Multifractal Analysis in Characterizing Adsorption Pore Heterogeneity of Middle- and High-Rank Coal Reservoirs

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ABSTRACT: Nanopore heterogeneity has a significant effect on adsorption, desorption, and diffusion processes of coalbed methane. The adsorption pore size distribution heterogeneity was calculated by combining N2 with CO2 adsorption data, and factors affecting multifractal and single-fractal dimensions were studied. The results indicate that pore size distribution of micropores (with pore diameters smaller than 2 nm) and meso−macro-pores (with pore diameters between 2 and 100 nm) in coal samples exhibit typical multifractal behavior. The overall heterogeneity of micropores in high-rank coal samples is higher than that in the middle-rank coal samples. The low-probability measure areas control the overall heterogeneity of pores with diameters of 0.40–1.50 nm. The high-probability measure area heterogeneity and spectral width ratio have a higher linear correlation with coal rank and pore structure parameters than those of low-probability measure areas. Heterogeneity of high-probability measure areas and overall pore size distribution are controlled by pores with diameters of 0.72–0.94 nm. Multifractal parameters of meso−macro-pores have no clear relationship with coal rank. The pore volume of 2–10 nm diameter shows a good linear correlation with heterogeneity of low-probability measure areas, and pores of this diameter range are the key interval that affected pore size distribution heterogeneity. The single-fractal dimension obtained using the Frenkel−Halsey−Hill (FHH) model shows a positive linear correlation with heterogeneity of the low-probability measure areas. It indicates that this parameter can effectively characterize the pore size distribution heterogeneity of low-probability measure areas in meso−macro-pores.

1. INTRODUCTION

Differing from conventional gas reservoirs, coal reservoirs are dominated by fracture and nanoscale pores. The pore-fracture system of coal reservoirs can be divided into seepage pores (pore diameter over 100 nm) and adsorption pores (pore diameter below 100 nm) by the different behaviors of methane and water in each of them during the drainage of coalbed methane (CBM). Seepage pores provide a migration channel for gas and water and control the seepage characteristics of gas and water. Adsorption pores affect the adsorption characteristics of the reservoir through adsorption of methane molecules on the surface and thereby affect gas-bearing characteristics.

Currently, the low-pressure nitrogen gas adsorption test (LPN2 GA) has become an effective method for characterizing adsorption pore structure in porous media among various testing technologies. However, it has limitations with regard to accurate characterization of the micropore structure because of the large molecular diameter (0.36 nm) of N2 and the instrument precision. Due to its smaller molecular diameter (0.33 nm) and stronger adsorption capacity, CO2 can enter pores with diameters ranging from 0.3 to 1.5 nm at a temperature of 273.15 K. Therefore, the CO2 adsorption test (LPCO2 GA) is considered to be the best method for the quantitative characterization of micropores. Comprehensive characterization of adsorption pore structures in coal reservoirs has also been achieved through LPN2 GA and CO2 GA tests.

Adsorption experiment results have been used to characterize quantitatively the complexity and heterogeneity of adsorption pores by fractal theory. Linear fitting of LPN2 GA
data by the Frenkel–Halsey–Hill (FHH) model has become the most widely used method to describe adsorption pore heterogeneity. Many studies indicate that the fractal dimension of a sample is composed of $D_1$ and $D_2$ (with the relative pressures corresponding to $0−0.5$ and $0.5−1$, respectively), and both have physical significance.\textsuperscript{14−18} This physical significance of the fractal dimension parameter is studied in terms of various aspects, e.g., coal rank, tectonic deformation, adsorption capacity, and pore structure parameter. The majority of studies indicate that $D_1$ can be adopted to characterize surface heterogeneity of adsorption pores, and $D_2$ can be used to characterize its pore volume (PV) heterogeneity.\textsuperscript{19−21}

It is noted that the above two parameters only characterize the heterogeneity of pores with diameters ranging from 2 to 100 nm, and cannot characterize micropore heterogeneity. Hence, to make up for the shortcoming of heterogeneity characterization of micropores, Zhang et al.\textsuperscript{12} and Yu et al.\textsuperscript{22} derived a fractal model to describe the fractal characteristics of micropores.

However, the above model can only describe the pore size distribution (PSD) heterogeneity through a single-fractal dimension. For coal reservoirs with strong heterogeneity, the PSD curve generally fluctuates randomly, and self-similarity may differ from pore diameter intervals. Therefore, it is difficult to characterize the PSD heterogeneity with a single-fractal dimension.\textsuperscript{23−26} In contrast to single-fractal dimensions, multiple-fractal dimensions can be separated into many small regions with different singularity exponents. The fine structure of the pore network can be studied by the fractal of different regions. Hence, multiple-fractal dimensions of PSD in sedimentary rocks and soil were studied using image analysis, mercury injection, $N_2$ adsorption, and the nuclear magnetic resonance method.\textsuperscript{27−33}

Multifractal features of tectonically deformed and different bituminous coal reservoirs were analyzed using mercury intrusion curves and NMR technology.\textsuperscript{34−36} Those results indicate that multifractal parameters (e.g., $D_1$ and Hurst index) were strongly related to macropore PSD and seepage porosity of tectonically deformed coal. Zheng et al. used the NMR test curve to calculate multifractal parameters and derived a calculation model for the transverse relaxation time ($T_2$) cutoff value.\textsuperscript{37}

However, based on the experimental pore range and instrument accuracy, multifractal research on coal reservoirs focuses on the fractal characteristics of seepage pores, but the separate description of adsorption pores is rarely studied. The comparison between single-fractal and multifractal parameters of pore diameters also needs further investigation.

This paper will focus on the analysis of the multifractal characteristics of micropores (below 2 nm) and meso–macropores (MMPs) (2−100 nm) of middle- and high-rank coal samples based on the LPN$_2$ and CO$_2$ GA data, and investigate multifractal parameters determining the PSD of adsorption pores. Single-fractal and multifractal analyses of pore data of all coal samples will be compared. The research aims to provide a theoretical basis for the quantitative evaluation of PSD heterogeneity of coal reservoirs.

Figure 1. Distribution of the sampling and tectonic sketch map of the study area.

Table 1. Summary of Sample Information\textsuperscript{a}

| sample name | sampling area | coalbed number | $R_{\text{max}}$ (%) | $M_{\text{ad}}$ | $A_{\text{ad}}$ | $V_{\text{daf}}$ | $\text{FC}_{\text{ad}}$ |
|-------------|---------------|----------------|----------------------|----------------|----------------|---------------|----------------|
| T1          | Tucheng       | 12             | 0.93                 | 2.64           | 4.48           | 27.59         | 88.58         |
| T2          | 9             | 0.95           | 1.48                 | 5.82           | 27.16          | 68.60         |
| T3          | 8 + 9         | 1.32           | 0.88                 | 25.04          | 27.71          | 54.19         |
| T4          | 12            | 1.45           | 1.34                 | 10.54          | 29.76          | 62.31         |
| T5          | 7             | 2.06           | 1.39                 | 13.43          | 14.93          | 77.59         |
| L1          | Laochang      | 3              | 2.31                 | 1.52           | 11.41          | 8.64          | 73.64         |
| L2          | 7             | 2.46           | 1.06                 | 11.38          | 12.31          | 77.71         |
| L3          | 9             | 2.7            | 1.86                 | 14.09          | 7.83           | 79.18         |
| L4          | 3             | 2.76           | 2.33                 | 8.57           | 7.60           | 84.48         |
| L5          | 3             | 2.9            | 1.06                 | 8.48           | 31.88          | 62.34         |
| L6          | 13            | 3.01           | 1.29                 | 9.1            | 11.71          | 80.25         |
| L7          | 8             | 3.2            | 2.44                 | 9.89           | 7.13           | 83.68         |

\textsuperscript{a}$M_{\text{ad}}$ is the moisture, air-drying basis; $A_{\text{ad}}$ is the ash yield, air-drying basis; $V_{\text{daf}}$ is the volatile, dry ash-free basis; and $\text{FC}_{\text{ad}}$ is the fixed carbon content, air-drying basis.
2. MATERIALS AND METHODS

2.1. Sampling. The western Guizhou and eastern Yunnan areas are in the Yangtze Block and cover an area of about 2.58 × 10^4 km^2 (Figure 1). CBM resource is about (2.20−2.75) × 10^{12} m^3. The coal-bearing strata are the late Permian Longtan Formation and Changxing Formation, which belong to a delta–tidal–lagoon sedimentary system. These sampling areas were subject to the Indosinian–Yanshan–Himalayan tectonic movements. Faults and folds generated at multiple periods control the distribution of CBM resources.\cite{40,41} Coal maturity in this region varies from bituminous to anthracite during the Yanshanian period.\cite{40,41}

Samples from two areas are selected for comparison. Twelve (15 × 15 × 15 cm^3) underground fresh coal samples were selected for this study, of which six were from the Laochang area (five coal mines) and six were from the Tucheng area (seven coal mines). The basic parameters of the coal samples are shown in Table 1.\cite{12} According to the value of R_{0, max} and the volatile content of all of the samples, they were classified into two groups, that is, middle (sample T1−T5)- and high (sample L1−L7)-rank coal sample groups.

2.2. Experimental Method. The samples collected were placed in a sample tank, which was quickly transported to the laboratory for pretest processing and a series of tests according to the standard GB/T 19222-2003. Macroscopic coal petrography was performed according to the Chinese national standard GB/T 18023-2000. Microscopic maceral analysis was performed on 3 × 3 cm^2 polished slabs with a total of 500 observational points (based on GB/T 6948-1998). Proximate analysis was conducted on all samples following GB/T 212-2001.

Fresh block samples collected from underground are ground to 40−60 mesh, and an LPN2 GA experiment is performed at 77 K using a Tristar II 3020 Quanta Chrome Autosorb-I physical adsorption instrument. This test can analyze the PSD of meso--macro-pores. The Barrett–Joyner–Halenda (BJH) model is used to study the PSD and specific surface area (SSA). An ASAP2020 specific surface area and pore analyzer is employed to perform LP CO2 GA tests at 273.1 K. The density functional theory (DFT) model was used to study the micropore PSD.

2.3. Fractal Theory. The FHH model is used to describe the single-fractal dimensions of meso–macro-pores using LPN2 GA results.\cite{14,22−44}

\[
\ln \left( \frac{V}{V_m} \right) = C + A \left[ \ln \left( \frac{P}{P_0} \right) \right] \\
D = 3A + 3
\]  

where \( P \) is the relative pressure, MPa, \( P_0 \) is the saturation pressure of N_2, MPa, \( V \) is the adsorption volume of nitrogen at equilibrium pressure \( P \), cm^3 g^{-1}, \( V_m \) is the monolayer adsorption volume, cm^3 g^{-1}, C is constant, and A is the power-law exponent depending on the fractal dimension (D) and adsorption mechanism.

The box-counting method is adopted to study the multifractal dimensions of adsorption data using LPN2 and CO2 GA technologies.\cite{29−31} When analyzing the volume probability of PSD in the interval [A, B], the scale and measure value need to be determined. The scale and resolution are expressed as:

\[
e = 2^k L
\]

\[
\Delta n_k = \frac{\Delta n_{min} - \Delta n_{min}}{\sum_{i=1}^{N} (\Delta n_i - \Delta n_{min})}
\]

where \( e \) is the scale size, \( k \) is a positive integer, and \( L \) is the interval length.

For adsorption data, relative pressure is divided into several boxes of equal lengths for gas adsorption and the box size is represented by scale size. The analysis interval of LP N2 GA ranges from 0 to 0.99, where the interval of LP CO2 GA is 0.01−0.03. Therefore, the corresponding scale size is different.\cite{30,43}

In the case of different scales, the distribution probability of pore volume in the interval [A, B] satisfies:

\[
p_i(e) \sim e^{-a_i}
\]

where \( p_i(e) \) is the mass probability function of the i-th box, and is used to analyze the distribution of total gas adsorption in each box, and \( a_i \) is the singularity index.

The value of \( a_i \) characterizes the singularity strength in the i-th box, and a higher value indicates higher smoothness or regularity. Conversely, a smaller value indicates a greater change in degree or stronger irregularity. \( a_i \) is related to its location, reflecting the probability of the area.

After obtaining the singularity index \( a_i \), the research object is divided into a series of subsets, and therefore, the small units in each subset have the same singularity index. Then, the number of units in this subset is measured and the relationship between the number and the scale is defined as:

\[
N_i(e) \sim e^{-f(a_i)} \rightarrow 0
\]

where \( N_i(e) \) is the number of subsets with the same singular index and \( f(a) \) is a multifractal spectrum, which is the fractal dimension of a subset with the same singularity index.

The singularity indices \( a \) and \( f(a) \) can be obtained by eqs 7 and 8, and can be expressed as:

\[
a(q) \propto \sum_{i=1}^{N(e)} [u_i(q, e) \log \epsilon]
\]

\[
f(a) \propto \frac{\sum_{i=1}^{N(e)} [u_i(q, e) \log u_i(q, e)]}{\log \epsilon}
\]

\[
u_i(q, e) = \frac{p^q_i(e)}{\sum_{i=1}^{N(e)} p^q_i(e)}
\]

where \( q \) is the order of the statistical matrix.

When the value of \( q \) is much larger than 1, the information of higher probability measure areas (HPMAs) is amplified; when the value of \( q \) is much lower than 1, the information of lower probability measure areas (LPMAs) is amplified. In this study, \( q \) lies within [−10, 10] with a step of 1; \( a \) and \( f(a) \) can be acquired by linear regression of the above equations.

The plot with \( a \) as the horizontal coordinates and \( f(a) \) as the vertical coordinates is called the multifractal singularity spectrum, which is used to investigate the nonuniform distribution of gas adsorption on the fractal structure. If the
research object is multifractal, f(x) generally presents a unimodal curve.

The parameters of f(x) include amax, amax, admin, and A. The variable amax is the singularity index of the minimum q, which can be used to characterize the heterogeneity of the lowest probability measure areas. Similarly, amax is the singularity index of the maximum q, which can be used to characterize the heterogeneity of the highest probability measure areas. Furthermore, ad min is the singularity index corresponding to the peak of the singularity spectrum. Larger width of the right branch (ad max - ad min) indicates predominant heterogeneity in the LPMA, whereas larger width of the left branch (ad min - a max) indicates predominant heterogeneity in the HPMA. The symmetry of the singularity spectrum can be expressed as A = (ad max - ad min)/(ad min - amax). A left-skewed shape (A is lower than 1) indicates that the measured value is affected by large fluctuations, whereas a right-skewed shape (A is lower than 1) indicates that the measured value relies on small fluctuations. Δf = f10 - f10 represents the ratio of the maximum number and minimum number of elements in the relevant physical parameter subset.13,35,37,51

Besides the curve of x=f(x), another set q=D(q) is introduced from the perspective of information theory and is called the generalized fractal dimension.

For multifractals, the denominator in eq 2−9 is the partition function, and it is written as

\[ x(q, \varepsilon) = \sum_{i=1}^{N(\varepsilon)} P_i^q(\varepsilon) \sim \varepsilon^{\tau(q)} \]  

(10)

where \( x(q, \varepsilon) \) is a probability distribution function. Moreover, \( \tau(q) \) is the mass scaling function of order q. The function \( \tau(q) \) can be defined as

\[ \tau(q) = \lim_{\varepsilon \to 0} \frac{\ln \sum_i P_i^q(\varepsilon)}{\ln(1/\varepsilon)} \]  

(11)

Then, generalized fractal dimension spectrum D(q) can be determined by

\[ D_q = \frac{1}{q - 1} \lim_{\varepsilon \to 0} \frac{\ln x(q, \varepsilon)}{\ln \varepsilon} = \frac{\tau(q)}{q - 1} \]  

(12)

For q = 0, 1, and 2, \( D_q \) can be defined as the capacity dimension, information dimension, and correlation dimension, respectively. For q = 1, \( D_1 \) can be derived from

\[ D_1 = \frac{1}{q - 1} \lim_{\varepsilon \to 0} \frac{\ln \sum_i P_i^q(\varepsilon)}{\ln(1/\varepsilon)} \]  

(13)

The parameter \( D_q \) includes Dmin, Dmax, D0, D1, D2, D0 - D1, D1 - D2, D1-10, D0 - D10, and D10 - D0. \( D_q \) is a monotonically decreasing function with a sigmoidal shape. A narrower \( D_q \) distribution corresponds to weaker heterogeneity of the measures contained in the multifractal set. Dmin is influenced by the lowest probability measure areas, whereas Dmax is influenced by the highest probability measure areas. \( D_1 \) is the information dimension and characterizes the degree of disorder in the PSD. A value of \( D_1 \) of 1 represents a uniform pore size distribution. \( D_2 \) is the correlation dimension and characterizes the association between the measures contained in the multifractal set. D0 - D10 and D10 - D0 are the amplitudes of the right and left branches of \( D_q \), which represents the high- and low-probability measure area heterogeneities, respectively.

**Figure 2.** Generalized fractal dimension of micropore size distribution ((a) relationship between \( \log[a(q)] \) and \( \log(\varepsilon) \), (b) relationship between \( i(q) \) and \( q \), (c) relationship between \( D(q) \) and \( q \) in middle-rank coal samples, (d) relationship between \( D(q) \) and \( q \) in high-rank coal samples.)
3. RESULTS AND DISCUSSION

3.1. Multifractal Evolution of Micropore Size Distribution.

3.1.1. Generalized Fractal Variation.

Using the CO2 adsorption data of a representative sample T1, a double-logarithmic plot of the partition function $u_q(\epsilon, \epsilon)$ and the scale size $\epsilon$ was studied by eqs 2−10 (Figure 2). Figure 2a shows that $\log[u_q(\epsilon, \epsilon)]$ and $\log(\epsilon)$ exhibit a clear linear relationship, and Figure 2b illustrates that $i_q(\epsilon)$ strictly monotonically increases with the increase of $q$, which indicates that the PSD of micropores has multiple-fractal behaviors. For a value of $q$ lower than 0, there is a negative correlation between $\log[u_q(\epsilon, \epsilon)]$ and $\log(\epsilon)$, whereas they have a positive correlation for $q$ larger than 0. This indicates that the quality index function varies from negative to positive as the statistical matrix varies from small to large values. Meanwhile, the fitting line gradually varies from sparse to dense, indicating that the PSD range of micropores is small.

Multifractal parameters of micropores were calculated by combining eqs 2−11 and eqs 2−12. Figure 2c,d shows that $q$ versus $D(q)$ spectra of all samples have a distinct reverse-shaped curve, which further confirms that the PSD is multifractal (Figure 2). This spectral curve can characterize the PSD complexity at different $q$ values. The generalized spectral width of the high-rank coal sample group is larger than that of the middle-rank coal sample group (Figure 2c,d), indicating that the former has higher heterogeneity.

Table 2. Summary of Generalized Fractal Parameters of Micropores

| samples | $D_{10}$ | $D_{-10}$ | $D_0$ | $D_1$ | $D_2$ | $D_0 - D_1$ | $D_2 - D_0$ | $D_1 - D_0$ | $D_0 - D_{-10}$ |
|---------|----------|-----------|-------|-------|-------|-------------|--------------|------------|-----------------|
| T1      | 0.70     | 1.59      | 1     | 0.90  | 0.84  | 0.16        | 0.59         | 0.30       | 0.89            |
| T2      | 0.67     | 1.70      | 1     | 0.89  | 0.82  | 0.18        | 0.70         | 0.33       | 1.03            |
| T3      | 0.70     | 1.63      | 1     | 0.91  | 0.85  | 0.15        | 0.63         | 0.30       | 0.93            |
| T4      | 0.71     | 1.32      | 1     | 0.93  | 0.87  | 0.13        | 0.32         | 0.29       | 0.60            |
| L1      | 0.77     | 2.21      | 1     | 0.91  | 0.88  | 0.12        | 1.21         | 0.23       | 1.44            |
| T5      | 0.82     | 1.73      | 1     | 0.94  | 0.91  | 0.09        | 0.73         | 0.18       | 0.91            |
| L2      | 0.80     | 1.70      | 1     | 0.93  | 0.90  | 0.10        | 0.70         | 0.20       | 0.90            |
| L3      | 0.79     | 2.04      | 1     | 0.93  | 0.90  | 0.10        | 1.04         | 0.21       | 1.25            |
| L4      | 0.90     | 1.84      | 1     | 0.95  | 0.95  | 0.05        | 0.84         | 0.10       | 0.94            |
| L5      | 0.84     | 1.70      | 1     | 0.95  | 0.93  | 0.07        | 0.70         | 0.16       | 0.86            |
| L6      | 0.88     | 2.05      | 1     | 0.95  | 0.95  | 0.05        | 1.05         | 0.12       | 1.17            |
| L7      | 0.88     | 1.86      | 1     | 0.95  | 0.94  | 0.06        | 0.86         | 0.12       | 0.98            |

Figure 3. PSD of micropores in all of the coal samples ((a) relationship between incremented pore volume and diameter, (b) relationship between incremental pore volume and pore diameter).

Figure 4. Multifractal singularity spectrum of micropore size distribution ((a) relationship between $f(a)$ and $a$ in middle-ranking coal samples, (b) relationship between $f(a)$ and $a$ in high-ranking coal samples).

3. RESULTS AND DISCUSSION
micropores. The 1.06 average value of the high-rank coal sample group is greater than that of the middle-rank coal sample group, indicating that the micropore size distribution in the former is more heterogeneous. Moreover, the $D_{-10} - D_{10}$ variation of samples in the same rank is distinct, indicating that $D_{-10} - D_{10}$ may also be affected by ash yield, moisture and volatile content, etc. Amongst the middle-rank coal sample group, $D_{-10} - D_{0}$ shows a larger variation in comparison to $D_{0} - D_{10}$ (with a maximum of 0.03), indicating that the heterogeneity of these samples is controlled by the LPMA (Figure 2c).

$D_{-10} - D_{0}$ and $D_{0} - D_{10}$ both show distinct differences in the high-rank coal sample group, indicating that the pore volume variation in each pore diameter range is remarkable. The 0.17 variation value of $D_{0} - D_{10}$ in the high-rank coal sample group is smaller than that of the middle-rank coal sample group, which indicates that the heterogeneity of HPMA in the former exhibits a larger variation than that in the latter. This result is caused by the trimodal PSD of micropores in the middle-rank coal sample group in comparison with the bimodal PSD in the high-rank coal sample group (the PSDs of micropores in all of the coal samples are shown in Figure 3(2)). The HPMA in the middle-rank coal sample group have a larger range, resulting in a relatively larger variation in heterogeneity.

3.1.2. Multifractal Singularity Variation. The singularity spectrum of micropore size distribution was calculated using eqs 2–7 and 2–8. Figure 4 shows that the $a$ versus $f(a)$ spectra of all samples have a clear parabolic-shaped distribution. The singular spectral width of the high-rank coal sample group is larger than that of the middle-rank coal sample group, and the generalized spectral width of the right branch is larger, indicating that the heterogeneity of the micropore size distribution in the former is higher. According to Section 2.3, the singular spectrum fractal parameters corresponding to each sample are listed in Table 3.

The average value of $a_{-10}$ for the middle-rank coal sample group is 1.70, which is less than that of 2.01 for the high-rank coal sample group (Table 3). This shows that there is a minimum pore volume. The 0.64 average $a_{10}$ value of the middle-rank coal sample group is smaller than the 0.80 average value of the high-rank coal sample group, which is in good agreement with Figure 2b. The singularity index $a_{0}$ represents the degree of uniformity of the PSD. The results show that the average value of both middle- and high-rank coal samples is 1.12. However, this value varies obviously amongst samples, indicating that it is affected by other factors.

The spectral width $\Delta a = a_{-10} - a_{10}$ can characterize the complexity of the PSD, and a higher value represents larger differences within the multifractal system. Table 3 shows that the 1.28 average value of the high-rank coal sample group is larger than that of the middle-rank coal rank samples, indicating that the heterogeneity of micropores in the former is higher. However, $a_{-10}$ and $a_{10}$ variations are slightly different. In one sample, except for sample T4, $A$ is greater than 1, which indicates that the heterogeneity variation of the LPMA in all samples is stronger than that of HPMA. This result is consistent with the results shown in Table 2.

Among different samples, the average value (0.57) of $a_{-10} - a_{0}$ in the middle-rank coal sample group is smaller than the average value (0.95) in the high-rank coal sample group, whereas the average value (0.48) of $a_{0} - a_{10}$ is larger than that of the latter. This indicates that the pore size distribution variation of LPMA in the high-rank coal sample group is distinct. Except for samples T1 and T4, the multifractal singularity spectrum of each sample is left-hook-shaped (Figure 4), indicating that the number of large probability subsets in the micropores is dominant.

| Sample | $a_{-10}$ | $a_{10}$ | $a_{0}$ | $a_{0} - a_{10}$ | $a_{-10} - a_{0}$ | $a_{10} - a_{-10}$ | $A$ | $f_{10} - f_{-10}$ |
|--------|-----------|---------|-------|----------------|-----------------|---------------------|-----|------------------|
| T1     | 1.72      | 0.65    | 1.13  | 0.49           | 0.58            | 1.07                | 1.20 | −0.10           |
| T2     | 1.86      | 0.62    | 1.15  | 0.54           | 0.71            | 1.25                | 1.32 | 0.03            |
| T3     | 1.80      | 0.65    | 1.12  | 0.47           | 0.68            | 1.15                | 1.45 | 0.16            |
| T4     | 1.40      | 0.65    | 1.08  | 0.32           | 0.32            | 0.74                | 0.76 | −0.35           |
| T5     | 2.43      | 0.73    | 1.20  | 0.47           | 1.24            | 1.71                | 2.66 | 0.36            |
| L1     | 1.90      | 0.79    | 1.10  | 0.31           | 0.80            | 1.11                | 2.54 | 0.49            |
| L2     | 1.86      | 0.76    | 1.13  | 0.36           | 0.73            | 1.09                | 2.03 | 0.35            |
| L3     | 2.25      | 0.76    | 1.15  | 0.39           | 1.10            | 1.49                | 2.80 | 0.45            |
| L4     | 2.02      | 0.85    | 1.10  | 0.25           | 0.92            | 1.17                | 3.71 | 0.43            |
| L5     | 1.86      | 0.81    | 1.10  | 0.29           | 0.77            | 1.06                | 2.63 | 0.49            |
| L6     | 2.25      | 0.83    | 1.13  | 0.30           | 1.12            | 1.42                | 3.72 | 0.41            |
| L7     | 2.05      | 0.84    | 1.10  | 0.26           | 0.94            | 1.2                 | 3.59 | 0.46            |
It is known that the generalized fractal parameters and the singular fractal parameters are clearly related. Tables 2 and 3 also demonstrate that each parameter exhibits a good linear relationship. To avoid information duplication, the singular spectrum parameters will be analyzed in the next part.

Correlation analysis was performed on the singular fractal spectrum parameters in Table 3 using SPSS software; then, correlation coefficients among those parameters were calculated (Table 4). The results indicate that there is a good correlation among some parameters. A -10 has a good positive correlation with A -10 - A 10 and A 0 and A -10 - A 10 (Figure 5a). A 10 has a positive correlation with A 0 - A 10, whereas there is no clear relationship with A -10 - A 10 (Figure 5b).

Figure 5c shows that singularity index A 0 presents a positive linear correlation with A -10 - A 10, indicating that this value can be utilized to characterize the uniformity of the PSD. A higher value indicates that the local distribution has a larger fluctuation and narrower distribution interval, and the occurrence of local agglomeration of pores. The linear positive correlation between A -10 - A 0 and A -10 - A 10 also demonstrates that the interval with low-probability density in these samples dominates the spatial distribution of the PSD (Figure 5d).

Therefore, four multifractal parameters A 0 - A 10, A -10 - A 10, A -10 - A 0, and A are selected to investigate the factors affecting multifractal parameters.

3.1.3. Factors Affecting Multifractal Parameters. In this section, the factors that affect multifractal parameters are discussed in terms of three aspects, including coal rank, pore parameter, and proximate analysis, e.g., moisture, ash, volatile matter, etc.

3.1.3.1. Coal Rank. R o,max was used to analyze the effect of coal rank on multifractal parameters (Figure 6). A 0 - A 10 shows a weak negative correlation with R o,max (Figure 6a), indicating that the heterogeneity variation of the HPMA gradually decreases with higher R o,max. There is no clear linear relationship between A -10 - A 0 and A 0 - A 10 - A 10, and A are selected to investigate the factors affecting multifractal parameters.
in the former are more heterogeneous in the LPMA. It is related to the distribution variation of pores with diameters of 0.40–0.94 nm (Figure 3). An increase in coal rank leads to a decrease in peak 3 in the PSD curves, an increase in peak 1, and change from trimodal to bimodal distribution states (Figure 3). Samples with a higher rank have a greater number of smaller pores, so they have smaller $a_{0}$–$a_{10}$, and an increase of the pore diameter range in the LPMA causes a larger variation of the LPMA heterogeneity.

The value of $A$ increases with the increase of $R_{o,max}$ and the value of $A$ in all samples exceeds 1.0 (Figure 6b), indicating that the LPMA controls the heterogeneity of the PSD. This relates to a decrease of $a_{0}$–$a_{10}$ and an increase of $a_{-10}$–$a_{0}$. However, $a_{-10}$–$a_{10}$ which characterizes the overall distribution of micropores, has no significant correlation with $R_{o,max}$ which relates to their regular variation in the right-half spectral width. The above results reveal that the variations of $a_{-10}$–$a_{0}$ and $a_{-10}$–$a_{10}$ are not only affected by $R_{o,max}$ but are also influenced by other factors.

3.1.3.2. Pore Structure Parameters. Pore parameters of all samples were obtained using CO2 adsorption data (Table 5). The results show that the pore parameters of the middle-versus high-rank coal sample groups are different. The relationships between the pore structure parameter and multifractal parameters were analyzed for average pore diameter, pore volume (PV), specific surface area (SSA), and incremental pore volume percentage.

Figure 7a shows that $a_{0}$–$a_{10}$ linearly increases with the average pore diameter. Samples with larger average pore diameters belong to middle-rank coal (Figure 7b); the HPMA interval in this type is 0.42–0.92 nm (Figure 3a). In contrast, samples with smaller average pore diameters belong to high-rank coal; the HPMA interval of the samples in this type is 0.42–0.80 nm (Figure 3b). The high pore size interval of the

### Table 5. PSD Parameters of Micropores

| sample | average pore diameter (nm) | total pore volume (cm$^3$ g$^{-1}$) | surface area (m$^2$ g$^{-1}$) | $0.40$–$0.72$ | $0.72$–$0.94$ | $0.94$–$1.50$ |
|--------|---------------------------|-------------------------------------|-------------------------------|----------------|----------------|----------------|
| T1     | 0.69                      | 0.021                               | 56.73                         | 0.51           | 0.26           | 0.23           |
| T2     | 0.75                      | 0.023                               | 60.60                         | 0.47           | 0.30           | 0.23           |
| T3     | 0.72                      | 0.027                               | 72.89                         | 0.50           | 0.27           | 0.23           |
| T4     | 0.70                      | 0.023                               | 65.90                         | 0.55           | 0.21           | 0.24           |
| T5     | 0.70                      | 0.05                                | 138.96                        | 0.57           | 0.19           | 0.24           |
| L1     | 0.62                      | 0.054                               | 158.63                        | 0.63           | 0.16           | 0.21           |
| L2     | 0.63                      | 0.048                               | 138.77                        | 0.62           | 0.19           | 0.19           |
| L3     | 0.63                      | 0.057                               | 164.80                        | 0.62           | 0.17           | 0.21           |
| L4     | 0.50                      | 0.053                               | 165.08                        | 0.72           | 0.10           | 0.18           |
| L5     | 0.60                      | 0.068                               | 197.63                        | 0.63           | 0.14           | 0.23           |
| L6     | 0.52                      | 0.056                               | 182.92                        | 0.82           | 0.10           | 0.08           |
| L7     | 0.42                      | 0.06                                | 186.15                        | 0.70           | 0.12           | 0.18           |
former is larger than that of the latter, resulting in a significant difference in $a_0 - a_{10}$. Similarly, an increase in the average pore diameter leads to a linear increase in $a_0 - a_{10}$ resulting in a gradual decrease of the value of $A$ (Figure 7c).

PV and SSA of micropores both show a linear relationship with multifractal parameters $a_0 - a_{10}$ and $A$ (Figure 8). The HPMA heterogeneity decreases with the increase of PV and SSA, whereas LPMA heterogeneity increases, due to the increase in the number of micropores. With the increase of $R_{o,max}$ the pore diameter becomes smaller, which results in an increase of the SSA, the distribution interval of HPMA decreases, and that of LPMA increases. The correlation of the SSA to $a_0 - a_{10}$ and $A$ is higher than that of the total PV (Figure 8), which shows that the SSA of micropores is more sensitive to variations of pore size.

However, the specific range of the HPMA characterized by this parameter has not been discussed in previous studies. Three peaks have been identified here in the PSD curves of micropores, which are defined as peak 1, peak 2, and peak 3 (corresponding to 0.40–0.72, 0.72–0.94, and 0.94–1.50 nm, respectively). Figure 9 shows that pore volume percentages of pores with diameters of 0.40–0.72 and 0.72–0.94 nm both show a linear relationship with $a_0 - a_{10}$ and $A$. The correlation between $a_0 - a_{10}$ and pores with a diameter in the range of 0.72–0.94 nm is stronger than pores with a diameter of 0.40–0.72 nm, indicating that the porosity variation in peak 3 mainly controlled the variation of $a_0 - a_{10}$ (Figure 9c,d).

There is no clear relationship between PV of pores with diameters of 0.94–1.50 nm and multifractal parameters (Figure 9e,f). The PV percentage of samples in the same rank in this pore range has only small differences (Table 5), which results in small variations of $a_{0.94} - a_{1.50}$. A higher $R_{o,max}$ leads to a lower PV percentage of pores with diameters of 0.40–0.72 nm, inducing increased LPMA heterogeneity.

3.1.3.3. Proximate Analysis Parameters. The correlation between the multifractal parameters and volatile and ash content was studied (Figure 10). The volatile content has a weak negative correlation with LPMA heterogeneity, indicating that these parameters are smaller for higher volatile content in a sample of the same coal rank (Figure 10a). The volatile contents of sample T4 and sample L5 in the middle-rank coal sample group are higher than those of other samples of the same coal rank. The fixed carbon content is the smallest, resulting in underdevelopment of micropores below 0.94 nm, and the PSD is relatively uniform. Therefore, this value of $a_{0.94} - a_0$ is the smallest. Contrary to volatile components, ash yield and other components have no significant effect on multifractal parameters (Figure 10c,d).

3.2. Multifractal Evolution of Meso–Macro-Pore Size Distribution. 3.2.1. Generalized Fractal Variation. Using the LPN$_2$ GA of a representative sample T1, a double-logarithmic plot of the partition function $x(q,\varepsilon)$ and scale size $\varepsilon$ was obtained using eqs 2–10 (Figure 11). The results illustrate that $\log[x(q,\varepsilon)]$ and $\log(\varepsilon)$ show a clear linear relationship, indicating that the PSD obtained from the N$_2$ adsorption has multifractal characteristics.

The multifractal singularity spectrum of MMP distribution in each sample was obtained (Figure 12), and the $a$ versus $f(a)$ spectra of all samples have a clear parabolic-shaped distribution. The singularity spectrum can be classified into two types, i.e., left-hooked and right-hooked. The singularity spectra of the middle-rank coal sample group are left-hook-shaped with larger right-half spectral width, and the LPMAs control the overall heterogeneity of meso–macro-pores (Figure 12a). The singularity spectra of the high-rank coal sample group are different, and can be classified into two types according to their spectral shapes: (i) left-hook-shaped, including samples L1, L2, and L7 (Figure 12b), and (ii) right-hook-shaped; samples L1, L3, L4, and L6 all belong to
this type (Figure 12c). Coal rank is not the main factor affecting the multifractal characteristics of meso-macro-pores (Figure 12b,c).

According to Section 2.3, fractal parameters of the singularity spectrum corresponding to each sample were calculated and are listed in Table 6.

Table 6 shows that there are significant differences in $a_{-10}$ amongst the samples. The $a_{-10}$ values of samples L1, L2, and L7 are the largest, indicating that the LPMAs in these samples have the widest range. Contrary to $a_{-10}$, $a_{10}$ of each sample shows a smaller difference of 0.30. The PSDs of MMP in all samples are shown in Figure 13. The PVs of 20–80 nm are relatively higher, and each pore size range is relatively uniform based on the PSDs. Comparing the singularity index $a_0$ of different samples, the difference between middle- and high-rank coal is slight, which suggests that coal rank has no significant effect on the PSD.

$\Delta a$ of the high-rank coal sample groups L1, L2, and L7 is up to 1.92, indicating that PSD of this type has the highest heterogeneity. It is worth noting that the $\Delta a$ of other samples in the same coal rank is only 0.30, which indicates that PSD of these samples is relatively uniform. Comparing the left and right spectral widths, the differences of $a_0 - a_{10}$ between samples L2, L1, and L7 are small, whereas $a_{-10} - a_{0}$ shows a large difference, indicating that the development of LPMAs directly affects the overall heterogeneity of the PSD. For other high-rank coal samples, $a_{-10} - a_{10}$ differences are small, whereas the differences of $a_0 - a_{10}$ are large, indicating that variations of HPMA have a larger effect on the overall heterogeneity of PSD.

3.2.2. Factors Affecting Multifractal Parameters. A correlation analysis was performed on the singularity fractal spectrum parameters in Table 6 using SPSS software, and the results are listed in Table 7. There is a good correlation between some parameters. The correlation of $a_{-10} - a_{10}$ with $a_{-10} - a_{0}$ of the high-rank coal sample groups L1, L2, and L7 is up to 1.92, indicating that PSD of this type has the highest heterogeneity.
other multifractal parameters in N₂ adsorption was significantly higher than that in CO₂ adsorption (Table 4). However, the determination coefficient between \( a_{-10} - a_{10} \) and \( a_{0} - a_{10} \) is only 0.44, which indicates that development of LPMA has a weak effect on the PSD heterogeneity. The four multifractal parameters \( a_{0} - a_{10}, a_{-10} - a_{10}, a_{-10} - a_{10}, \) and \( A \) are discussed in relation to the coal rank, pore parameter, and proximate components.

3.2.2.1. Coal Rank. The effect of coal rank on multifractal parameters is analyzed through \( R_{\text{max}} \) (Figure 14). There is no clear linear relationship between fractal parameters and \( R_{\text{max}} \) (Figure 14a), which is different from that of the micropores (Figure 6). In contrast to micropores, the pore structure of meso–macro-pores is not only controlled by coal rank but also affected by other parameters, e.g., moisture and ash yield, which results in the lack of a significant linear relationship of \( R_{\text{max}} \) with PV and SSA (Figure 14c). The \( R_{\text{max}} \) of all samples in this paper has a wide range; the MMP volume and surface area first decrease with the increase of coal rank and abruptly increase when the value of \( R_{\text{max}} \) is larger than 2.50% because of the fifth coalification jump.52

3.2.2.2. Pore Structure Parameter. Multifractal parameters are controlled by pore structure parameters, and the pore diameter range characterization by different fractal parameters still needs to be discussed. The relationship between pore parameters and multifractal parameters was analyzed using pore volume and incremented pore volume percentage. There is no clear linear relationship between total PV and each fractal parameter, although the samples with lower pore volume correspond to higher \( a_{-10} - a_{10} \) and \( a_{-10} - a_{10} \) (Figure 15a). Except for samples L1, L2, and L7, differences in the multiple parameters of most samples are small (Table 6), which also results in poor correlation.
Meso–macro-pores can be divided into pores with diameters in the range of $2^{-10}$, $10^{-10}$–$50$, and $50^{-10}$–$100$ nm using PSD curves (Figure 13). The PV of pores with diameters of $2^{-10}$ nm has a good linear correlation with $a^{-10}$ and $a^{-10}$–$a_0$ (Figure 15c,d). For a PV percentage in this range of less than $10\%$, the heterogeneity of LPMA significantly decreases, resulting in an increase in the overall heterogeneity of the PSD (Figure 13).

Table 6. Summary of the MMP Singularity Spectrum

| sample | $a_{-10}$ | $a_{10}$ | $a_0$ | $a_{-10} - a_{10}$ | $a_{10} - a_0$ | $a_{-10} - a_{10}$ | $A$ | $f_{10} - f_{-10}$ | $D_{v1}$ | $D_{v2}$ |
|--------|-----------|--------|------|----------------|-------------|----------------|----|----------------|--------|--------|
| T1     | 1.18      | 0.96   | 1.01 | 0.05           | 0.17        | 0.22           | 3.27 | 0.53           | 2.49   | 1.18   |
| T2     | 1.20      | 0.90   | 1.02 | 0.12           | 0.18        | 0.30           | 1.55 | 0.39           | 2.53   | 2.24   |
| T5     | 1.24      | 0.66   | 1.04 | 0.38           | 0.20        | 0.58           | 0.52 | -0.51          | 2.61   | 2.03   |
| L1     | 2.14      | 0.74   | 1.13 | 0.40           | 1.01        | 1.40           | 2.54 | 0.42           | 2.37   | 2.88   |
| L2     | 2.61      | 0.79   | 1.14 | 0.35           | 1.47        | 1.83           | 4.18 | 0.88           | 2.31   | 2.65   |
| L3     | 1.17      | 0.90   | 1.02 | 0.12           | 0.15        | 0.27           | 1.33 | 0.06           | 2.53   | 2.62   |
| L4     | 1.15      | 0.89   | 1.01 | 0.13           | 0.13        | 0.26           | 1.05 | 0.01           | 2.54   | 2.65   |
| L5     | 1.20      | 0.93   | 1.01 | 0.08           | 0.19        | 0.27           | 2.45 | 0.46           | 2.5    | 2.45   |
| L6     | 1.19      | 0.77   | 1.03 | 0.25           | 0.17        | 0.42           | 0.66 | -0.15          | 2.61   | 2.33   |
| L7     | 3.24      | 0.72   | 1.22 | 0.50           | 2.02        | 2.52           | 4.02 | 0.57           | 2.12   | 2.79   |

Figure 12. Multifractal singularity spectrum of meso–macro-pores ((a) relationship between $f(a)$ and $a$ in samples T1 and T2, (b) relationship between $f(a)$ and $a$ in samples L2, L1, and L7, (c) relationship between $f(a)$ and $a$ in samples L1, L3, L4, and L6).

Figure 13. Pore size distribution of MMP in all samples ((a) relationship between incremented pore volume and diameter in samples T1, T2, T4, L1, L2, and L7, (b) relationship between incremented pore volume and pore diameter in samples T3, T5, L4, L5, and L7).

Meso–macro-pores can be divided into pores with diameters in the range of $2^{-10}$, $10^{-10}$–$50$, and $50^{-10}$–$100$ nm using PSD curves (Figure 13). The PV of pores with diameters of $2^{-10}$ nm has a good linear correlation with $a_{-10} - a_0$ and $a_{-10} - a_{10}$ (Figure 15c,d). For a PV percentage in this range of less than $10\%$, the heterogeneity of LPMA significantly decreases, resulting in an increase in the overall heterogeneity of the PSD (Figure 13). $R_{v_{max}}$ of this type of sample is in the
stage of coalification transition, and the number of pores in 2–10 nm is lower, resulting in significant differences of $a_{-10}$ and $a_{-10} - a_{0}$ in comparison to other samples. It can be concluded that there is a critical value of pore volume percentage, which affects the distribution interval of the high- and low-probability intervals.

When the PV percentage of pores with diameters of 2–10 nm is less than 10%, this pore size range belongs to LPMA. In the pore size range from 2 to 10 nm, the effect of pore volume variation on the value of $a_{-10} - a_{0}$ is more obvious. When the pore volume percentage of pores with diameters of 2–10 nm is larger than 10%, this pore size range belongs to the part of the high-probability area. The pore size interval of HPMA is large (Figure 13b), so the variation of pore volume in the local interval of 2–10 nm has a weak effect on the values of $a_{-10} - a_{0}$ and $a_{-10} - a_{10}$.

To confirm this interpretation, the relationship between PV percentage of pores with diameters of 10–50 nm and multifractal parameters was analyzed (Figure 13e,f). The results show that the volume percentage in this interval is strongly correlated with $a_{0} - a_{10}$, whereas there is a lack of correlation with $a_{-10} - a_{0}$ and $a_{-10} - a_{10}$. The results indicate that pores in this diameter range belong to HPMA, and have a higher correlation with $a_{0} - a_{10}$.

### 3.2.3. Comparison of Single- and Multifractal Dimensions.

The values of ln(ln($P_{0}/P$)) and ln($V$) corresponding to each sample were calculated using eqs 2 and 1, and the single-fractal parameters $D_{v1}$ and $D_{v2}$ of each sample were obtained (Table 6). Figure 16 shows that $D_{v1}$ had a good linear positive correlation with $a_{-10} - a_{0}$ and $a_{-10} - a_{10}$, indicating that single-fractal $D_{v1}$ can effectively characterize the PSD heterogeneity in the LPMA of MMP, i.e., heterogeneity of volume distribution of pores with diameters of 2–10 nm. This is also consistent with the conclusion from previous work that $D_{v1}$ can be used to study the volume roughness of pore structure and to characterize the pore morphology.19

However, the linear relationship between $D_{v2}$ and each multiple parameter is not clear. Specifically, the samples with $D_{v2}$ of less than about 0.4 correspond to the larger values of $a_{-10} - a_{0}$ and $a_{-10} - a_{10}$. For $D_{v2}$ values greater than 0.4, $a_{-10}$ and $a_{-10} - a_{10}$ tend to stabilize.
4. CONCLUSIONS

Based on the comprehensive description of micropores and meso–macro-pores through N₂ and CO₂ adsorption tests, the multifractal theory was applied to quantitatively characterize pore distribution heterogeneity of the middle- and high-rank coal sample groups. Relying on the calculated multifractal parameters, factors affecting pore size distribution heterogeneity of adsorption pores were investigated. The correlation of fractal parameters obtained by different calculation methods was compared, and the pore range characterized by fractal parameters was determined. The conclusions are as follows:

(1) Pore size distribution of adsorption pores in the middle- and high-rank coal sample groups exhibits typical multifractal behavior, and correlations of multifractal parameters and factors affecting micropores and meso–macro-pores are significantly different.

(2) The correlation of multifractal parameters of micropores indicates that the low-probability measure areas dominate the heterogeneity of pores with diameters from 0.40 to 1.50 nm. The high-probability measure areas only affect the heterogeneity of the partial interval of the micropores and have a weak effect on the overall heterogeneity of micro-pore-size distribution.

(3) The linear correlation of the heterogeneity with coal rank and pore structure parameters in the high-probability measure areas is stronger than that in the low-probability measure areas. The percentage of pore volume of pores with 0.72–0.94 nm diameter decreases with the increase of coal rank, and the heterogeneity of high-probability measure areas decreases linearly. The diameter range of 0.72–0.94 nm is a key interval causing the distribution heterogeneity variations of micropores.

(4) Heterogeneity in the low-probability measure areas is affected by the pore distribution of 0.94–1.50 nm diameters. However, the variation of pore volume percentage in this interval is smaller, which results in smaller changes in \( a_{-10} - a_0 \) of samples in the same coal rank. Moreover, the proximate parameter also affects the heterogeneity of pore size distribution; highly volatile samples of the same coal rank present smaller \( a_{-10} - a_0 \).
There is no clear correlation between the multifractal parameters and coal rank. Pores with a diameter range from 2 to 10 nm have a good linear correlation with $a_{-10} - a_{10}$ and $D_{v1}$, which is the key interval that affects the low-probability measure areas and the overall heterogeneity of the PSD.

Single-fractal parameters present a good correlation with multifractal parameters. The single-fractal $D_{v1}$ is linearly positively correlated with $a_{-10} - a_{10}$ and $a_{-10} - a_{10}$, which can effectively characterize the pore distribution heterogeneity in the low-probability measure areas of meso–macro-pores.

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