Modified Dubinin–Astakhov Model for the Accurate Estimation of Supercritical Methane Sorption on Shales

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ABSTRACT: In order to evaluate the total shale gas-in-place (GIP) resources in deep formations, it is important to study the sorption of supercritical methane in shales. At present, the Dubinin–Astakhov model is used to describe sorption isotherms. However, it still has some shortcomings. The main objective of this study is to establish an optimized model for supercritical methane sorption in shales. A series of high-pressure methane sorption isotherms were measured at different temperatures (from 293 to 333 K) for shale samples collected in the Cengong block, Guizhou, China. The characteristics and causes of shale gas sorption capacity changes were analyzed. By comparing the fitting results of several conventional sorption models, the characteristics and applicable scope of these models are obtained. A four-parameter (V_0, D, m, and ρ_a) modified supercritical D−A model was developed to accurately estimate the sorption of supercritical methane on shales based on Polanyi sorption potential theory. The results show that the sorption characteristic curve of methane on the shale surface under high pressure is obviously different from that under low pressure. The density of the sorption phase and the virtual saturated vapor pressure have a great influence on the fitting results of the sorption models. The density of the adsorption phase directly determines the ultimate sorption capacity of the shale sample. Also, the modified D−A model can improve the accuracy of the prediction of supercritical methane sorption on shales, and it can accurately describe the isothermal sorption law of gas in the supercritical state.

1. INTRODUCTION

The adsorbed gas on the surface of shale pores is an important part of shale gas. The research by Curtis¹ on five shale gas basins in the United States, such as Fort Worth, Illinois, shows that the proportion of adsorbed gas in shale gas is 20–80%. Also, it is generally believed that during the development of a gas reservoir, the flow of gas from the shale matrix to the wellbore undergoes three processes: desorption, diffusion, and percolation.²−⁴ Therefore, the study of shale gas sorption and desorption is the key to the rational and effective development of shale gas reservoirs.

It is a time-consuming and expensive process to measure the sorption/desorption characteristics of shale using experiments. How to use mathematical models to describe sorption isotherms is a research hotspot. By establishing a sorption model to fit experimental data and verifying the established mathematical model, it can reveal the gas sorption/desorption mechanisms and provide effective guidance for the evaluation and development of shale gas reservoirs.

At present, multiple sorption models have been proposed in the field of sorption research, and they are widely used in the fields of coal, shale, activated carbon, and molecular sieves. The Langmuir isothermal sorption model is the most popular model to describe shale sorption. In addition to the Langmuir isothermal model, the Freundlich model, the Toth model, the BET model, the Dubinin–Radushkevich volume filling model (D–R model), and the Dubinin–Astakhov volume filling model (D–A model) are also commonly used. Summarizing...
previous research results, the current mathematical models of shale sorption of methane are divided into three categories: (1) monolayer sorption model or empirical equation, including the Langmuir model (L model), the extended Langmuir model (E-L model), the Freundlich model, and the Toth model; (2) multilayer sorption model, such as the BET model; (3) sorption model based on the micropore sorption filling theory, also known as the sorption potential model, such as the D−R model and the D−A model.

Langmuir first proposed a model of gas sorption on a solid surface in 1916. This model describes an ideal sorption. It is assumed that the adsorbed molecules undergo monolayer sorption, and there is no interaction between them. The surfaces of the adsorbent are uniform, and the energy of each sorption site is equal. The Langmuir model is widely used in the fitting of shale sorption experimental results. Weniger et al.5 and Zhang et al.6 fitted the shale sorption isotherms using Langmuir’s equation. Zhao et al.7 used several-layer sorption models to fit the experimental data of coal and shale sorption. The results show that the ranking of fitting accuracy of sorption models for shale from high to low is: T model > E-L model > L-F model > L model > F model; the fitting results of coal are different, and the order of fitting accuracy of each model is as follows: L-F model > E-L model > L model > T model > F model. Fan et al.8 presented a conceptual Bi-Langmuir model to predict methane absorption capacity by accommodating the effect of the moisture content.

In 1938, Brunauer et al.9 proposed the BET multimolecular layer sorption theory. The BET sorption theory shows that there is a molecular force between adsorbent molecules. Therefore, it can produce mutual sorption and form multimolecular layer sorption. The BET model can be divided into a two-parameter BET model (B-BET model) and a three-parameter BET model (T-BET model) according to the number of fitting parameters. The T-BET model is a modification of the B-BET model, which takes the heterogeneity between various sorption layers into consideration and improves the fitting accuracy. However, more fitting parameters lead to certain limitations of the T-BET model. The BET model can take the van der Waals interactions between molecules into account, and it fits the experimental data of sorption better than the Langmuir model. However, the BET model also has defects. Although it takes the limitation of the number of sorption layers in the capillary pore space into consideration, it does not involve the phenomenon of capillary condensation in the micropores. Therefore, it is not ideal for sorption in small pores and micropores.10−12

The micropore filling theory can describe the sorption characteristics in the micro-nanopores. It is generally believed that in relatively large pores, the sorption characteristics of gas molecules are not affected by the pore size and the radius of curvature. However, under supercritical conditions, “capillary condensation” occurs in gas molecules. In this case, the existing state of gas in pores cannot be described by the single-layer or multi-layer sorption theory. Therefore, the micropore filling theory can make up for the shortcomings of the single-layer or multilayer sorption theory. It provides an important means for the reasonable evaluation of shale sorption characteristics and revealing the gas−solid interface sorption mechanism. Dubinin and Astakhov5,14 proposed the D−R model and the D−A model, and they extended the application of the theory to the supercritical field based on the gradual characteristics of the sorption value. Zhou et al.15 Sudibandriyo16 and Choi et al.17 studied the sorption characteristics of hydrogen and methane in high-surface activated carbon. Kaneko and Murata18 studied the calculation method of the potential energy of nitrogen, methane, carbon monoxide, and water molecules in the pores of the slit under supercritical conditions, and they observed that the molecules showed a high-pressure state under the action of a special molecular field in nanospace.

However, the D−R model and the D−A model also have some shortcomings. Richard Sakurovs et al.19 put forward that the D−R model requires a “saturation pressure” in its calculation, which is not defined for supercritical conditions. Therefore, in the isothermal sorption fitting, where the experimental temperature exceeds the critical temperature, many scholars have proposed the concept of virtual saturated vapor pressure. The virtual saturated vapor pressure was used to replace the vapor pressure in models to fit the experimental data of supercritical methane. However, the isothermal sorption law obtained using the hypothetical “virtual saturated vapor pressure” has its own limitations under this hypothesis.

Richard Sakurovs et al.20 studied the adsorption behavior of supercritical gas on coals. The results show that the sorption isotherm can be reasonably fitted when the gas density replaces the gas pressure as an independent variable in the model. Therefore, in this study, a modified model with four parameters (\(V\), \(D\), \(m\), and \(p_s\)) for supercritical sorption was established based on the Polanyi sorption potential theory and the derivation of the D−A model. It overcomes the limitation of virtual saturated vapor pressure. The isothermal sorption data of experimental samples and North American shale were fitted and analyzed in this study. A series of high-pressure methane sorption isotherms were measured at different temperatures (from 293 to 333 K) for shale samples collected in the Cengong block, Guizhou, China. The characteristics and causes of shale gas sorption capacity changes were analyzed. The details of this study and the results are presented in the following sections.

2. MODIFIED D−A MODEL

According to the Polanyi sorption potential theory, there is a sorption potential at every point in the sorption space. For a gas molecule, its sorption potential is the work of moving it from its location to infinity. Therefore, the sorption potential is mainly generated by the intermolecular forces of the adsorbate molecules and the adsorbent molecules. It can be inferred that for sorption in porous media, the larger the pore size, the smaller is the sorption potential of the adsorbate molecules therein, and the smaller the pore diameter, the greater is the sorption potential energy of the adsorbate molecules. Polanyi believes that the sorption phase of gas on a solid surface can be considered as the liquid phase, and as long as the sorption potential is greater than its work of compressing from the current pressure to the liquid phase, sorption of gas molecules on the solid surface can occur.21

The molar sorption work of gas is that the work of 1 mol of an ideal gas is compressed from equilibrium pressure \(P\) to saturated vapor pressure \(P_0\) at temperature \(T\).

\[
A = \int_{P_f}^{P_0} V \, dP = \int_{P_f}^{P_0} \frac{RT}{P} \, dP = RT \ln \frac{P_0}{P_f}
\]

where \(A\) is the sorption potential, J/mol; \(V\) is the adsorption capacity, cm\(^3\)/g; \(T\) is the sorption temperature, K; \(P_0\) is the
saturated vapor pressure of gas at temperature $T$, MPa; $P$ is the equilibrium pressure, MPa; and $R$ is the universal gas constant, 8.314 J/(mol·K).

Equation 1 is based on defining the sorption phase as the liquid phase. The applicable condition is that the sorption temperature $T$ is far lower than the gas critical temperature $T_c$. When the experimental temperature $T$ is higher than the gas critical temperature $T_c$, the saturated vapor pressure does not exist. Polanyi believes that when the sorption temperature $T$ is slightly lower than the critical temperature $T_c$, the sorption phase is a mixture of liquid and supercritical states, and when the sorption temperature $T$ is greater than the critical temperature $T_c$, the sorption phase is in a supercritical state.

Aiming at supercritical sorption, Dunbinin believes that the sorption amount is a function of the sorption potential. He put forward the concept of virtual saturated vapor pressure and Polanyi sorption potential theory to establish a D–A isothermal sorption model. In this model, the sorption phase is defined as an approximate liquid phase.

However, the isothermal sorption law obtained using the hypothetical "saturated vapor pressure" has its own limitations under this hypothesis.

Deriving from the Dubinin–Astakhov sorption model, the pore-filling ratio can be expressed as

$$\theta = \frac{W}{W_0} = \frac{V_{ab}}{V_0}$$

where $\theta$ is the pore-filling ratio; $W_0$ is pore volume of adsorbent, cm$^3$; $W$ is pore volume occupied by adsorbent molecules, cm$^3$; $V_{ab}$ is the absolute sorption amount, cm$^3$/g; $V_0$ is adsorbent pore volume, cm$^3$/g.

If the pore size distribution of the adsorbent obeys the Weibull distribution, the relationship between the molar sorption work derived from Dunbinin and the pore filling ratio is expressed as

$$\theta = e^{-\left(\frac{A}{\rho}\right)^m}$$

$$V_{ab} = V_0 e^{-\left(\frac{A}{\rho}\right)^m}$$

where $E$ is the sorption characteristic energy, J/mol; $m$ is a constant that characterizes adsorbent heterogeneity.

Substituting eq 1 in eq 4 yields

$$V_{ab} = V_0 e^{-\left(\frac{RT \ln \rho_a}{P}\right)^m} = V_0 e^{-D \ln \left(\frac{\rho a}{P}\right)^m}$$

where $D$ is a constant related to the net heat of adsorption.

Equation 5 is the D–A model equation in the general form. When solving the D–A model, Dunbinin assumes that the sorption phase is an approximate liquid phase, $P_0$ is the corresponding saturated vapor pressure at the sorption temperature, and it is the virtual saturated vapor pressure.

Obviously, the approximate liquid phase and its corresponding saturated vapor pressure do not exist. When the gas sorption temperature $T$ is higher than the critical temperature $T_c$, sorption is in a supercritical state.

For the sorption of supercritical gas, it is assumed that the sorption phase is in a supercritical state with a density of $\rho_a$, and it is only related to the temperature and the properties of the adsorbent. The molar sorption work is expressed as

$$A = RT \ln \frac{P_a}{P}$$

where $P_a$ is pressure at temperature $T$ when the gas density is $\rho_a$, MPa.

The ideal gas state equation is written as

$$P_s = \frac{\rho a RT}{M}$$

where $\rho_a$ is gas density, g/cm$^3$; $M$ is gas molar mass, g/mol.

Substitution of eqs 6, 7 in eq 8 gives

$$V_{ab} = V_0 e^{-\left(\frac{RT}{P}\ln \frac{\rho a}{P}\right)^m} = V_0 e^{-D \ln \left(\frac{\rho a}{P}\right)^m}$$

The conversion relationship between the experimentally sorption amount and absolute sorption amount is expressed as

$$V = \frac{\rho_s - \rho_a}{\rho_s} V_{ab}$$

where $V$ is sorption amount measured using the experiment, cm$^3$/g.

Sorting out the abovementioned equations, the modified D–A isothermal sorption model is expressed as

$$V = \left(1 - \frac{\rho_a}{\rho_s}\right) V_0 e^{-D \ln \left(\frac{\rho a}{P}\right)^m}$$

The modified D–A isothermal sorption model consists of four parameters ($V_{ab}$, $D$, $m$, and $\rho_s$).

3. RESULTS AND ANALYSIS

3.1. Analysis of the Characteristics of Sorption Capacity. From Figure 1, we can see that the sorption
includes the Dubinin, Amankwah, Dubinin–Astakhov models. The F model and T model are empirical models. The D model also has clear physical meanings. The L model and the BET model are based on the theory and multimolecular layer adsorption theory, respectively. Also, every parameter in them model has a clear physical meaning. The D–R model is a special form of the D–A model when \( m = 2 \). The physical parameters in the D–R model and the D–A model also have clear physical meanings.

The calculation method of virtual saturated vapor pressure includes the Dubinin, Amankwah, Dubinin–Astakhov, and Reid method, in which the Amankwah method is an improvement of the Dubinin method. According to Amankwah, the adsorption system will affect the saturated vapor pressure of the adsorbate in the supercritical state. However, the undetermined coefficient \( k \) of the Amankwah method needs to be substituted into the adsorption model for the solution. In other words, the undetermined parameters of the original adsorption model are increased by a certain coefficient. The Antoine equation is a classical empirical equation for calculating saturated vapor pressure, and the Dubinin–Astakhov empirical method is a special form of Antoine equation extrapolation. Both of the two methods extend the application range of the original equation to the supercritical temperature range.

At a certain temperature, the virtual saturated vapor pressure obtained using the Dubinin, Dubinin–Astakhov, Antoine, and Reid methods is constant. In the Amankwah method, the virtual saturation vapor pressure is associated with a coefficient. Also, this coefficient is related to the sorbent and adsorbate. For the saturated vapor pressure of materials, the change is only related to temperature, but the virtual saturated vapor pressure obtained using the Amankwah method is not only related to temperature but also to the adsorption system.

The density of the sorption phase needs to be determined to convert the experimental sorption capacity to absolute adsorption capacity. There are many calculation methods for the density of the adsorption phase. The normal boiling point density (NBPD) and the Ozawa method were used in this study.

The calculation results of the virtual saturated vapor pressure and sorption phase density required for fitting are shown in Table 1.

Table 1. Values of Different Pseudo-Saturation Vapor Pressures at Different Temperatures

| T/K | Dubinin/MPa | Amankwah/MPa | Dubinin–Astakhov/MPa | Reid/MPa | normal boiling point density/kg/cm³ | Ozawa method/kg/cm³ |
|-----|-------------|--------------|----------------------|---------|-------------------------------------|---------------------|
| 393 | 10.885      | 30.642       | 9.793                | 422.3   | 268.30                              |                     |
| 303 | 11.64       | 34.412       | 10.257               | 422.3   | 261.68                              |                     |
| 313 | 12.42       | 38.373       | 10.711               | 422.3   | 255.22                              |                     |
| 323 | 13.226      | 42.495       | 11.156               | 422.3   | 248.92                              |                     |
| 333 | 14.057      | 46.773       | 11.591               | 422.3   | 242.772                             |                     |

Figure 2. Langmuir model fitting results of sorption capacity of TK1. (a) Langmuir model. (b) Langmuir model + NBPD. (c) Langmuir model + Ozawa method.
The Langmuir model has a good fitting effect on the two absolute adsorption quantities. According to the data of isotherm adsorption, when the pressure increases to a certain degree, there is almost no change or even a downward trend in the measured adsorption capacity, but it will not appear in the Langmuir model based on the single molecular layer adsorption theory. At low pressures, the Langmuir model has a good fitting effect on adsorption capacity, but at high pressures, the fitting effect is not good. The Langmuir volume and Langmuir pressure fitted using two different methods are very different. The density of the adsorption phase obtained using the normal boiling point density-correction method is higher, and the Langmuir adsorption phase obtained using the normal boiling point density must be considered in the pressure is far from the Langmuir pressure. Therefore, the Ozawa method is not convergent, and the experimental results of the two-parameter BET model are relatively large. The density of the adsorbed phase calculated using the Ozawa method is generally small, but the Langmuir volume and Langmuir pressure fitted using the Ozawa method are relatively large.

Figure 2 shows that the Langmuir model has a good fitting effect on the two absolute adsorption quantities. According to the density of the adsorption phase, the pressure increases to a certain degree, there is almost no change or even a downward trend in the measured adsorption capacity, but it will not appear in the Langmuir model based on the single molecular layer adsorption theory. At low pressures, the Langmuir model has a good fitting effect on adsorption capacity, but at high pressures, the fitting effect is not good. The Langmuir volume and Langmuir pressure fitted using two different methods are very different. The density of the adsorption phase obtained using the normal boiling point density-correction method is higher, and the Langmuir volume and Langmuir pressure obtained by the final fitting are relatively small. The density of the adsorbed phase calculated using the Ozawa method is generally small, but the Langmuir volume and Langmuir pressure finally fitted using the Ozawa method are relatively large.

Figure 2a shows that the sorption capacity obtained using the normal boiling point density correction method is still convergent in general, indicating that the adsorption tends to be balanced. However, the sorption capacity calculated using the Ozawa method is not convergent, and the experimental pressure is far from the Langmuir pressure. Therefore, the adsorption phase density must be considered in the fitting of the isotherm adsorption curve under high pressure. The final fitting parameters of the Langmuir model are directly affected by the density of the adsorption phase.

3.2.2. BET Isothermal Sorption Model. In the process of fitting, it is necessary to use the saturated vapor pressure in the BET isothermal sorption model. Therefore, the virtual saturated vapor pressure of three algorithms was used in this study. The two-parameter BET model characterizes adsorption in an infinite space, while the three-parameter BET model characterizes adsorption in a finite space. Therefore, the three-parameter model has one more parameter (n) to limit the number of adsorption layers.

3.2.2.1. Two-Parameter BET Model. The two-parameter BET model is given by

$$V = \frac{V_m CP}{(P^0 - P)(1 + (C - 1)(\frac{P}{P^0})^n)}$$

where V is the sorption capacity, cm$^3$/g; $V_m$ is the single layer maximum adsorption capacity, cm$^3$/g; C is a constant related to the heat of adsorption; $P^0$ is the saturated vapor pressure, MPa; P is the equilibrium pressure, MPa.

The experimental data and the adsorption quantity corrected using the normal boiling point density method cannot be fitted effectively using the two-parameter BET model. However, for the adsorption amount obtained using the Ozawa method, the two-parameter BET model can fit it well. This is directly related to the convergence of the isotherm adsorption curve. Combined with the Langmuir model fitting of the adsorption quantity calculated using the Ozawa method, it can be concluded that the adsorption quantity obtained using the Ozawa method is far from the adsorption capacity limit. The two-parameter BET model represents the adsorption in infinite space, which can be used to fit the adsorption isotherm curve that is far from the adsorption capacity limit.

The fitting results of the two-parameter BET model are shown in Figure 3.

It can be seen from Figure 3 that the two-parameter BET model can well fit the saturated steam pressure calculated using the two calculation methods. In general, the fitting effect of virtual saturated steam pressure obtained using the Amankwah method is better than that using the Dubinin–Astakhov method, and the saturated steam pressure obtained using the Amankwah method is greater than that with the Dubinin–Astakhov method.

According to the two-parameter BET model, the adsorption capacity limit is the adsorption capacity when equilibrium pressure is equal to the virtual saturated vapor pressure. Therefore, the more the adsorption capacity is far away from the adsorption capacity limit, the more consistent the two-parameter BET model characterizing adsorption in infinite space is, and the higher is the fitting accuracy.

In conclusion, the selection of adsorption phase density and virtual saturated vapor pressure determines the fit of the two-parameter BET model. Amankwah virtual saturated vapor pressure essentially adds a parameter to the two-parameter BET model, so as to increase the virtual saturated vapor pressure to a certain extent to meet the fit of the two-parameter BET model.

3.2.2.2. Three-Parameter BET Model. Three-parameter BET model is given by
Figure 4. Three-parameter BET model fitting results of sorption capacity of TK₁. (a) Dubinin–Astakhov method. (b) NBPD + Dubinin–Astakhov method. (c) Ozawa method + Dubinin–Astakhov method.

Figure 5. Dubinin–Radushkevich model fitting results of adsorption capacity. (a) Experimental data + Dubinin–Astakhov. (b) Experimental data + Amankwah. (c) NBPD + Dubinin–Astakhov. (d) NBPD + Amankwah. (e) Ozawa + Dubinin–Astakhov.

\[ V = \frac{V_m C_p}{(P^0 - P) \left[ 1 - (n + 1) \left( \frac{P}{P^0} \right)^n + n \left( \frac{P}{P^0} \right)^{n+1} \right]} \]

Figure 4 shows that the three-parameter BET model has a good fitting effect on the absolute adsorption capacity. For the three-parameter BET model, when the parameter \( n = 1 \), it is converted to the Langmuir model. When the three-parameter BET model is used to fit the experimental adsorption capacity and the absolute adsorption capacity obtained using the normal boiling point density method, the parameter \( n \) is less than 1, indicating that it is still in the single molecular layer adsorption, which makes the three parameter BET model meaningless for its fitting.

For the absolute adsorption capacity obtained using the normal boiling point density method, the adsorption curve shows a convergence trend, and the parameter \( n \) obtained using the three-parameter BET model is small. For the absolute adsorption obtained using the Ozawa method, the
parameter $n$ obtained using the three-parameter BET model is larger. For the BET model, the adsorption phase density has a great influence on the fitting results of the model.

3.2.3. Dubinin–Radushkevich Isothermal Sorption Model. Dubinin–Radushkevich isothermal sorption model (D–R) is given by

$$ V = V_0 e^{-D \ln \left( \frac{P}{P^0} \right)} $$

where $V$ is sorption capacity, cm$^3$/g; $V_0$ is the pore volume of the adsorbent, cm$^3$/g; $D$ is a constant related to the net heat of adsorption; $P^0$ is saturated vapor pressure, MPa; $P$ is equilibrium pressure, MPa.

The fitting result of the D–R model is shown in Figure 5. For the sorption capacity corrected using the Ozawa method, the virtual saturation vapor pressure of the Amankwah method cannot be used to fit it effectively.

It can be seen from Figure 5 that the D–R model has the best fitting effect on the sorption capacity corrected using the NBPD method. For the experimental data, the downward trend of the isotherm adsorption curve cannot be effectively fitted using the D–R model. For the sorption capacity corrected using the Ozawa method, it is difficult to be fitted using the D–R model reasonably and effectively. The sorption capacity data can be fitted well when the Amankwah method is used to calculate the virtual saturation vapor pressure. However, the virtual saturated vapor pressure obtained using the Amankwah method is less than the maximum equilibrium pressure of the experiment, which makes the D–R model lose its physical significance. As the temperature increases, the virtual saturation vapor pressure obtained using the Amankwah method decreases accordingly, which does not meet the definition of virtual saturation vapor pressure.

3.2.4. Dubinin–Astakhov Isothermal Sorption Model. Dubinin–Astakhov isothermal sorption model (D–A) is given by

$$ V = V_0 e^{-D \ln \left( \frac{P}{P^0} \right)} $$

where $m$ is a characterization constant related to the heterogeneity of the adsorbent.

The fitting result of the D–A model is shown in Figure 6. For the sorption capacity corrected using the Ozawa method, the virtual saturation vapor pressure of the Amankwah method cannot be used to fit it effectively.

It can be seen from Figure 6 that the D–R model can fit the sorption capacity which was corrected by the NBPD and Ozawa method well. Because of the difference between the sorption-phase density and the virtual saturated vapor pressure, the parameters obtained by the fitting differ greatly. In addition, although the D–A model can fit the data well when the virtual saturated vapor pressure was calculated using the Amankwah method, the virtual saturated vapor pressure obtained by it decreases with increasing temperature, which does not meet the definition of virtual saturated vapor pressure. Using the Amankwah method actually improves the original model from three parameters to four parameters, and the fitting accuracy increases accordingly. However, the original physical meaning of the model is lost.
According to the comparison of the fitting effects of the abovementioned sorption models, it can be found that these models all have a better fitting effect on the adsorption capacity when the pressure is low. The density of the adsorption phase and the virtual saturated vapor pressure have a great influence on the fitting results of the sorption model. The density of the adsorption phase directly determines the ultimate adsorption capacity of the shale sample. In addition, the BET, D–A, and D–R models are based on the assumption of virtual saturated vapor pressure. Although different methods can be used to obtain high-precision fitting results, the shale isotherm adsorption law obtained using different methods is only based on the assumption of each method.

### 3.3. Modified D–A Model Fitting

The isothermal sorption data of three rock samples were fitted using the modified D–A model. The fitting results are shown in Figure 7, and the fitting parameters are shown in Table 2.

From Figure 7 and Table 2, we can see that the modified supercritical D–A model can fit the experimentally measured sorption amounts of the high-pressure stage more accurately than the D–A model. Both the R-squared value and the adjusted R-squared values are above 0.99. The results show...
that the model fits the supercritical isothermal sorption model well.

3.4. North American Shale Sorption Data Fitting. The isothermal sorption data of the North American Green River Formation, Woodford, and Barnett (Blakely #1) shale were selected to be fitted using the modified D–A model. The fitting results of the modified D–A model are shown in Figure 8, and the fitting parameters are shown in Table 3.

As can be seen from Figure 8 and Table 3, the modified D–A model fits the Green River Formation, Woodford, and Barnett (Blakely #1) shale well. The fitting results of the experimental data and North American shale isothermal sorption data show that the modified D–A model can describe the isothermal sorption law of gas in the supercritical state well, and it has high fitting accuracy.

4. CONCLUSIONS

(1) A four-parameter \((V_0, D, m, \rho_a)\) modified model of a D–A sorption model was established. The isothermal sorption data of experimental samples were fitted and analyzed. The results show that the modified D–A model can accurately describe the isothermal sorption law of gas in the supercritical state, and it has high fitting accuracy.

(2) The density of the adsorption phase and the virtual saturated vapor pressure have a great influence on the fitting results of the sorption models. The density of the adsorption phase directly determines the ultimate adsorption capacity of the shale sample.

(3) The BET, D–A, and D–R models are based on the assumption of virtual saturated vapor pressure. Although different methods can be used to obtain the high-precision fitting results, the shale isotherm adsorption law obtained using different methods is based on the assumption of the calculation method of virtual saturation pressure.

(4) The sorption characteristic curve of methane on the shale surface under high pressure is obviously different from that under low pressure. In the low-pressure stage, the sorption amount increases rapidly with the increase of pressure and finally reaches a maximum value. In the high-pressure stage, the sorption amount slowly decreases with the increase of pressure. At the same pressure, the sorption amount of shale samples decreases with increasing temperature. The decline is

| samples             | T/K | \(V_0/\text{cm}^3/\text{g}\) | \(D\)  | \(M\)  | \(\rho_a/\text{g/cm}^3\) | \(R^2\) | Adj \(R^2\) |
|---------------------|-----|----------------------------|-------|-------|--------------------------|--------|------------|
| green river formation | 308 | 9.157                      | 0.4805| 1.199 | 2.886                    | 1.000  | 0.9999     |
|                     | 323 | 9.054                      | 0.516 | 1.256 | 3.265                    | 0.9998 | 0.9999     |
|                     | 338 | 7.745                      | 0.3029| 1.518 | 5.036                    | 0.9999 | 0.9999     |
| woodford            | 308 | 9.317                      | 0.5445| 1.099 | 2.471                    | 0.9999 | 0.9999     |
|                     | 323 | 8.134                      | 0.4187| 1.268 | 3.034                    | 0.9999 | 0.9999     |
|                     | 338 | 7.919                      | 0.3680| 1.375 | 3.971                    | 1.000  | 0.9999     |
| Barnett (Blakely #1)| 308 | 6.202                      | 0.4852| 1.034 | 2.003                    | 0.9994 | 0.9992     |
|                     | 323 | 4.532                      | 0.2692| 1.377 | 2.509                    | 0.9997 | 0.9996     |
|                     | 338 | 4.985                      | 0.3424| 1.295 | 2.633                    | 0.9999 | 0.9999     |

Figure 9. Diagram of experiment system. 1—Gas storage tank; 2—gas booster pump; 3—air compressor; 4—buffer container; 5—pressure regulating valve; 6—pneumatic valve; 7—thermostatic oil bath; 8—pneumatic valve; 9—standard chamber 10—sample chamber 11—filter 12—vacuum container 13—gas drying tank 14—vacuum pump 15—data acquisition system.
samples are shown in Table 4. In order to ensure the were selected for this study. The basic parameters of shale gas reservoirs in China.28

The reservoir temperature and pressure conditions of almost all pressure are 453 K and 40 MPa, respectively. They can meet gas sorption and desorption. The highest test temperature and therm sorption system mainly completes data sampling, data processing, and curve analysis in the whole process of shale gas sorption and desorption. The highest test temperature and pressure are 453 K and 40 MPa, respectively. They can meet the reservoir temperature and pressure conditions of almost all shale gas reservoirs in China.29–30

5. SUPERCritical methane sorption experiments

5.1. Experimental apparatus. In this study, an experimental research method for shale isothermal sorption under high temperature and high-pressure reservoir conditions is established. The KDDXF-II high-temperature and high-pressure isothermal sorption system of China University of Petroleum (East China) public test platform is used in this study. The basic principle of this instrument is shown in Figure 9.

The KDDXF-II high-temperature and high-pressure isotherm sorption system mainly completes data sampling, data processing, and curve analysis in the whole process of shale gas sorption and desorption. The highest test temperature and pressure are 453 K and 40 MPa, respectively. They can meet the reservoir temperature and pressure conditions of almost all shale gas reservoirs in China.29–30

5.2. Shale samples. Three representative shale samples (TK1, TK2, and TK3) from Cengong block, Guizhou, China, were selected for this study. The basic parameters of shale samples are shown in Table 4. In order to ensure the consistency of the experimental samples at each temperature, we did not reuse the samples, and the following steps were adopted: sieved 500 g of 60–80 mesh sand particles that have been crushed of each sample, and divided them into 5 parts after mixing. Then, the samples were dehydrated at 383.15 K for 8 h and vacuum-degassed for 10 h before testing to fully remove impurity gases. The isothermal sorption experiments were performed at 293.15, 303.15, 313.15, 323.15, and 333.15 K, respectively.

Table 4. Basic Parameters of Shale Samples

| samples | detrital minerals/% | illite/% | kaolinite/% | chlorite/% | brittle mineral/% | TOC/% | R_0/% | porosity/% | permeability/μD |
|---------|---------------------|--------|-------------|------------|-----------------|------|------|-----------|----------------|
| TK1     | 46.2                | 29.1   | 1.7         | 0.4        | 22.6            | 6.14 | 2.71 | 2.11      | 0.1773         |
| TK2     | 56.7                | 24.8   | 1.4         | 0.6        | 16.5            | 5.61 | 2.58 | 3.14      | 0.2560         |
| TK3     | 71.2                | 18.9   | 0.7         | 0.2        | 11.8            | 4.98 | 2.61 | 3.97      | 0.2819         |

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Notes

The authors declare no competing financial interest.

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