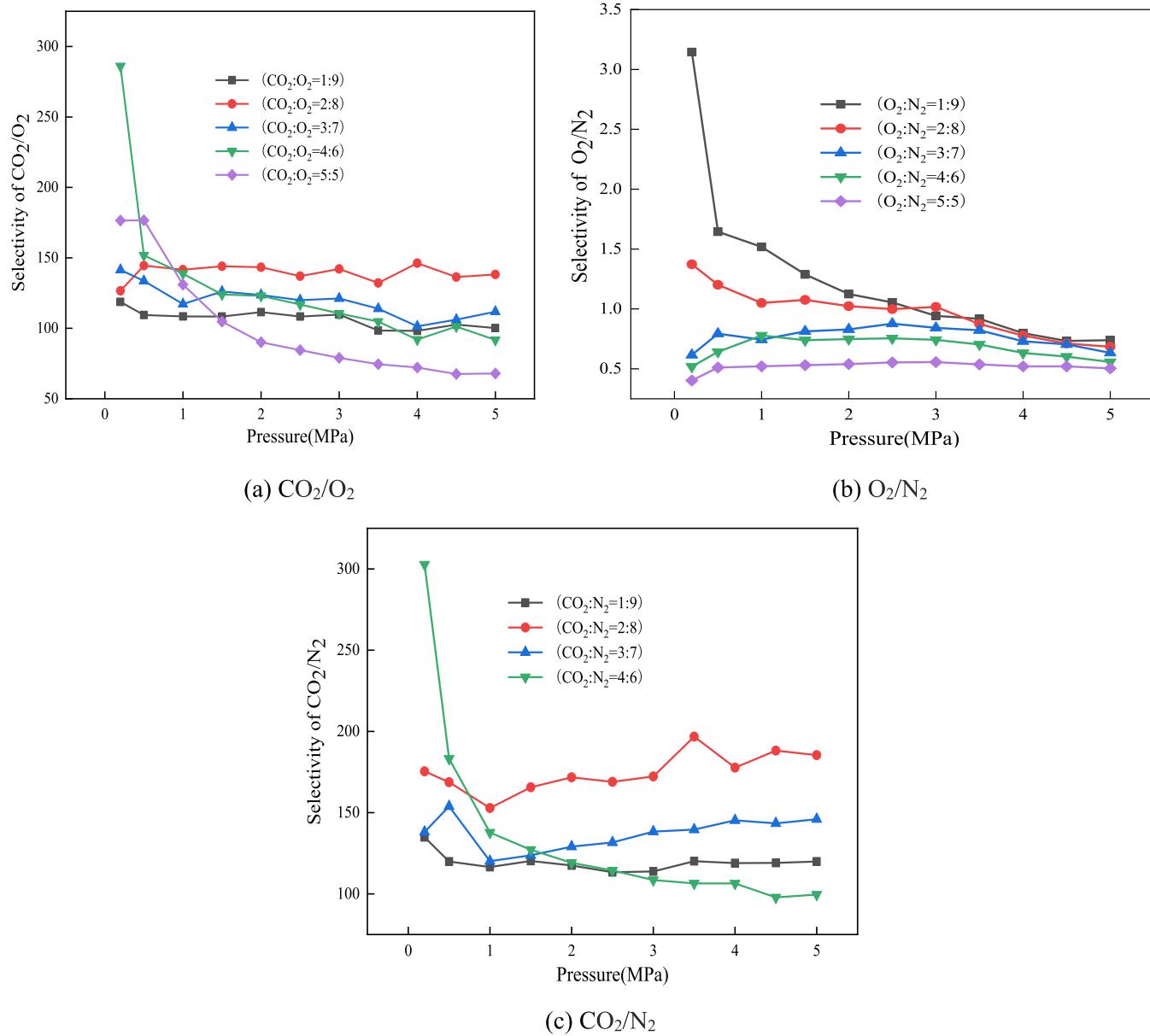


Fig. 9. Adsorption selectivity in binary gas mixtures with different proportions.

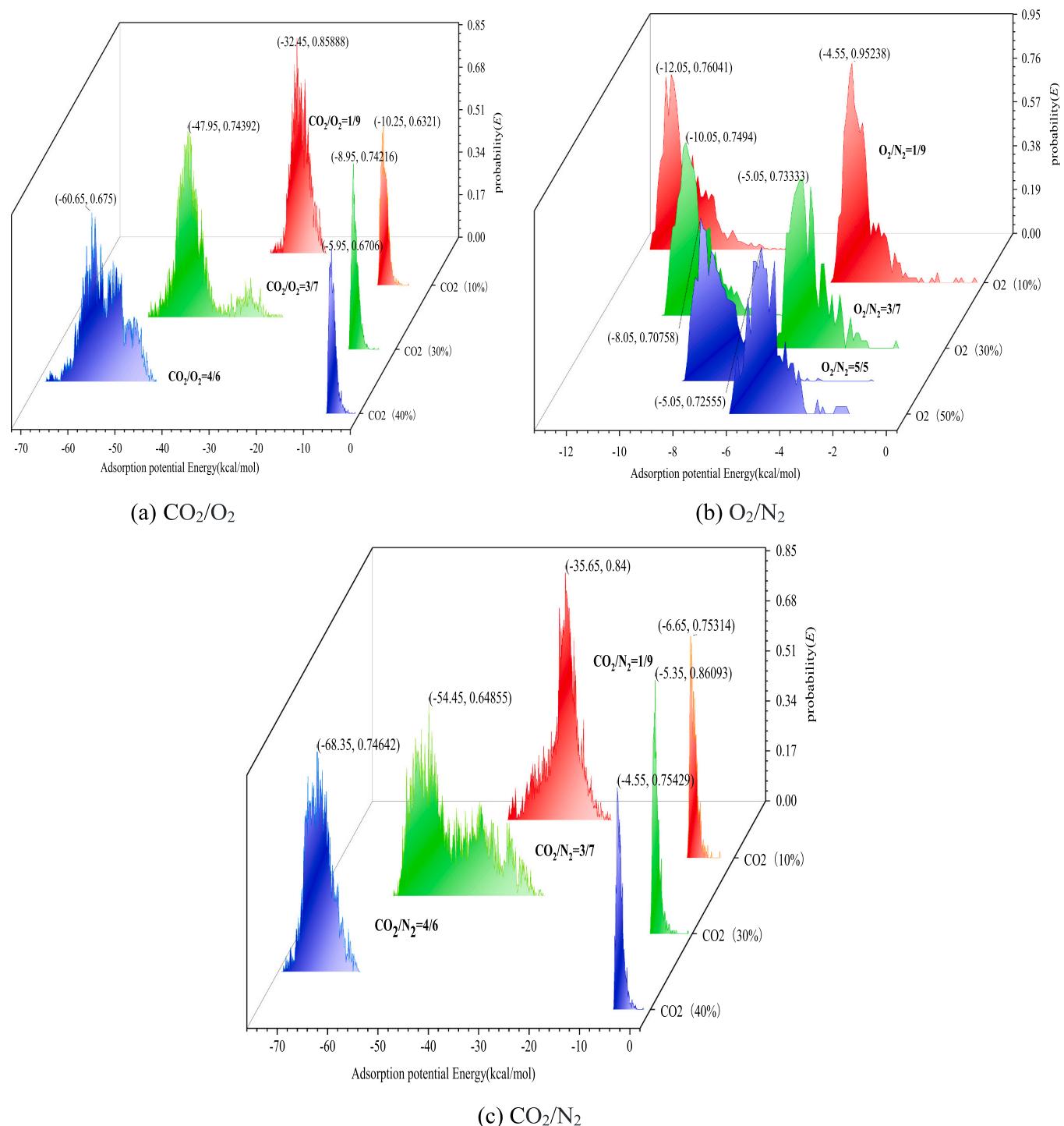
#### 3.4. Analysis of adsorption heat of binary gas mixtures

From Fig. 11, it can be observed that the adsorption heat of  $\text{CO}_2$  in  $\text{CO}_2/\text{O}_2$  mixed components initially decreases by a certain value with increasing pressure, then stabilizes. On the other hand, the adsorption heat of  $\text{O}_2$  initially rises for a period and then gradually stabilizes, following the same pattern as observed in single-component systems. This phenomenon can be attributed to the fact that the adsorption energy distribution of  $\text{CO}_2$  is much larger than that of  $\text{O}_2$ , and it has a wider range. Furthermore, with the increase in  $\text{CO}_2$  concentration, the adsorption heat also gradually increases, and there is a stable linear relationship between adsorption amount and adsorption heat.

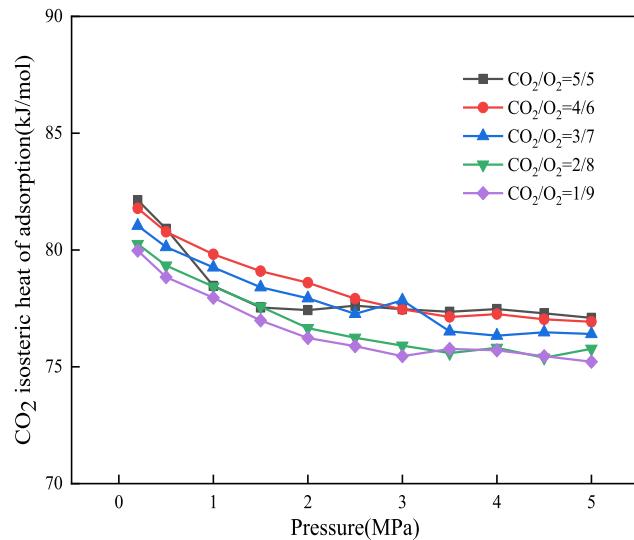
From Fig. 12, it can be observed that the variation in adsorption heat of individual components in the  $\text{N}_2/\text{O}_2$  mixture follows a similar pattern to that of single-component systems. The adsorption heat of both components in the mixed gas increases with increasing pressure. This is attributed to the fact that the differences in the size and distribution of energy sites between the two gas components are not significant, resulting in relatively small differences in the change of adsorption heat.

The concentration of the gas components is the primary factor influencing the variation in adsorption heat, with higher concentrations corresponding to higher adsorption heat. The adsorption amounts of  $\text{N}_2$  and  $\text{O}_2$  are positively correlated with adsorption heat.

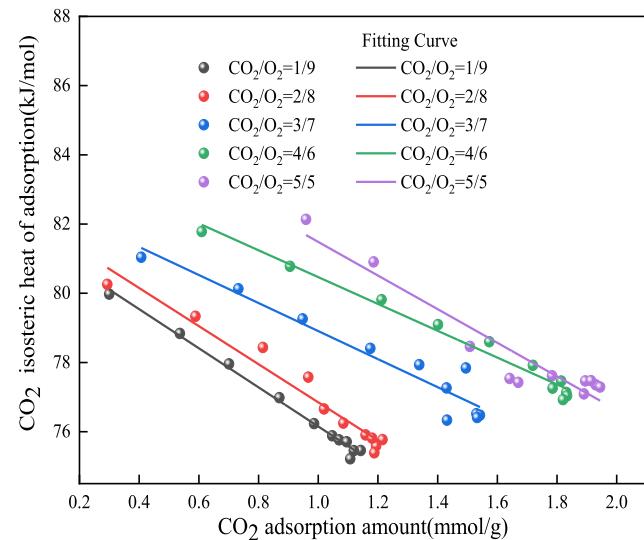
In conclusion, the relationship between the adsorption heat and adsorption amount of competitive components  $\text{N}_2$  and  $\text{O}_2$  exhibits a positive correlation. Yang et al. [37] found that the adsorption amount of single-component oxygen also shows a positive correlation with adsorption heat. The impact of  $\text{CO}_2$  is manifested in the negative correlation between adsorption heat and adsorption amount, possibly due to  $\text{CO}_2$  being a strongly adsorbing gas. In  $\text{CO}_2/\text{N}_2$  mixtures, the relationship between adsorption heat and pressure, as well as adsorption amount, remains consistent with that of  $\text{CO}_2/\text{O}_2$  components overall. Due to different interactions, within the same concentration range, the adsorption heat of  $\text{CO}_2$  in  $\text{CO}_2/\text{N}_2$  mixtures is slightly higher than that in  $\text{CO}_2/\text{O}_2$ , with the reason still stemming from  $\text{O}_2$  having a greater influence on  $\text{CO}_2$  than  $\text{N}_2$ .



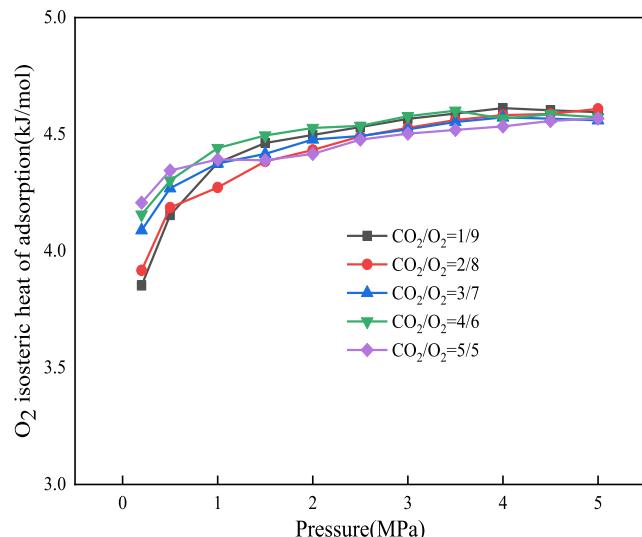
**Fig. 10.** Potential energy distribution in a binary hybrid system with different  $\text{CO}_2/\text{O}_2$  ratios.



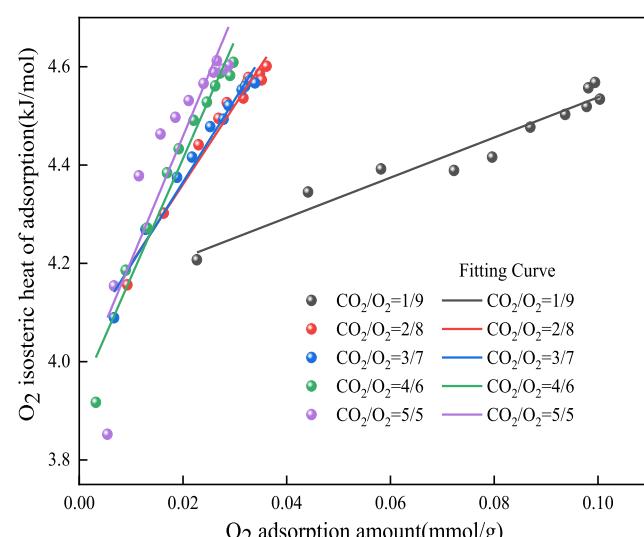
(a)



(b)



(c)



**Fig. 11.** Relationship between adsorption heat and adsorption capacity of CO<sub>2</sub>/O<sub>2</sub> competitive components. (a) Equivalent adsorption heat of CO<sub>2</sub> in CO<sub>2</sub>/O<sub>2</sub>; (b) Relationship between the adsorption heat and adsorption amount of CO<sub>2</sub> in CO<sub>2</sub>/O<sub>2</sub>; (c) Equivalent adsorption heat of O<sub>2</sub> in CO<sub>2</sub>/O<sub>2</sub>; (d) Relationship between the adsorption heat and adsorption amount of O<sub>2</sub> in CO<sub>2</sub>/O<sub>2</sub>.

### 3.5. Analysis of interaction energy of binary gas mixtures

The interaction energy reflects the stability of the adsorption system. The larger the absolute value, the more stable the adsorption system [38, 39]. The adsorption process is primarily influenced by interaction energy. To fundamentally understand the contribution of interaction energy to adsorption, the interaction energies during the adsorption process of binary systems are illustrated in Fig. 14.

From Fig. 14, it can be observed that in the competitive adsorption of binary gases, the adsorption energy of the gas increases rapidly with increasing pressure, then gradually levels off. This indicates that the influence of pressure on adsorption energy is similar to its effect on adsorption quantity. There is a close connection between adsorption quantity and adsorption energy.

Van der Waals energy and electrostatic energy can reflect the strength of coal in gas adsorption from an energy perspective. In a system composed of CO<sub>2</sub> and O<sub>2</sub>, as the partial pressure of CO<sub>2</sub> increases, the Van der Waals energy rises by 317.6%, while the electrostatic energy

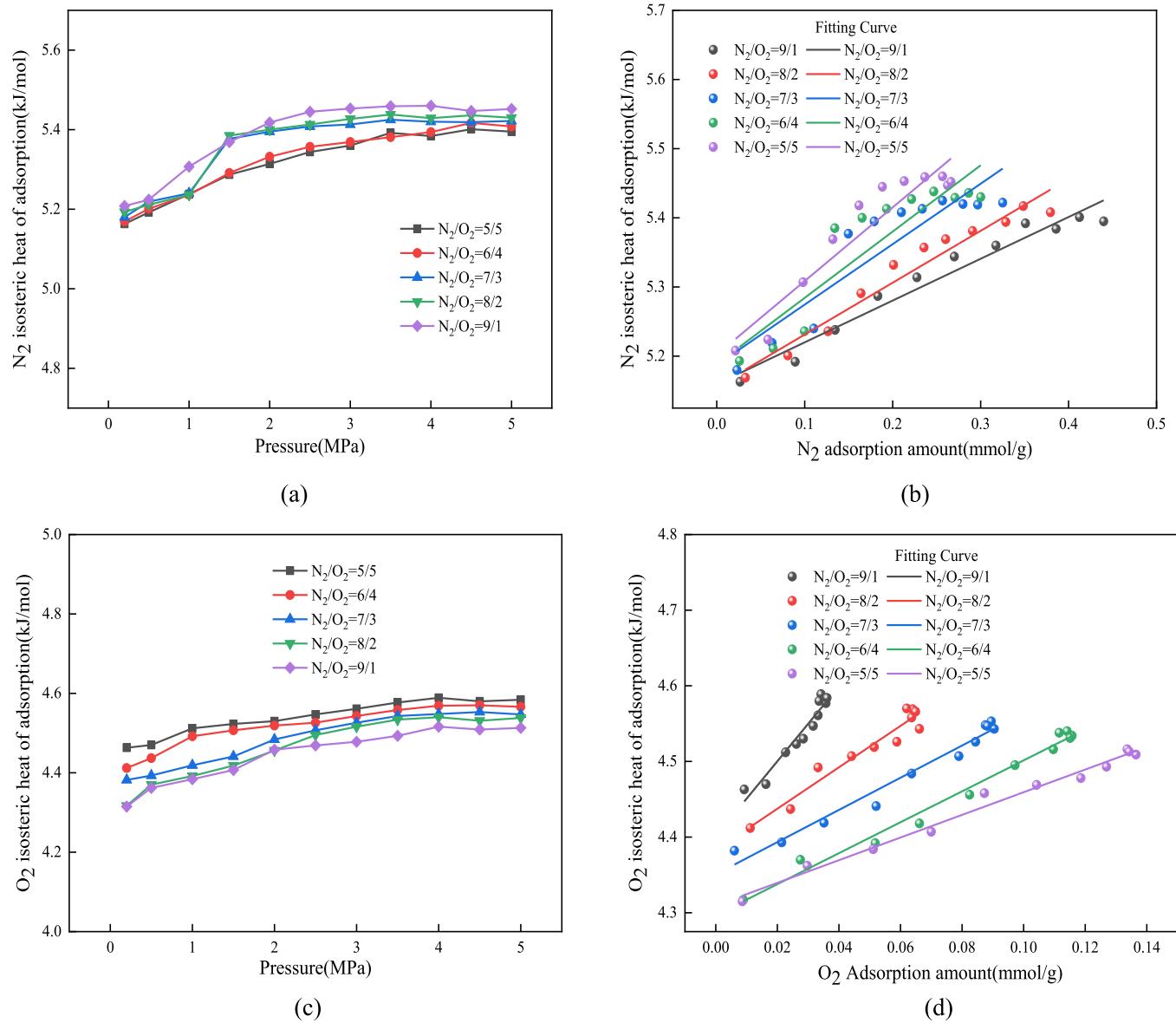
increases by 217%. The increase in Van der Waals energy is most significant, followed by electrostatic energy. This is because with the increase in CO<sub>2</sub> partial pressure, the adsorption quantity of CO<sub>2</sub> increases significantly, leading to a rise in the total adsorption quantity within the system.

In the competitive adsorption system of N<sub>2</sub>/O<sub>2</sub>, as the amount of O<sub>2</sub> decreases, the interaction energy continues to rise, which demonstrates that N<sub>2</sub> still dominates the Van der Waals energy in mixed components. The interaction energy in the system mainly originates from two aspects: the interaction between gas and coal molecules, and the interaction between the two adsorbate molecules.

## 4. On-site application of competitive inert gas components underground

### 4.1. Framework for selection of inert gas components underground

This page investigates the competitive adsorption mechanism of



**Fig. 12.** Relationship between adsorption heat and adsorption capacity of  $N_2/O_2$  competitive components. (a) Equivalent adsorption heat of  $N_2$  in  $N_2/O_2$ ; (b) Relationship between the adsorption heat and adsorption amount of  $N_2$  in  $N_2/O_2$ ; (c) Equivalent adsorption heat of  $O_2$  in  $N_2/O_2$ ; (d) Relationship between the adsorption heat and adsorption amount of  $O_2$  in  $N_2/O_2$ .

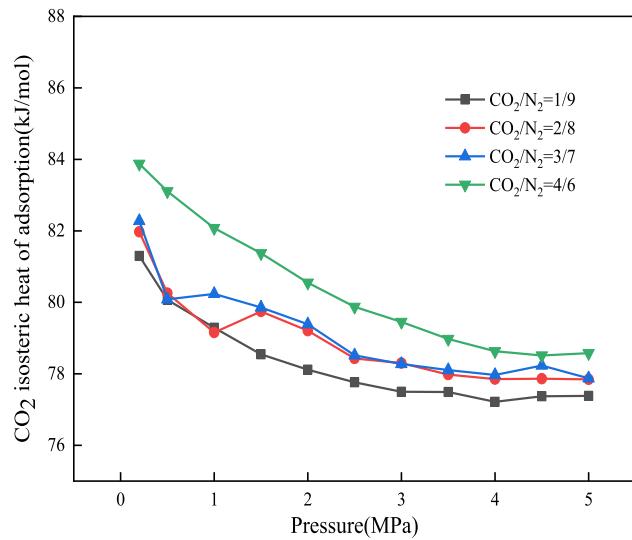
$CO_2/O_2/N_2$  from five dimensions: adsorption capacity, adsorption selectivity, potential energy distribution, competitive adsorption heat, and interaction energy. Among these, potential energy distribution and interaction energy explain the micro mechanism, while adsorption heat, adsorption capacity, and adsorption selectivity can be used to measure the effect of oxygen adsorption inhibition and select appropriate injection parameters. The specific approach involves using isothermal adsorption curves to identify the interval where adsorption capacity tends to flatten with pressure changes. The lower limit of this interval serves as the maximum critical point for injection pressure, beyond which adsorption tends toward saturation. The magnitude of adsorption capacity reflects the effectiveness of injection; therefore, it is recommended that the injection pressure in the actual application of this bituminous coal mine be less than 2.5 MPa. By analyzing the adsorption capacity of gases at different pressures, the combination with the maximum adsorption capacity in binary mixed components is determined, and the injection proportion interval belonging to the maximum saturation adsorption capacity is identified. However, further consideration of the actual on-site conditions of the coal mine is required to

determine the injection proportion range.

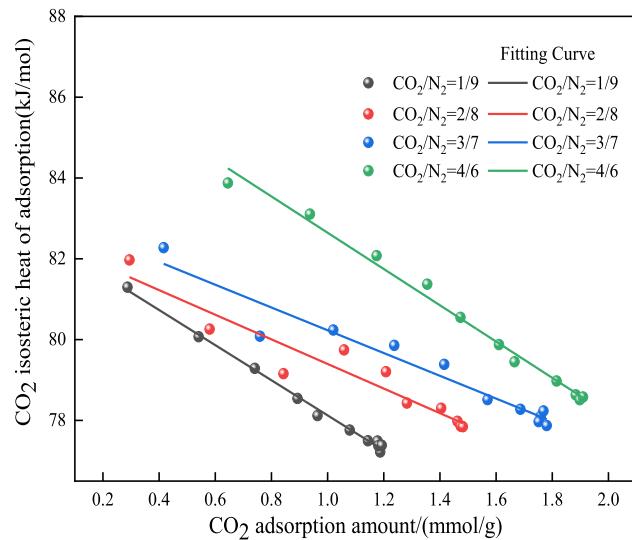
The adsorption effectiveness is determined by the magnitude of the saturation adsorption capacity. Through this study, three modes of underground inert gas composition selection were identified, based on the determination of whether competitive adsorption and single-component adsorption effects are the same. Therefore, a systematic logical framework for underground inert gas composition selection is proposed based on these three modes, as shown in Fig. 15. It is determined whether the adsorption effect of single-component gas or binary-component gas is better. If the injection effect of the binary-component gas is better, then binary-component injection is directly adopted. If the injection effects of both gases are the same, then considerations such as process complexity and gas cost are taken into account to make a decision. If the injection effect of the single component is better, then single-component injection is chosen directly.

#### 4.2. Underground mobile inert gas injection process

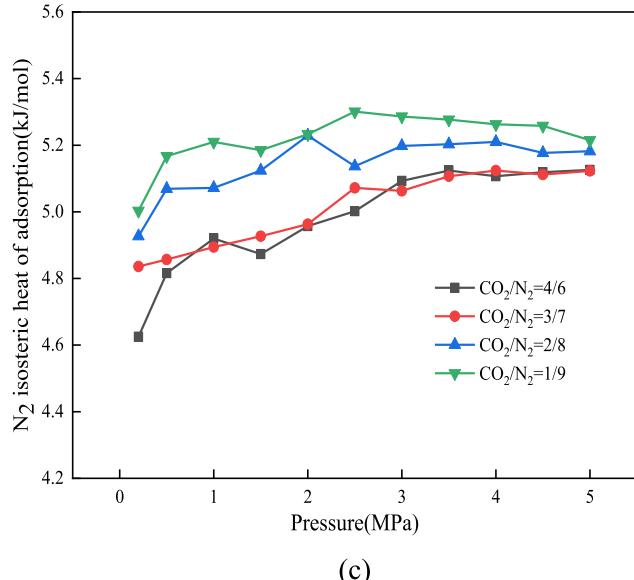
Zhang et al. proposed three liquid  $CO_2$  injection processes [40]. The



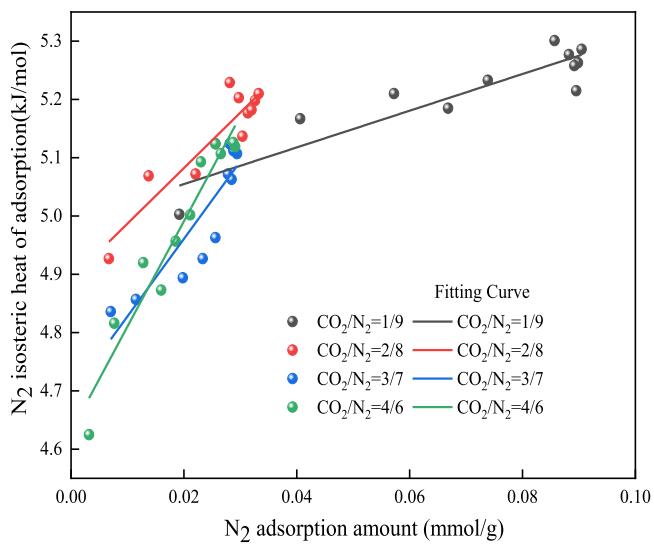
(a)



(b)



(c)



(d)

**Fig. 13.** Relationship between adsorption heat and adsorption capacity of CO<sub>2</sub>/N<sub>2</sub> competitive components. (a) Equivalent adsorption heat of CO<sub>2</sub> in CO<sub>2</sub>/N<sub>2</sub>; (b) Relationship between the adsorption heat and adsorption amount of CO<sub>2</sub> in N<sub>2</sub>/O<sub>2</sub>; (c) Equivalent adsorption heat of N<sub>2</sub> in N<sub>2</sub>/O<sub>2</sub>; (d) Relationship between the adsorption heat and adsorption amount of N<sub>2</sub> in N<sub>2</sub>/O<sub>2</sub>.

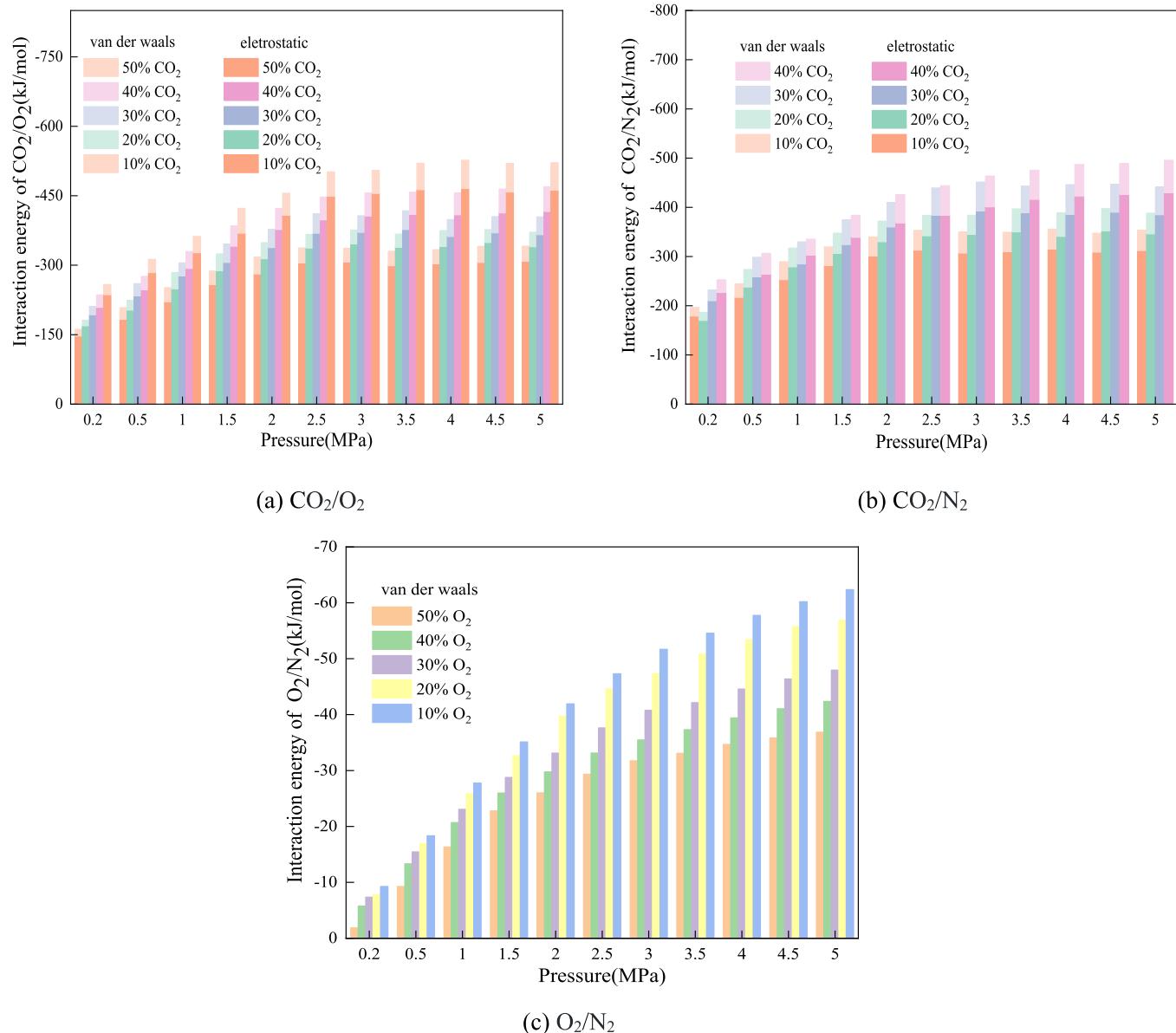
underground mobile injection process has the advantages of good maneuverability, considering both fire extinguishing and cooling, and can be directly transported to the vicinity of the underground goaf, thus achieving higher targeting and precision. Considering the actual conditions of the mine, the research team chose the underground mobile injection process of liquid CO<sub>2</sub> and conducted on-site practice of CO<sub>2</sub> injection. The injection process system is shown in Fig. 16. The underground mobile injection process involves transferring the liquid from the storage tank to small tanks for transportation and mobility, and using existing underground tracks to transport these small tanks to areas requiring fire prevention and extinguishing underground. Due to the high density of CO<sub>2</sub>, it tends to settle at the bottom of the goaf and coal accumulation area, with less significant effects in deeper parts of the goaf. On the other hand, nitrogen (N<sub>2</sub>) has strong diffusivity and permeability. Combining the two gases may achieve a more advantageous fire prevention and extinguishing effect. However, there is currently a lack of optimal analysis of the gas injection ratio. Therefore, through molecular simulation studies, we aim to clarify the

oxygen-blocking properties of competitive inert gas components. In the future, based on the research results, we will conduct underground mobile mixed inert gas injection, further strengthening the previous research efforts.

## 5. Conclusions

Competitive adsorption behaviors of mixed gases (CO<sub>2</sub>/N<sub>2</sub>/O<sub>2</sub>) at five different concentration ratios were conducted at a temperature of 303.15 K and pressures ranging from 0 to 5 MPa. A systematic logical framework for selecting underground inert gas composition was proposed, providing a basis for the selection of gas injection ratios in inert gas fire prevention and extinguishing in goaf. The main conclusions are as follows:

- (1) In the competitive adsorption of CO<sub>2</sub>/N<sub>2</sub>/O<sub>2</sub>, CO<sub>2</sub> exhibits a strong adsorption advantage, i.e., CO<sub>2</sub> > N<sub>2</sub>, O<sub>2</sub>, because CO<sub>2</sub> has more and higher energy distribution sites during the competition.



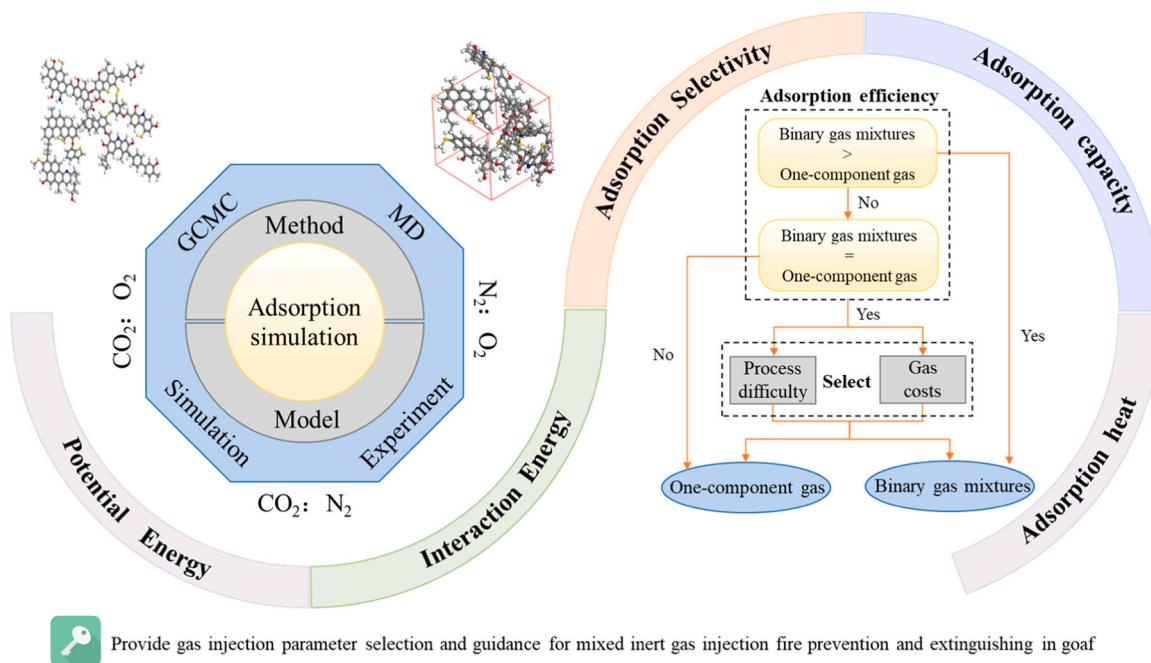
**Fig. 14.** Interaction energy in binary mixed systems with different ratios of CO<sub>2</sub>/O<sub>2</sub>.

The adsorption capacities of N<sub>2</sub> and O<sub>2</sub> are influenced by pressure and proportion. For O<sub>2</sub>/N<sub>2</sub> mixed components, at low pressures (<1 MPa) and when the O<sub>2</sub> concentration ratio is below 20%, the adsorption capacity of O<sub>2</sub> is greater than that of N<sub>2</sub>. Therefore, typically in goaf, N<sub>2</sub> occupies more space to reduce O<sub>2</sub> concentration and prevent coal spontaneous combustion.

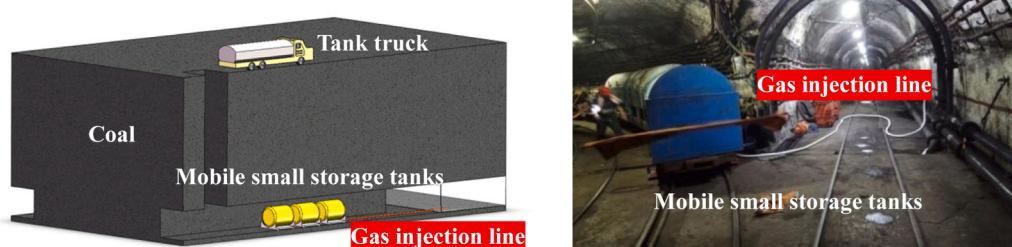
- (2) The relationship between the adsorption heat of N<sub>2</sub> and O<sub>2</sub> and the adsorption amount shows a positive correlation, while the adsorption heat and adsorption amount of CO<sub>2</sub> consistently exhibit a negative correlation. In the CO<sub>2</sub> and O<sub>2</sub> system, as the partial pressure of CO<sub>2</sub> increases, the van der Waals energy increases by 317.6%, and the electrostatic energy increases by 217%, thus the van der Waals energy plays a dominant role. It is recommended to inject gas at a pressure of less than 2.5 MPa during actual inert gas injection. Because under this pressure, the adsorption capacity of CO<sub>2</sub> and N<sub>2</sub> is close to their maximum, and the competitive effect is very significant. If the pressure continues to increase, the cost-effectiveness will be lower. The research results provide a certain theoretical basis for high-pressure injection in practical engineering.

- (3) As the partial pressure of CO<sub>2</sub> gradually increases, the competitive adsorption effect becomes less significant. The concentration range of mixed gas components CO<sub>2</sub>/N<sub>2</sub> is between 4:6 and 3:7. It is necessary to further determine the actual gas composition for injection based on factors such as process difficulty and gas cost in actual engineering. Therefore, a systematic logical framework for selecting underground inert gas composition is proposed, along with the determination of an underground mobile mixed inert gas infusion process.

In the future, the critical threshold of the "three zones" of spontaneous combustion in goaf will be determined through experiments and on-site testing methods. Experimental studies on inertization mechanisms at different oxygen concentrations will be conducted, along with adsorption simulation studies for optimizing gas injection ratios under environmental conditions or model reconstructions. This will provide a basis for quantifying fire prevention and extinguishing parameters in goaf.



**Fig. 15.** A system logic framework for the selection of downhole inert gas components.



**Fig. 16.** Underground mobile perfusion process system and field application.

#### CRediT authorship contribution statement

**Junchao Chen:** Project administration. **Lin Li:** Data curation, Funding acquisition. **Xuewei Yang:** Conceptualization, Writing – original draft, Writing – review & editing. **Bo Yang:** Supervision, Visualization. **Junhong Si:** Methodology, Resources.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

No data was used for the research described in the article.

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