Investigation of the fractal characteristics of adsorption-pores and their impact on the methane adsorption capacity of various rank coals via N2 and H2O adsorption methods

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Abstract
Coal seam is a sedimentary body with complex pore system. The gas adsorption property of coal is greatly determined by the adsorption-pores (<100 nm), and the fractal dimension can be used an index to estimate the impact of the adsorption-pores on the methane adsorption capacity of various rank coals. In this paper, low-temperature N2 adsorption and H2O adsorption methods were used to study the adsorption-pores structure and its fractal features. The results show that the development of adsorption-pores closely depends on the coalification, and the degree of pore development exhibits a U-shaped trend with increasing coal rank. Additionally, the pore size distributions of coal samples from N2 adsorption analysis and H2O adsorption analysis are similar, especially for samples LH7 and WLH8. Fractal analysis indicates that $D_2(N_2)$ ($0.5 < P/P_0 < 1$) can more accurately characterize the fractal features of adsorption-pores than $D_2(H_2O)$, which may be a result of the significant coal-H2O interaction. Moreover, $D_2(N_2)$ has stronger correlations with the coal pore parameters. With the increase in $D_2(N_2)$, the Langmuir volume first decreases and then increases, which is probably associated with the competition effect of the pore structure and surface irregularity of coal. When $D_2(N_2) < 2.7-2.8$, the pore structure plays a key role, while for $D_2(N_2) > 2.7-2.8$, the influence of the specific surface area is more prominent. The equilibrium moisture content of the coal samples also has a positive correlation with $D_2$, except for low-rank coal sample YZG2 due to the presence of a large amount of oxygen-containing functional groups, which increases its water-holding capacity.

KEYWORDS
coal rank, coalbed methane, fractal dimension, pore structure, water vapor sorption
1 | INTRODUCTION

China has increasingly attached importance to the development and utilization of coalbed methane (CBM) in recent years. This is because CBM not only causes disasters in coal mines but also provides a clean energy resource.\(^1\) Coal is characterized as a porous medium, and the CBM occurrence and migration are closely related to coal pore structure.\(^2\)-\(^5\) To define the coal pore system and its impact on the gas adsorption capacity and flow capability, several classifications have been given by multiple scholars.\(^6\)-\(^10\) Generally, the pores in coal reservoirs can be classified as follows\(^11\): micropores (<10 nm), transition pores (10-100 nm), mesopores (>100 nm), and macropores (>1000 nm). Cai et al.\(^12\) further indicated that the adsorption-pores (<100 nm) supply the main storage space for gas, while the seepage-pores (consisting of mesopores and macropores) play an important role in CBM flow, which has been accepted by many scholars.\(^13\),\(^14\) Hence, the adsorption-pores can greatly influence the adsorption and diffusion of gas in the coal matrix. This paper focuses on the adsorption-pores and their impact on the gas adsorption properties of coal.

Many parameters have been proposed to characterize the pore structure of coal, such as the specific surface area (SSA), pore volume (PV), pore diameter, pore size distributions (PSDs), and pore type. A series of test techniques have been adopted to evaluate the pore structure of coals, as shown in Figure 1. Among them, the adsorption method (with low-temperature N\(_2\) adsorption (LN\(_2\)GA) and CO\(_2\) adsorption) has been widely used in the pore analysis of coal because of its simple test procedure and convenient data analysis. The LN\(_2\)GA method is more commonly used to analyze pores with widths greater than 2 nm, while the CO\(_2\) adsorption method is superior in the analysis of smaller micropores (<2 nm) due to the stronger activity of CO\(_2\) molecules.\(^15\),\(^16\) The water vapor adsorption (WVA) method uses water molecules as probes and is based on the adsorption principle to estimate the microscopic pore characteristics of a given solid. Many studies have been conducted on water adsorption in shale or coal and the applicability of sorption models,\(^17\)-\(^21\) and some conclusions about the influence of water on the pore characteristics in these rock types have been discussed.\(^22\),\(^23\) Some scholars have applied the WVA method to study the pore structure of building materials and food.\(^24\),\(^25\) However, there are few reports on water vapor analysis for the pore structure of coal.\(^26\)

Previous studies have concluded that the gas adsorption capacity of coal is related to its pore structure.\(^27\),\(^28\) However, this work is still insufficient to comprehensively understand the relationship between the pore structure and adsorption properties of coal by using only the pore parameters due to the heterogeneity and anisotropy of coal.\(^29\)-\(^32\) As an important tool to describe the structural characteristics of natural materials, fractal geometry theory provides a new perspective to quantitatively describe the pore irregularity of coal reservoirs. Some scholars have introduced the fractal dimension to study the irregularity of the pore structure of coal or rock.\(^33\) The fractal dimension can be determined by processing data from many measurement techniques, such as the adsorption method, mercury intrusion porosimetry, optical image analysis, small-angle X-ray scattering (SAXS), and nuclear magnetic resonance (NMR) relaxation method.\(^34\)-\(^36\) Among

![FIGURE 1 Test techniques to evaluate the pore structure of coals (modified after ref.\(^37\),\(^38\))](image-url)
them, the adsorption method has a significant advantage since the surface fractal analysis can be performed with only one complete adsorption isotherm.\textsuperscript{39,40} The easiest way to calculate the value of the fractal dimension is to use the fractal Frenkel-Halsey-Hill (FHH) model.\textsuperscript{39} Regarding the FHH fractal analysis of LN\textsubscript{2}GA isotherms, it has been concluded that the fractal dimension is correlated with the methane adsorption capacity of coals.\textsuperscript{41,42} The fractal Brunauer-Emmett-Teller (BET) model has also been applied to calculate the fractal dimension based on the LN\textsubscript{2}GA isotherms of coal.\textsuperscript{43,44}

In terms of the WVA method, the WVA isotherms have been applied to the fractal analysis of soil, and the $D_s$ value is ideal.\textsuperscript{45,46} However, no research has been conducted on the fractal analysis of coal pores using WVA isotherms.

The WVA method was first applied in combination with the LN\textsubscript{2}GA method to study the pore structure of coal. Subsequently, combined with the experimental results of the methane adsorption capacity and equilibrium moisture content of various rank coals, three research components were performed: (a) investigating the pore structure characteristics of coals by using the LN\textsubscript{2}GA and WVA methods; (b) adopting the fractal FHH and BET models to calculate the fractal dimension of various rank coals, then analyzing the relationship between the pore parameters and fractal dimension; and (c) studying the impact of the fractal dimension on the methane adsorption capacity and water-holding capacity. This study will be useful to further reveal the influence mechanism of the adsorption-pores structure on the adsorption properties of coal.

| Sample no. | Coal mine | Coal seam | $R_{\text{max}}$, % | $M_{\text{ad}}$, % | $A_{\text{ad}}$, % | $V_{\text{ad}}$, % | $F_{\text{C_{ad}}}$, % | $V_{L}$, (cm$^3$/g) | $P_{L}$, MPa | Coal rank |
|------------|-----------|-----------|----------------|----------------|----------------|----------------|----------------|----------------|-------------|------------|
| YZG2       | Yuanzigou | 2         | 0.65           | 6.33           | 26.59          | 40.52          | 39.90          | 39.97          | 1.93        | Low-rank coal |
| LH7        | Linhuan   | 7         | 1.16           | 0.53           | 27.74          | 28.75          | 51.11          | 23.22          | 1.15        | Medium-rank coal |
| YL10       | Yangliu   | 10        | 1.32           | 1.28           | 8.97           | 22.95          | 67.01          | 26.99          | 0.94        | Medium-rank coal |
| HZ9        | Haizi     | 9         | 2.20           | 1.63           | 14.38          | 14.20          | 72.07          | 32.86          | 0.75        | High-rank coal |
| WLH8       | Wolonghu  | 8         | 3.18           | 2.40           | 9.94           | 8.03           | 80.61          | 52.80          | 0.66        | High-rank coal |

2 | MATERIALS AND METHODS

2.1 | Sample characterization

Five coal samples collected from different mining areas of China were selected: long-flame coal from the Yuanzigou coal mine in Baoji city, Shaanxi Province; fat coal from the Linhuan coal mine; coking coal from the Yangliu coal mine; lean coal from the Haizi coal mine; and anthracite from the Wolonghu coal mine in Huaiabei city, Anhui Province. The vitrinite reflectance of coal can reflect the coalification degree, which was determined by following the ISO7404-5:2009 standard. In the ISO11760:2005 standard, the classification of coal rank is given, namely, low-rank coal ($R_{r}$ < 0.5%), medium-rank coal (0.5% ≤ $R_{r}$ < 2.0%), and high-rank coal (2.0% ≤ $R_{r}$ < 6.0%). Notably, long-flame coal with a maximum vitrinite reflectance less than 0.65% is always classified as low-rank coal in China.\textsuperscript{28} Following ISO17246:2010 standard, the proximate analysis of coal samples with sizes of 0.074-0.2 mm was conducted on an automatic proximate analyzer. The Langmuir volume ($V_{L}$) and Langmuir pressure ($P_{L}$) are the key parameters that represent the adsorption capacity of coal. Following MT/T752-1997, methane adsorption tests of dried coal samples with sizes of 0.2-0.25 mm were conducted using high-pressure volumetric equipment. The procedures of the above tests are described in An et al.\textsuperscript{47} and Chen et al.\textsuperscript{48} The results of the proximate analysis, methane adsorption constant, and coal rank for the coal samples are shown in Table 1.

2.2 | Experiments

The instrument used for the WVA studies was an AQUADYNE dynamic vapor sorption (DVS) analyzer (Quantachrome Ins, USA). It can measure the water vapor adsorption isotherms and the corresponding kinetics at preset relative humidity ($P/P_0$) steps. Before the measurements, approximately 50 mg of the fresh samples was vacuum dried at 363 K. During the sorption process, the relative humidity ($P/P_0$) was increased or decreased to a fixed value, and the change in the sample mass vs time was recorded with high resolution (0.1 μg) until sorption equilibrium. The measurements were performed at a temperature of 293 K and 0%-90% relative humidity. In particular, the change gradient in the relative humidity is 2% in the 40%-60% range and 5% outside this range.

The nitrogen gas adsorption at 77 K (LN\textsubscript{2}GA) was evaluated on an Autosorb-iQ2 analyzer (Quantachrome Ins,
USA). The relative pressure \((P/P_0)\) was observed over the range from 0.001 to 0.995. Prior to the experiments, the particle samples with a size range of 0.2-0.25 mm should be vacuum dried at 60°C for at least 24 hours. The Barrett-Joyner-Halenda (BJH), quenched solid-state density functional theory (QSDFT), and BET methods were used to determine the pore parameters of the materials via the software tool ASiQwin™. Detailed descriptions of the theoretical methods are provided in the research of Lowell et al.\(^{49}\)

2.3 | Theoretical fractal methods

The fractal feature of the solid surface can be characterized by adsorption isotherms with a given fractal model.\(^{39}\) In this study, both the fractal FHH and BET models are adopted to calculate the fractal dimensions and then estimate the pore structure and surface irregularity of various rank coals.

2.3.1 | Fractal FHH model

Based on the fractal FHH method, the fractal dimension \(D\) can be determined by an analysis of the multiplayer adsorption on the fractal surface. The commonly used expression is

\[
\ln \frac{M}{M_m} = m + A \ln \left( \frac{P_0}{P} \right) \quad \text{or} \quad \ln \frac{V}{V_m} = m + A \ln \left( \frac{P_0}{P} \right)
\]

(1)

where \(M\) (or \(V\)) is the amount of adsorbed gas at an equilibrium pressure \(P\); \(M_m\) (or \(V_m\)) is the adsorption amount of monolayer coverage; \(P_0\) is the saturation pressure of the gas; \(m\) is a constant; and \(A\) is the fractal parameter, which is dependent on the fractal dimension.

Generally, by fitting the curves of \(\ln M\) (or \(\ln V\)) vs \(\ln(P/P_0)\), the slope of the linear segments should be equal to \(A\). The coefficient \(A\) in Equation (1) depends on the van der Waals force and capillary condensation adsorption mechanism.\(^{40,45,50}\) For the van de Waals interaction, the fractal dimensions, \(D\), can be calculated by the following formula:

\[
D = 3 + 3A
\]

(2)

For the capillary condensation effect, the following equation can be applied:

\[
D = 3 + A
\]

(3)

2.3.2 | Fractal BET model

Fripiat et al.\(^{51}\) indicated that with an increasing number of adsorption layers, the adsorption interface tends to shrink, and the number of adsorption sites decreases. Then, the fractal BET model for multilayer adsorption on the fractal surface was proposed. The expression is as follows:

\[
\frac{M}{M_m} = \frac{C}{1 + (C - 1)x} \sum_{n=1}^{\infty} n^{2-D}x^n
\]

(4)

where \(C\) is the BET constant, \(n\) is the number of adsorbed layers, and \(x\) is the relative pressure \((P/P_0)\). In the low relative pressure range, \(x\) is considerably less than 1, and \(D\) is 2-3. Then,

\[
x > 2^{2-D}x^2 > 3^{2-D}x^3 > 4^{2-D}x^4
\]

Therefore, Equation (4) can be transformed into the following expression:

\[
\frac{M}{M_m} = \frac{C}{1 + (C - 1)x} \left( x + 2^{2-D}x^2 + 3^{2-D}x^3 \right)
\]

(5)

The three parameters \(M_m\), \(C\) and \(D\) were optimized using a least squares routine coupled with a multiparameter optimization algorithm in MATLAB software. Here, Equation (5) is mainly used to calculate \(D\) based on the adsorption isotherms in the low relative pressure region.

2.4 | Mathematical PSD model for water adsorption isotherms

For isothermal adsorption of water vapor in a solid, Huang et al.\(^{52}\) proposed a model for calculating the PSDs of materials based on the cylindrical pore assumption, that is,

\[
\Delta V_i = R_i \left( \Delta v_i - 2\Delta t_i \sum_{j=1}^{i-1} \frac{\Delta V_j}{\bar{r}_j^2} + 2\bar{t}_i \Delta t_i \sum_{j=1}^{i-1} \frac{\Delta V_j}{r_j^2} \right)
\]

(6)

\[
R_i = \left( \frac{\bar{r}_i}{\bar{r}_i - \bar{t}_i} \right)^2
\]

(7)

\[
\bar{r}_i = \frac{1}{2} (r_{i-1} + r_i)
\]

(8)

\[
\bar{t}_i = \frac{1}{2} (t_{i-1} + t_i)
\]

(9)

\[
\Delta t_i = t_{i-1} - t_i
\]

(10)

where \(\Delta V_i\) is the volume of a pore with radius \(r_i\); \(\Delta v_i\) is the amount of water adsorbed on the coal at relative pressure \(P_i/P_0\); \(r_i\) corresponds to the pore radius at \(P_i/P_0\) Å; and \(t_i\) is the thickness of the adsorption layers at \(P_i/P_0\). The real pore diameter...
(d_i) includes the effective pore radius (r_{ki}) and the adsorption layer thickness (t_i), namely,

\[ d_i = 2r_i = 2(r_{ki} + t_i) \] (11)

The relationship between the parameters \( r_{ki} \) and \( P_i/P_0 \) can be expressed by the Kelvin equation, that is,

\[ r_{ki} = -\frac{2\gamma v_m}{RT \ln \left( \frac{P_i}{P_0} \right)} \] (12)

where \( \gamma \) is the surface tension of water, equal to 0.072735 N/m at 293 K; \( v_m \) is the molar volume of water, 18.0323 cm³/mol; \( R \) is the universal gas constant, 8.314 J/(mol·K); and \( T \) is the experimental temperature, 293 K. The formula for calculating the thickness of the water vapor adsorption layer is\(^52\)

\[ t_i = -\frac{3.48}{\left( \log \left( \frac{P_i}{P_0} \right) \right)^{1/3}} \] (13)

Hence, the real pore diameter \( d_i \) can be expressed as

\[ d_i = 2\left( -\frac{4.67}{\log \left( \frac{P_i}{P_0} \right)} - \frac{3.48}{\left( \log \left( \frac{P_i}{P_0} \right) \right)^{1/3}} \right) \] (14)

Thus, the PSDs curves (\( \Delta V/\Delta d \) vs \( d \)) of coal can be plotted.

3 | RESULTS AND DISCUSSION

3.1 | Characteristics of the coal pore structure

3.1.1 | LN2GA analysis

The nitrogen ad/desorption isotherms of the coal samples are illustrated in Figure 2. Based on the original International Union of Pure and Applied Chemistry (IUPAC) Recommendation of 1985, the IUPAC classification increases the number of adsorption isotherms from six to eight and the number of hysteresis loops from four to six.\(^53\) The adsorption isotherms of all the samples have a sigmoidal profile and correspond to type II, and the hysteresis loop features are close to those of types H3 and H4.

For nitrogen adsorption at 77 K, the surface tension of nitrogen \( \gamma \) is 8.85 ergs/cm², and the molar volume of liquid nitrogen \( v_m \) is 34.7 cm³/mol. The calculation equation of the nitrogen adsorption layer thickness is

\[ t_{N_2} = \left[ \frac{13.99}{\log \left( \frac{P_0}{P} \right) + 0.034} \right]^{1/2} \] (15)

Thus, according to Equations (11), (12), and (15), the relationship between the real pore diameter and relative pressure can be obtained based on the LN₂GA tests.

In the low relative pressure stage \( (P_i/P_0 < 0.01) \), samples YZG2 and WLH8 have very significant adsorption amounts due to the micropore filling effect, indicating that there are many micropores in the two coals. Sample YL10 has the lowest adsorption amount at \( P_i/P_0 < 0.01 \), suggesting that the medium-rank coal contains relatively few micropores. The adsorption curves of all the samples increase sharply in the high relative pressure stage \( (P_i/P_0 > 0.9) \), which depends on the capillary condensation effect. Moreover, although \( P_i/P_0 \) approaches 1.0, the adsorption amount of the coals still increases indefinitely. This can be attributed to (a) the existence of numerous mesopores and macropores in the coal and (b) the nonrigid aggregated plate-like particles forming to slit-shaped pores.\(^49,55\)

The hysteresis loop of a coal can be classified into three types based on LN₂GA tests.\(^54-56\) For the L1 type, such as sample YL10, the adsorption and desorption branches essentially coincide at \( P_i/P_0 < 0.35 \) (corresponding to \( d > 2.9 \) nm), and very narrow hysteresis loops are formed at \( 0.35 < P_i/P_0 < 1.0 \). There are mainly semiclosed pores, such as semiclosed cylindrical cavities, observed in the range of 2.9-300 nm. Samples LH7 and HZ9 are assigned to the L3 type. Unlike the L1 type, the L3 type corresponds to a prominent inflection point in the desorption curve at a \( P_i/P_0 \) value of approximately 0.5, which may be due to the existence of ink-bottle-shaped pores.\(^56,57\)

Additionally, the distinct desorption hysteresis loop occurring at \( P_i/P_0 > 0.35 \) for the two samples suggests that the two samples have many open pores, such as parallel plate pores with four open ends.

Moreover, the hysteresis loop of the anthracite sample WLH8 and low-rank coal sample YZG2, which can be classified as the L4 type, is not mentioned in the above classification but appears in many published reports.\(^2,57-59\) Its main characteristic is that the adsorption and desorption curves do not coincide, even in a very low relative pressure range \( (P_i/P_0 < 0.35) \). The low-pressure hysteresis may be related to the change in the volume of the adsorbent, for example, the sorption-swelling effect of the coal.\(^49,60\) When \( P_i/P_0 \) is within the range 0.35-0.90, with increasing relative pressure, the adsorption branches of samples YZG2 and WLH8 increase more rapidly, reflecting that the low-rank coal sample YZG2 and anthracite sample WLH8 have greater pore openness. In addition, the analysis of the pore types shows that the open-type pores in low-rank and high-rank coals are well developed, which is conducive to gas diffusion, while the development of open-type pores in the other three coal samples is relatively poor.

The pore parameters of coal samples analyzed using the LN₂GA method are shown in Table 2. After integrating the SSA or PV from the QSDFT model \((1 < d < 10 \text{ nm})\) and
BJH model (10 < d < 300 nm), the SSA and PV percentages of the micropores, transition pores, and mesopores are calculated. The PSDs curves of the coal samples are shown in Figure 3. The QSDFT curves show a bimodality for samples YZG2 and WLH8 (main peaks at ~1.5 nm and ~5 nm), and the BJH curves suggest that samples YZG2 and WLH8 exhibit a unimodality with a main peak at ~3 nm. In contrast, for both the QSDFT and BJH curves, the other three coal samples show multimodality. Therefore, the PSDs of samples YZG2 and WLH8 are more concentrated in micropores.

![Figure 2](image-url)

**FIGURE 2** Low-temperature N\textsubscript{2} ad/desorption isotherms of coal samples

**TABLE 2** Pore parameters of the coal samples analyzed using the LN\textsubscript{2}GA method

| Sample no. | SSA (m\textsuperscript{2}/g) | PV (×10\textsuperscript{-3} cm\textsuperscript{3}/g) | BET SSA (m\textsuperscript{2}/g) | Average pore diameter (nm) |
|------------|-----------------|------------------|---------------------|-----------------------------|
|            | S1   | S2   | S3   | Total SSA | V1   | V2   | V3   | Total PV |                      |                      |
| YZG2       | 16.44 | 1.12 | 0.10 | 17.66     | 18.79 | 7.20 | 4.83 | 30.82     | 22.17 | 5.66 |
| LH7        | 1.50  | 0.40 | 0.06 | 1.97      | 1.48  | 3.36 | 3.26 | 8.11      | 2.35  | 13.84 |
| YL10       | 0.21  | 0.11 | 0.03 | 0.34      | 0.29  | 0.97 | 1.30 | 2.56      | 0.45  | 22.01 |
| HZ9        | 0.60  | 0.28 | 0.04 | 0.93      | 0.64  | 2.47 | 2.17 | 5.28      | 1.17  | 18.24 |
| WLH8       | 16.35 | 1.07 | 0.07 | 17.49     | 13.10 | 7.47 | 3.50 | 24.07     | 21.62 | 4.59 |

*Note: S1 (V1), S2 (V2), and S3 (V3) represent the surface area (or volume) of the micropores (<10 nm), transition pores (10-100 nm), and mesopores (100-300 nm), respectively.*
indicating that the low-rank coal and high-rank anthracite have relatively nonuniform PSDs and complex pore structures.

As shown in Table 2, the SSA and PV of sample YZG2 are approximately 8.97-52.09 and 3.80-12.04 times those of samples YL10, LH7, and HZ9. In addition, sample WLH8 has an SSA of 8.89-51.60 times and a PV of 2.97-9.40 times those of the medium-rank coal samples. Hence, with increasing coalification, both the SSA and PV show a U-shaped change trend. As shown in Figure 3, the SSA of samples YZG2 and WLH8 is dominated by micropores, accounting for more than 90% of the SSA, and the PV is also dominated by micropores, accounting for more than 50% of the PV. The SSA of the other three samples is also dominated by micropores, accounting for 61.2%-76.2% of the SSA, which is significantly less than that of samples YZG2 and WLH8. Hence, the low-rank coal and high-rank anthracite both have well-developed micropore structures, which is beneficial to CBM occurrence. Additionally, the total PV percentage of transition pores and mesopores in samples YL10, LH7, and HZ9 exceeds 80%, which is greater than the corresponding 39% of sample YZG2 and 45.6% of sample WLH8. However, the PV of samples YZG2 and WLH8 is still greater than that of the other three samples, indicating that the diffusion capability of methane gas in low-rank coal and high-rank anthracite may be relatively strong.

The development of adsorption-pores is closely related to the coal rank. Xie indicates that in the low coalification stage, coal includes more nonaromatic structures and oxygen-containing functional groups, a large amount of long side chains and a loose spatial structure. Therefore, the pore structure of low-rank coal is more developed than that of higher-rank coal, which is conducive to gas adsorption. With increasing coalification, the number of both oxygen-containing functional groups and alkyl side chains decreases, the aromatization degree increases and the molecular structure becomes tight, so the porosity of medium-rank coal is relatively small. Hence, medium-rank coal always exhibits a low adsorption capacity. The further increase in coalification leads to the orderly arrangement of the coal macromolecular structure and a tighter aromatic layer. Moreover, the intense polycondensation reaction makes the coal shrink and then form new pores and fissures, which leads to a more developed pore structure for higher-rank coal. Therefore, anthracite always has more significant adsorption performance than low- and medium-rank coals.

### 3.1.2 WVA analysis

The water vapor ad/desorption isotherms of the coal samples are illustrated in Figure 4. The coal samples have different adsorption isotherm characteristics and adsorption hysteresis morphologies. Samples YZG2 and WLH8 exhibit more pronounced hysteresis features than the other three samples, and a sharp step-down of the desorption isotherms can be observed at a $P/P_0$ of approximately 0.5. In contrast, the desorption curves of the other three samples follow a path...
The hysteresis loops obtained from the WVA method exhibit some differences with those obtained from the LN$_2$GA method: (a) The extent of water vapor uptake of sample WLH8 decreases significantly with increasing $P/P_0$, even in the low relative pressure range. (b) The inflection point of the desorption branches at a $P/P_0$ of approximately 0.5 disappears for samples HZ7 and HZ9. (c) The desorption curves of samples YL10, LH7 and HZ9 are not closed in the low relative pressure range, which may be attributed to the swelling effect due to the presence of adsorbed water in the micropores. The great differences in the hysteresis loops between the WVA method and the LN$_2$GA method were previously observed for carbon and shale.

The possible surface chemical interactions between the water molecules and coal play a key role due to the existence of numerous oxygen-containing functional groups in coal. These functional groups have a controlling effect on the WVA in the low relative pressure stage, which affects the water ad/desorption behaviors and the hysteresis characteristics of the coal. Moreover, the adsorption hysteresis is also related to the experimental conditions such as temperature. Hence, because of the discrepancy in the surface chemical interactions between water and coal and the experimental conditions, different hysteresis features are observed for H$_2$O adsorption (293 K) and N$_2$ adsorption (77 K).

A comparison of PSDs curves determined with Huang’s model for H$_2$O adsorption and the BJH model for N$_2$ adsorption is shown in Figure 5. The coal sample PSD curves obtained from H$_2$O adsorption appears to exhibit unimodality or bimodality with a main peak at approximately 3 nm, indicating the existence of many micropores in the coal. In particular, for samples LH7 and WLH8, the PSDs features determined from H$_2$O adsorption using Huang’s model are similar to those determined from N$_2$ adsorption using the BJH model.

### 3.2 Calculation of the fractal dimension

Many scholars have regarded 0.5 as the demarcation point of relative pressure for two different adsorption behaviors. When $P/P_0 < 0.5$, the adsorption behavior is controlled by...
van der Waals forces; when $P/P_0$ is 0.5-1.0, the capillary condensation effect plays a major role.\textsuperscript{69,70} As shown in Figure 2, $P/P_0 = 0.5$ is a prominent demarcation point for the change in the desorption rate of the adsorbed nitrogen in the coal. The same results can be observed in the water vapor desorption isotherms of the coal samples, especially samples YZG2 and WLH8.

The FHH plots of $\ln V$ vs $\ln(\ln(P_0/P))$ reconstructed from the $N_2$ adsorption isotherms are shown in Figure 6. The results of the fractal dimension $D$ calculated by the FHH model are illustrated in Table 3. When $P/P_0 > 0.5$ (corresponding to $d > 4$ nm), the fractal dimension is calculated by the formula $D = 3 + A$, and $D$ ranges from 2.547 to 2.860. While $P/P_0 < 0.5$, the adsorption process is dominated by the monolayer and multilayer adsorptions, and $D$ is still calculated by $D = 3 + A$ rather than $D = 3 + 3A$. As shown in Table 3, the $D$ value calculated by $D = 3 + A$ is less than 2, which is unrealistic. Conversely, the $D$ value calculated by $D = 3 + A$ is 2.073-2.563, and the results are realistic. The highly developed micropores of the coals, especially pores with widths less than or equal to 2 nm (corresponding to $P/P_0 = 0.2$), can lead to a large amount of $N_2$ adsorption in coal at a very low relative pressure, namely, micropore filling, which is different from the monolayer and multilayer adsorption mechanisms.\textsuperscript{60}

This may be one reason why the equation $D = 3 + 3A$ is not applicable at the low relative pressure section. In addition, Sahouli et al\textsuperscript{71} proposed the equation $D_s = 3 + s * A$ and further indicated that when the adsorption behavior is controlled by the solid-gas potential, the coefficient $s$ should be used to replace the theoretical value of 3. However, there is a lack of relevant research on the value of $s$.\textsuperscript{72}

Regarding the WVA of the coal samples, the relative pressure was divided into two segments of 0-0.5 and 0.5-1.0 for fractal analysis. The fitting results of the fractal analysis with the BET and FHH models are shown in Figure 7, and the calculation results of the fractal dimension are shown in Table 4. When $P/P_0 > 0.5$ (corresponding to $d > 4.1$ nm), the fractal dimension $D_2$ is calculated by the equation $D = 3 + A$ in the FHH method and ranges from 2.384 to 2.680. When $P/P_0 < 0.5$, the equations $D = 3 + A$ and $D = 3 + 3A$ are used to calculate the fractal dimension $D_1$; however, the corresponding calculated value is not within the range of 2-3, which is not realistic. In this case, the fractal BET model is adopted to calculate the fractal dimension. The correlation coefficients $R^2$ are all above 0.99, and $D_1$ varies from 2.023 to 2.232. Hence, the fractal BET model has a relatively good effect when used for the fractal analysis of the low relative pressure section ($P/P_0 < 0.5$).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{plot.png}
\caption{Plots of ln(V) vs ln(ln(P_0/P)) from the N_2 gas adsorption isotherms at 77 K}
\end{figure}

\begin{table}[h]
\centering
\caption{Results of the fractal analysis by using the FHH model for N_2 adsorption}
\begin{tabular}{|c|c|c|c|c|}
\hline
Sample no. & $P/P_0 < 0.5$ & $0.5 < P/P_0 < 1$ & & \\
\hline
 & $A_1$ & $D_1(N_2) = 3 + A_1$ & $D_2(N_2) = 3 + 3A_1$ & $R^2$ & $A_2$ & $D_2(N_2) = 3 + A_2$ & $R^2$ \\
YZG2 & -0.596 & 2.404 & 1.212 & 0.9802 & -0.140 & 2.860 & 0.9391 \\
LH7 & -0.482 & 2.518 & 1.554 & 0.9694 & -0.359 & 2.641 & 0.9947 \\
YL10 & -0.927 & 2.073 & 0.219 & 0.9769 & -0.453 & 2.547 & 0.9924 \\
HZ9 & -0.577 & 2.423 & 1.269 & 0.9326 & -0.414 & 2.586 & 0.9978 \\
WLH8 & -0.437 & 2.563 & 1.689 & 0.6953 & -0.143 & 2.857 & 0.9982 \\
\hline
\end{tabular}
\end{table}
As shown in Figure 8A, when \( P/P_0 < 0.5 \), the value of \( D_1(N_2) \) is close to that of \( D_2(H_2O) \) only for sample YL10. While \( P/P_0 > 0.5 \), the values of \( D_2(N_2) \) and \( D_2(H_2O) \) are the closest for samples LH7, YL10 and HZ9, followed by sample WLH8 with a difference of 0.177, and sample YZG2 has the largest difference. Sahouli et al.\(^{71}\) considered that the fractal dimension \( D_1 \) characterizes the surface irregularity of the coal pores.\(^{69}\) The relationships between the \( D_2 \) value and the average pore diameter and BET SSA are shown in Figure 9. \( D_2(N_2) \) and the average pore diameter show a strong positive correlation (\( R^2 = 0.9700 \)). For sample YZG2, \( D_2(H_2O) \) and the average pore diameter also exhibit a positive correlation (\( R^2 = 0.5307 \)). Smaller pore sizes may indicate the existence of more pore throats, which can lead to an increase in the complexity of the pore structure of coal and a significant enhancement in the \( D_2 \) value. Combined with the \( D_2 \) value obtained from LN2GA in the research of Yao et al.\(^{72}\) and Zhou et al.,\(^{44}\) the \( D_2(N_2) \) value shows a positive correlation with the BET SSA (\( R^2 = 0.5690 \)). With increasing BET SSA, \( D_2(N_2) \) rapidly increases at first and then more gradually increases, which is the same observation as in the research of Fu et al.\(^{76}\) Hence, \( D_2(N_2) \) has a significant correlation with the BET SSA, and the correlation weakens with increasing SSA. Similar to \( D_2(N_2) \), \( D_2(H_2O) \) of the coal samples and the BET SSA also show a positive correlation (\( R^2 = 0.5869 \)) except for sample YZG2.

As shown in Figure 10, \( D_2(N_2) \) is positively correlated with the micropore (<10 nm) volume and the volume of transition pores and mesopores (10-330 nm). The corresponding correlation coefficients are 0.8277 and 0.6888. Apart from sample YZG2, \( D_2(H_2O) \) is also positively correlated with the micropore volume, with an \( R^2 \) of 0.8287, and with the volume of transition pores and mesopores, with an \( R^2 \) of 0.4738. Clearly, for the two adsorbates of nitrogen and water, \( D_2 \) has a greater relevance to the micropore volume than to the volume of transition pores and mesopores. As illustrated in Figure 11, except for sample YZG2, both \( D_2(N_2) \) and \( D_2(H_2O) \) are positively correlated with the proportion of micropore volume and negatively correlated with the proportion of the volume.
of transition pores and mesopores. The corresponding correlation coefficients $R^2$ are 0.9178 and 0.8108, respectively. Therefore, the correlation between the fractal dimension and micropore volume is greater, indicating that the development of micropores has a more significant and positive impact on the fractal nature of the coal adsorption-pores. However, $D_2(H_2O)$ of sample YZG2 exhibits a different trend. It is likely that the large amount of oxygen-containing functional groups present in low-rank coal and the water molecules adsorbing on these oxygen-containing sites will influence the fractal analysis through the WVA method.

### 3.4 Relationship between the fractal dimension and adsorption properties of coal

The Langmuir volume ($V_L$) represents the maximum adsorption amount of coal, and the Langmuir pressure ($P_L$) characterizes the gas pressure when the adsorption gas content reaches 50% of the saturated adsorption amount. Along with the results of Li et al, the relationships between $D_2(N_2)$ and the Langmuir parameters ($V_L$ and $P_L$) are shown in Figure 12A,B, respectively, while the relationship between $D_2(H_2O)$ and the Langmuir parameters are illustrated in Figure 12D,E, respectively. $V_L$ shows a trend of first decreasing and then increasing with increasing $D_2(N_2)$, which may be related to the competition effect between the pore structure (eg, pore throat) and the pore surface irregularity of the coal (eg, SSA). When $D_2(N_2) < 2.7-2.8$, the methane adsorption capacity of coal decreases with increasing fractal dimension. It is concluded that although coal with a larger $D_2(N_2)$ has a greater SSA, the complexity of the pore structure has a more significant impact on the methane adsorption capacity of coal. A more complex pore structure may result in a greater liquid/gas surface tension, which is unfavorable for gas adsorption. When $D_2(N_2) > 2.7-2.8$, the methane adsorption capacity of the coal increases with the enhancement
in the fractal dimension. Moreover, the N₂-BET SSA of coal has will increase to a high value (Figure 9B). The developed pore surface can provide sufficient adsorption sites for gas molecules, which is conducive to gas adsorption in coal. As shown in Figure 12D, with the exception of sample YZG2, $V_L$ exhibits an increasing trend with increasing $D_2(H_2O)$.

With a larger $P_L$, the resistance to methane molecules being adsorbed in the coal pores increases, and the methane desorption efficiency decreases when the CBM pressure is reduced. ⁵⁷ As shown in Figure 12B,E, both $D_2(N_2)$ and $D_2(H_2O)$ have a weak correlation with $P_L$, indicating that $D_2$ has a weak influence on the resistance to gas desorption during CBM extraction.

The equilibrium moisture content (ie, the maximum inherent moisture content) represents the water-holding capacity of coal. ⁵⁸ Combined with the research of Yao et al, ⁷⁰ the
The relationship between $D_2(N_2)$ and $D_2(H_2O)$ and the equilibrium moisture content is shown in Figure 12C,F, respectively. Except for sample YZG2, both $D_2(N_2)$ and $D_2(H_2O)$ are positively correlated with the equilibrium moisture content of coal. The enhancement in $D_2$ indicates the increasing complexity of the pore structure and the surface irregularity of the pores in coal, which can provide more adsorption sites for water molecules. The adsorption of water is associated with not only the pore characteristics of coal but also the number of oxygen-containing functional groups in coal. As shown in Figure 12F, the low-rank coal sample YZG2 has a greater equilibrium moisture content, which is mainly due to the existence of a large amount of oxygen-containing functional groups in the low-rank coal. Conversely, the medium- and high-rank coals have few oxygen-containing functional groups, so their water-holding capacity is mainly influenced by the pore structure of the coal.
Therefore, compared with $D_2(H_2O)$, $D_2(N_2)$ has greater advantages in describing the fractal features of adsorption-pores structures for different rank coals. $D_2(N_2)$ can better characterize the impact of the pore structure on methane adsorption and water vapor adsorption in coal. Moreover, many other scholars have studied the relationship between the fractal dimension and coal parameters, showing consistent results. Therefore, $D_2(N_2)$ can be used as an index to reflect the impact of the adsorption-pores structure on the adsorption properties of coal. In addition, considering the anisotropy and heterogeneity of coal, the fractal dimensions determined by various fractal methods always exhibit significant differences. Hence, it is necessary to further study the validity of the application of various fractal methods for coals.

4 | CONCLUSIONS

In this paper, the adsorption method, including the LN$_2$GA and WVA methods, was selected to study the pore structure and its fractal features and their impact on the adsorption properties of various rank coals. The main conclusions are as follows:

1. Coalification is a key factor that affects the characteristics of adsorption-pores (eg, pore type, SSA, and PSD). Both the SSA and PV exhibit a U-shaped trend with increasing coal rank. Simultaneously, low-rank coal and high-rank anthracite exhibit more open-type pores, which favor gas adsorption and diffusion, while the openness of adsorption-pores in medium-rank coals is relatively poor. Additionally, the PSDs of coal samples from WVA adsorption analysis and LN$_2$GA adsorption analysis are similar, especially for samples LH7 and WLH8.

2. Considering the interaction between the water and oxygen-containing functional groups in coal (especially low-rank coal), $D_2(N_2)$ can more accurately reflect the fractal features of adsorption-pores than $D_2(H_2O)$. Furthermore, strong correlations are observed between $D_2(N_2)$ and the coal pore parameters. $D_2(N_2)$ increases rapidly and then tends to increase more gently with increasing SSA, indicating that the surface irregularity of coal pores also has a significant impact on $D_2(N_2)$, yet this effect weakens with increasing SSA. $D_2(H_2O)$ also has good correlations with the coal pore parameters of the coal samples, with the exception of sample YZG2.

3. The Langmuir volume first decreases and then increases with the increase in $D_2(N_2)$, which may be related to the competition effect of the pore structure and surface irregularity of coal. When $D_2 < 2.7-2.8$, the complexity of the pore structure plays a key role; when $D_2 > 2.7-2.8$, the influence of the SSA is more prominent. The equilibrium moisture content of the coal samples has a positive correlation with both $D_2(N_2)$ and $D_2(H_2O)$, with the exception of sample YZG2, due to its greater water-holding capacity, which may be mainly associated with the existence of a large amount of oxygen-containing functional groups in the low-rank coal.

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