Comparative analysis of pore structure and fractal characteristics of micropores in medium and high rank coals——Taking the typical mining area of western Guizhou and eastern Yunnan as an example

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Abstract. In order to clarify the micropore pore structure characteristics of medium and high rank coal reservoirs, based on low temperature CO₂ adsorption test and surface/volume fractal theory, the structure and fractal characteristics of medium and high coal rank micropores (0.40~2nm) were analyzed. The results show that with the increase of coal metamorphism, the pore size of coal reservoirs changes from 0.55~0.8nm to 0.5~0.7nm, and the pore size is 0.5~0.9nm. Microporous pores have good fractal characteristics, $D_{av1}<D_{av2}$, indicating stage the pore volume heterogeneity increases with the pore size in the pore range. $D_{av2}$ is positively correlated with the maximum vitrinite reflectance, indicating that the pore volume heterogeneity increases with the pore size in the micropore range. The heterogeneity of the surface area of the adsorption pore is far more complicated than the volume heterogeneity, $D_{as1}<D_{as2}<D_{as3}$, indicating that the surface heterogeneity of the micropore decreases with the decrease of the pore size and tends to be stable: As the degree of metamorphism of coal increases. And the study shows that the influence of coal rank on surface heterogeneity decreases with the decrease of pore size.

1. Introduction

The reservoir space of coal reservoir is mainly composed of the defect space (solid solution state) between the surface molecules of coal matrix and the tiny pores developed to the nanometer level, the gas is mainly physically adsorbed on the surface of the nanopore. [1-2]. Pore structure, pore size and distribution, and pore connectivity determine the pore and seepage characteristics of coal, which affects the adsorption and migration of gases [2-4]. Therefore, the homogeneity of pore structure has become an important factor in the enrichment and development of coal bed methane (CBM).

Fractal theory has become an effective method to study the homogeneity of pore structure in porous media [5]. At present, relevant scholars use different methods from different angles to study fractal dimension[6-8], such as Sierpinski model, FHH (Frenkel-Halsey-Hiss) model and Langmuir fractal model.
Based on Hodot's\cite{9} pore partitioning criteria, based on the adsorption and seepage characteristics of different pore sizes, the pores are divided into adsorption pores and percolation pores by the boundary of 100 nm\cite{10}, and the adsorption pores are divided into micropores (diameter < 2 nm) and mesopores (2~50nm in diameter) and large pores (10~100nm). It is generally believed that the medium and high coal rank micropores are widely developed and provide the vast majority (>99%) surface area (SSA) of coal pores and the micropore surface area has a good positive correlation with the adsorption capacity of CH4. At the same time, the study shows that the CO\textsubscript{2} adsorption test can more accurately characterize the micropore structure of coal reservoirs than the low temperature N2 adsorption test.

At present, microporous (d<2nm) pores have not been studied as the main pore type of medium-high coal rank reservoirs. Therefore, based on the low-temperature CO\textsubscript{2} adsorption test data, this paper uses the fractal theory of volume and surface area to achieve a comprehensive fractal study of the microporous pores of the middle and high coal ranks in the study area, and to explore its influencing factors.

2. Sample experimental test and theoretical basis

In this experiment, a total of 9 middle-high-order primary-fragmented structural coals (20*20*15cm\textsuperscript{3}) were collected from the Tucheng mining area and the old factory mining area in the Longxi-Yongdong area (Fig.1). The vitrinite group reflectance (R\textsubscript{0}.max) 0.93%~3.16%, mainly bituminous coal and anthracite coal. The coal rock type is mainly semi-bright-bright coal, and the coal structure is relatively simple. The coal-bearing strata in this area are the Permian Longtan Formation, and the sedimentary environment is the delta-tidal flat-lagoon sedimentary system. Due to the regional uplift, the depth of burial along the SE to the stratum is deepened. Among them, the Tucheng Mine is dominated by the middle coal rank coal seam, and the old mine mining area is dominated by the high coal rank coal seam.

![Figure 1. Schematic diagram of the Tucheng mining area and the old factory mining area](image)

2.1. Sample preparation and experimental testing

The newly collected samples are specially packaged and transported to the laboratory in accordance with the specification GB/T 19222-2003 for sample processing and series of experimental tests. Each group of samples was ground to 40 to 60 mesh, and then an appropriate amount of samples were taken for low temperature CO\textsubscript{2} adsorption desorption experiments. The experimental instrument was subjected to CO\textsubscript{2} adsorption and desorption experiments at a temperature of 273.15 K using Micrometitics' ASAP2020 specific surface area and pore analyzer.

2.2. Fractal theory

Based on the low temperature CO\textsubscript{2} adsorption test, the volume fraction and surface integral shape were comprehensively analyzed, and their values were respectively characterized by pore volume homogeneity and surface area homogeneity.
The Frenkel-Halsey-Hill (FHH) model is the most commonly used fractal model in LPN$_2$GA to characterize adsorption pores from 2 to 100 nm. The expression:

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

Where P is the equilibrium pressure, MPa; $P_0$ is the N$_2$ saturation pressure, MPa; V is the N$_2$ volume at a fixed pressure, cm$^3$/g; $V_m$ is the maximum volume of the monolayer, cm$^3$/g; C is a constant; A is a power exponent, which depends on fractal dimension (D) and adsorption mechanism.

There are two fractal relationships between volume fractal feature D and slope A at different adsorption stages, and it has been shown that both are more suitable for $D = A + 3$.

The micropore volume fractal is described by the Sierpinski fractal model [11], and the fractal expression:

$$\ln(V) = (3 - D_{sv})\ln(P - P_t) + \ln \tilde{\delta}$$

Where V is the adsorption volume, cm$^3$/g; P and $P_0$ are the experimental pressure and pore pressure, MPa; $D_{sv}$ is the micropore volume volume fraction; is a fitting constant.

The surface fractal calculation of the adsorption holes such as micropores and mesopores is carried out by introducing the formula (3).

$$\ln S(r) = \ln(S_0K_s) + C \ln r$$

In the formula, S(r) is Total surface area (TSS) ; $D_s$ is lnS/lnr Slope; r is the diameter, nm; Surface fractal dimension $D_s=2+C$ or $D_s=(C-3)/3$.

3. Results and discussion

3.1. Microporous pore distribution
Compared with the CO$_2$ adsorption curve (Fig. 2), the high coal rank gas adsorption capacity (13.67~18.75ml.g$^{-1}$) is much larger than that of the medium coal rank sample (5.67~6.29ml.g$^{-1}$), and the degree of coal metamorphism Increasing the shape of the curve gradually changes from near linear to concave.

![Figure 2. Adsorption curves of CO$_2$ adsorption for different rank samples](image)

The pore size of each sample was mainly distributed in three peaks (Fig. 3 and Fig. 4), which were peak 1 (0.50~0.53nm), peak 2 (0.60~0.62nm) and peak 3 (0.82nm). In this study, there was no significant change in the peak position of each peak with the increase of coal rank. The pore volume and specific surface area corresponding to peak 1 and peak 2 increased significantly, and the pore volume corresponding to peak 3 showed a trend decreasing. The dominant pore diameter was 0.55.~0.8nm (medium coal rank) is converted to 0.5~0.7nm (high coal rank).
Figure 3. Incremental pore volume plots of DFT-microporous for the middle and high coals

Figure 4. Surface area distribution characteristic map of stage holes based on DFT model
(a: medium coal sample; b: high coal sample)

3.2. Fractal characteristics
Fractal description of micropore volume characteristics, There is a good linear relationship between \( \ln V \) and \( \ln(P-P_t) \) with \( \ln(P-P_t) = -4.5 \) as the boundary. Therefore, \( D_{av1} \) \((r < 0.8 \text{ nm})\) and \( D_{av2} \) \((0.8 \text{ nm} < r < 2 \text{ nm})\) indicate that the pore volume of the microporous pores has a good Sierpinski fractal feature. At the same time, \( D_{av1} < D_{av2} \) indicates that the pore volume complexity of 0.8nm<r<2nm is stronger than that of r<0.82nm pore. On the other hand, the range of \( D_{av1} \) and \( D_{av2} \) in the middle and high coal ranks are (1.64~1.68, 2.10~2.23) and (1.50~1.77, 2.20~2.47), respectively.

\( D_{av1} \) performance tends to be stable within the same coal rank, but the difference is more obvious at different coal ranks; \( D_{av2} \) appears to increase gradually with the increase of coal metamorphism.

These trends indicate that the micropore pore \((0.8 \text{ nm} < r < 2 \text{ nm})\) volume homogeneity is more sensitive to the degree of coal metamorphism than the microporous pores \((r < 0.8 \text{ nm})\).

Figure 5. Volume Fractal Dimension Characteristic Map of Micropores Based on Sierpinski Model
(a: medium coal sample; b: high coal sample)
Using the formula 3 to describe the micropore surface area characteristics, we can find that the surface integral curve is obviously represented by three different fractal features with $\ln(r)=-0.45/-0.2$ as the boundary. This feature is also reflected in the $d=0.62\text{nm}/0.82\text{nm}$ pores, and this result is consistent with the double peaks corresponding to Figures 6-7. The above conclusions indicate that there are significant differences in pore surface area homogeneity between 0.40 nm and 0.62 nm, 0.62 nm to 0.82 nm, and 0.82 nm to 2.0 nm. It also shows that surface area heterogeneity is significantly stronger than volume heterogeneity. The specific surface shape dimension of microporous pores of 0.40nm–0.62nm, 0.62nm–0.82nm and 0.82nm–2.0nm is expressed by $D_{a1}$, $D_{a2}$ and $D_{a3}$ respectively, and it can be found that the range of medium and high order samples is $0.50$–$1.06$. And it shows a tendency to gradually decrease as the degree of deterioration increases. The results show that the surface heterogeneity of the micropores of $0.40\text{nm}<d<0.62\text{nm}$ is weak, and the pore complexity tends to decrease as the pore surface area increases (Figure 6). In addition, experiments have shown that the measured values of $D_{a2}$ and $D_{a3}$ are $2.04$–$2.70$ and $2.10$–$2.75$, respectively, which indicates that the pore edges of $0.62\text{nm}$–$2\text{nm}$ micropores have complex 2D surfaces.

![Figure 6](image)

Figure 6. Surface fractal curve of the micro-pores (a,b), the surface fractal dimension of $D_{a1}$ / $D_{a2}$ and $D_{a3}$ of all the samples (c), d: micropore volume / surface integral Relationship with R0%.

The microporous pores of medium and high rank coals exhibit two characteristics: $D_{a1}<D_{a2}\leq D_{a3}$ in the same sample, indicating that the surface heterogeneity of the micropores of the same coal rank from 0.62 nm to 0.82 nm is weaker than that of the pores of 0.82 nm to 2.0 nm in the same tectonic setting, and the surface homogeneity of the micropores tends to be stable as the pore diameter decreases; Secondly, the surface fractal dimension $D_{a1}$, $D_{a2}$ and $D_{a3}$ generally decrease with the increase of coal metamorphism. In the high coal stage, $D_{a2}$ and $D_{a3}$ gradually become consistent, reflecting that $\ln(s)$ and $\ln(r)$ increase with the increase of coalfication degree, and gradually evolved from three stages to two stages (Figure 14c, d). The above two important characteristics show that the effect of the coal rank on the heterogeneity of the pore surface is gradually weakened with the
decrease of the pore size. It also shows to some extent that micropores with different pore sizes bounded by 0.62 nm have completely different pore fractal characteristics.

3.3. Micropore volume/surface fractal correlation analysis

In summary, the micropore volume fractal features can be divided into two categories: $D_{av1}$ ($r < 0.8$ nm) and $D_{av2}$ (0.8 nm < $r < 2$ nm). The surface fractal features of the micropores are divided into three categories: $D_{as1}$ (0.40nm~0.62nm), $D_{as2}$ (0.62nm~0.82nm) and $D_{as3}$ (0.82nm~2.0nm). At the same time, Figure 7 also shows that the correlation between volume fractal features and surface fractal dimensions in the micropore stage is significantly better than that in other stages. In addition, $D_{av1}$ ($/D_{av2}$) and surface fractal dimension of each micropore stage exhibit a significant negative correlation, and this negative correlation is most pronounced in pores of 0.8 nm < $d$ < 2 nm.

Figure 7. Relationship between volume fractionation and surface integral shape of CO$_2$ adsorption pores (a: volume fractal and surface fractal relationship; b: volume fractal and surface fractal relationship)

4. Conclusion

1) With the increase of coal metamorphism, the micropore dominant pore size of coal reservoir will change from 0.55~0.8nm to 0.5~0.7nm, but the pore size of 0.5~0.9nm is still the main storage space.

2) The pore volume and average surface area of microporous pores have obvious fractal characteristics. The pore volume homogeneity of 0.8nm<$d$<2nm is more sensitive to coal metamorphism than $d$<0.8nm pore, and the volume heterogeneity increases as the pores increase.

3) The surface fractal features of micropores are significantly stronger than the volume fractal features. According to the fractal dimension of pore surface, the micropores can be divided into $D_{as1}$ (0.40nm~0.62nm), $D_{as2}$ (0.62nm~0.82nm) and $D_{as3}$ (0.82nm~2.0nm). The surface heterogeneity of micropores with different pore sizes is significantly different. The surface heterogeneity of micropores gradually decreases with the decrease of pore size, and the homogeneity of pore surface increases with the degree of coal metamorphosis and tends to be uniform. At the same time, at each stage of micropores, the volume heterogeneity of the pores and the surface fractal dimension show a significant negative correlation, indicating that the pore surface heterogeneity is relatively weakened as the pore structure complexity increases.

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