Pore Size Distribution Characteristics of High Rank Coal with Various Grain Sizes

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ABSTRACT: Particle void filling effects (\( P_f \)) under low pressure and coal matrix compressibility effects (\( P_c \)) at high pressure should not be ignored when using mercury intrusion porosimetry (MIP) to study the pore size distribution of coal. In this study, two coal samples (FX and HF) collected from western Guizhou were crushed into three different grain sizes; then, the subsamples were analyzed by MIP and low-pressure nitrogen adsorption to study the pore size distribution characteristics. The micro- and transition pore volumes contribute to the total pore volume of the FX and HF subsamples. With decreasing subsample grain sizes, the macropore volume of FX subsamples tends to increase, while mesopore volume decreases; the volumes of micropores and transition pores first increase and then decrease. In regard to the HF subsamples, the volumes of macropores and mesopores do not reveal any distinctive changes, while the 40–60 mesh subsample contains the greatest volume of micropores and transition pores. Fractal theory was introduced to determine \( P_f \) and \( P_c \). \( P_f \) barely changed as grain size decreased; it ranged from 0.1 to 0.15 MPa. However, \( P_c \) increased with reduced coal grain sizes. The coal matrix compressibility coefficients of the subsamples were calculated from the cumulative mercury volume curve, and the true pore volume was also modified. The modified volume of macropores does not change markedly, while the volumes of mesopores and transition pores decrease significantly, clearly indicating the coal matrix compressibility under high mercury injection pressure. The modified pore volume shows that the pore (<10,000 nm) still harbors fractal characteristics.

1. INTRODUCTION

Coal is composed of organic matter and inorganic substances, with complicated fractures and pore structures.\(^1\) As effects of coalification increase, the pore structure in the coal shifts mainly from mesopores in the low and medium rank coals to transition pores and micropores in high rank coal, and the pore structure tends to be more complicated at a higher coal rank. The properties of pores in the coal are mainly influenced by the size, shape, and quantity of pores.\(^2\)–\(^5\) Currently, the development of coalbed methane has been a focus point, and related research on coal pore structure has attracted increased attention.

There are various methods by which the pore structures in the coal can be measured, including mercury intrusion porosimetry (MIP),\(^6\)–\(^9\) constant-rate-controlled mercury porosimetry (CMP),\(^10\) low-pressure nitrogen adsorption (LP-N2A),\(^15\)–\(^18\) low-pressure carbon dioxide adsorption (LP-CO\(_2\)A),\(^12\) synchrotron small-angle X-ray scattering (SAXS),\(^13\) small-angle neutron scattering (SANS),\(^14\) low-field NMR spectral analysis (LFNMR),\(^15\)–\(^17\) microfocus X-ray computed tomography (\( \mu \)CT),\(^18\)–\(^20\) optical microscopy,\(^2\) scanning electron microscopy (SEM),\(^22\)–\(^23\) atomic force microscopy (AFM),\(^24\) and so on. The advantages, disadvantages, and the measured pore aperture ranges of different measurement methods are discussed,\(^7\)–\(^25\) while it is noted that the MIP is the most widely used method to test the pore distribution in the coal.\(^6\)–\(^7\) The interparticle voids at low pressure and coal matrix compressibility effects at high pressure are two key factors that determine the accuracy of pore distribution in the coal,\(^26\)–\(^27\) so they should not be ignored when the MIP method is used.

It was found that the mercury filled the interparticle voids when the mercury pressure was lower than 0.4 MPa with a grain size of 0.15 mm.\(^7\) Subsequently, the mercury tended to enter the pore voids in the coal with increased pressure. Therefore, 0.4 MPa was considered to be the reference pressure for coal grain sizes of 0.2–0.4 mm using MIP.\(^7\)–\(^29\) Although the reference pressure is not confirmed, it certainly has a great deal to do with coal grain size.\(^3\)–\(^5\),\(^10\) It is thought that the reference pressure would be influenced by both the
interparticle voids and microfractures in the coal, and it showed that the reference pressure was 0.12 MPa.\textsuperscript{32} The coal particles that exceeded 1 mm in size were used with MIP to show that the mercury volume commonly had an apparent change under low mercury injection pressure, and the corresponding reference pressure was only 0.02 MPa.\textsuperscript{26} There are many studies on coal matrix compressibility effects during the development of coalbed methane.\textsuperscript{35,34} When the MIP is used to determine the pore structure of coal, the coal matrix compressibility effect is apparent under high mercury injection pressure. The coal matrix compressibility pressure could be as low as 7.35 MPa.\textsuperscript{27} It is found that when the mercury injection pressure was higher than 10 MPa, the measured pore volume from MIP was mainly induced by the coal matrix compressibility volume.\textsuperscript{9} For coal samples of large particle size (exceeding 1 mm), this pressure can reach to almost 48 MPa.\textsuperscript{26} It can be concluded that coal matrix compressibility pressures have obvious variations between various coal samples, implicating the strong anisotropy of coal. The accurate interparticle void filling pressure ($P_i$) and coal matrix compressibility pressure ($P_c$) are the foundations for studying the pore structure of coal, and fractal theory provides a potential method to quantify these two pressures.

Previous studies on coal pore structure have mainly focused on the same coal particle size fraction with various coal samples, but minimal attention was given to the pore distribution characteristics of the same coal sample having various grain sizes. In this paper, two high rank coal samples were collected from western Guizhou, and each coal sample was crushed into three subsample grain sizes: 20–40, 40–60, and 60–80 mesh. The subsamples were analyzed by MIP and LP-N$_2$A, and then, fractal theory was introduced to determine the $P_i$ and $P_c$ of the subsamples. According to the MIP results, the coal matrix compressibility coefficients of the subsamples were calculated, and the true pore volumes were modified. Finally, the pore distribution characteristics of various subsample particles were studied.

2. GEOLOGICAL SETTING

Zhucang syncline is located in the northeastern portion of the Bide-Santang Basin and includes the Zhina coalfield of western Guizhou (Figure 1). The Upper Permian Longtan Formation is the most significant coal-bearing stratum in the study area. The Longtan Formation represents a typical transitional facies deposit, comprising a mainly deltaic and lagoon-tidal system.\textsuperscript{36} Multiple coal seams are developed in the study area, and the distribution of these seams is quite constant.\textsuperscript{37} The thickness of the Longtan Formation is approximately 320 m in the Zhucang syncline, and there are 30–35 layers of coal seams. The cumulative thickness of all coal seams is 22.4 m, with the thickness of single coal seams varying from 0.1 to 8.5 m and an average coal seam thickness of 1.78 m. The tectonic movements of the late Yanshanian and Himalayan orogenies have resulted in the large number of folds and faults in the Zhucang syncline, which determined the current tectonic framework, and the Upper Permian Longtan Formation coal seams are well-preserved in the syncline. The faults are quite well-developed in the Zhucang syncline and are mainly normal faults with an NE-NNE trend. The dip angles of these faults are high ($>60^\circ$), while the extension distances are short. The faults deformed the coal structure of the shallow coal seams and had only a minor weakness impact on the deep coal seams (Figure 2).

3. RESULTS AND DISCUSSION

3.1. Pore Distribution Characteristics of Subsamples with MIP. Currently, Hotot’s and IUPAC’s pore classification methods are most commonly used. According to Hotot’s pore classification, the pores in the porous material include macropores ($>1000$ nm), mesopores ($100–1000$ nm), transition pores ($10–100$ nm), and micropores ($<10$ nm). IUPAC divided the pores into three types, macropores ($>50$ nm), mesopores ($2–50$ nm), and micropores ($<2$ nm). In this paper, Hotot’s pore classification is adopted. It can be seen that the cumulative mercury injective curves do not coincide for the subsamples, especially for the 40–60 mesh coal subsample (Figure 3), which indicates that the pore structure had been affected by the various coal grain sizes. Under low mercury injection pressure ($<0.03$ MPa), the cumulative pore volume shows a clear increase. However, this does not reflect the true pore volume in the coal; this mercury simply filled the interparticle voids of the coal particles. With increasing mercury injection pressure, the cumulative pore volume reveals a trend of stable increase. There is a significant increase of cumulative pore volume when the mercury injection pressure exceeds 40 MPa. The incremental pore volumes show a clear decrease under low pressure. With increasing pressure, the incremental pore volumes reveal a smooth and consistent increase. When the pressure exceeds 100 MPa, the incremental pore volumes tend to stabilize, which may have to do with damage incurred by the subsamples.

It is thought that pore volumes having pore diameters greater than 10,000 nm, from the MIP, were not true pores in the coal.\textsuperscript{32} Therefore, these pore volumes should not be considered when analyzing the pore distribution; this approach is adopted in this paper. The micropores ($7.5–10$ nm) and transition pores are dominant in the HF and FX coal samples,
which is a typical property of high rank coals (Figure 4). The total pore volume presents a similar trend of micropores and transition pores. For the HF and FX subsamples, different pore sizes reveal different variation characteristics. For FX subsamples, with the decreasing of the coal grain sizes, the macropore volume shows a continuous increase, while the mesopore decreases. The micropore volume and transition pore volume first decrease and then increase. The macropore and mesopore volume almost remain steady with the decreasing grain sizes for HF subsamples, and the 40–60 mesh coal subsample had the greatest micro- and transition pore volume (Figure 4). The coal has strong anisotropy,
leads to the various trends of different coal grain sizes. However, the MIP also has some defects in regard to determining the pore distribution, such as particle void filling effects under low pressure, coal matrix compressibility effects under high pressure, destructive effects with high mercury injection pressure, and so on. Therefore, the pore volume calculated from MIP should be modified before analyzing the pore distribution characteristics in the porous material.

3.2. Pore Distribution Characteristics of Subsamples with LP-N$_2$A. The porous material has six isotherm types and four hysteresis loops, which can present the adsorption characteristics of the porous material. The hysteresis loops can be utilized to determine the pore shape in the coal. The adsorption and desorption curves of FX and HF subsamples are similar to the IUPAC type IV isotherm and H$_4$ hysteresis loop, which indicates that the dominant pore diameter in the subsamples is less than 100 nm and that these pores are narrow slit-shaped pores with good interconnectivity (Figure 5). The pore volume of various pore diameters continually increases with decreasing coal grain sizes in the HF subsamples (Figure 6). For the FX subsamples, the transition pore volume increases with decreasing coal grain sizes, while the mesopore and micropore volumes first decrease and then increase (Figure 5). Comparing MIP and LP-N$_2$A, it can be found that the pore volume acquired from the MIP is significantly greater than that from LP-N$_2$A, and this phenomenon is largely a function of coal matrix compressibility effects under high pressure in MIP.

3.3. The Modifying of the Pore Volume of Coal Subsamples. 3.3.1. The Fractal Characteristics of Pores in the Coal. Coal is a typical porous material, and its pore structure has fractal characteristics. The pore fractal is influenced by the composition of the coal (including ash content, moisture content, and volatile content) and the pore parameters of coal (such as pore diameter and micropore structure). Greater pore fractal dimensions indicate complicated pore structure and strong anisotropy. The classic geometry model and thermodynamics model are the most commonly used pore fractal theories, with the former having a better applicability. Using the Washburn equation, the relationship between mercury injection volume and mercury injection pressure can be acquired (eq 1).

$$\Delta V = \frac{\text{P}}{\text{D}}$$

where $V$ is the mercury injection volume under pressure $P$, cm$^3$/g, and $D$ is the pore fractal dimension.

Equation 1 can alternately be written as

$$\text{lg}(\Delta V) = (4 - D)\text{lg}(P)$$

Figure 4. Histogram of pore volume and total pore volume with different grain sizes of coal subsamples from MIP.

Figure 5. Adsorption and desorption curves of low-temperature nitrogen sorption with different grain sizes of coal subsamples.

Figure 6. Histogram of pore volume and total pore volume with different grain sizes of coal subsamples from low-temperature nitrogen sorption porosimetry.
Previous studies showed that $D$ values should be included in the interval (2, 3), and it features three clear linear regimes.\textsuperscript{29,41} In this study, the three linear regimes are also found (Figure 7). However, depending on the particular purposes of various studies, the pressures for dividing the three linear regimes vary. The $D$ can be divided into three linear regimes with pressures of 0.1 and 10 MPa.\textsuperscript{29} The fractal theory is utilized, and MIP results of coal are used to determine the particle void filling pressure and the coal matrix compressibility pressure.\textsuperscript{35} Under low mercury injection pressure, the mercury mainly injects into particle voids. Due to the wide pore diameter range, the $D$ in this regime is commonly less than 2. For the intermediate pressure range, the $D$ ranges from 2 to 3, indicating that the Hg mainly enters into pores in the coal. If the $D$ approaches 3, the coal matrix tends to be compressed.

Figure 7. Fractal characteristics of various coal grain sizes.
Here, the values of $D$ at various pressures are used to
determine the $P_f$ and $P_c$ of different subsamples (Table 1).

**Table 1. The $P_f$, $P_c$, and $D$ of the Subsamples**

| Sample | Particle size (mesh) | $P_f$ (MPa) | $P_c$ (MPa) | $D_1$ | $D_2$ | $D_3$ |
|--------|----------------------|-------------|-------------|-------|-------|-------|
| FX-1   | 20–40                | 0.12        | 24.06       | 1.929 | 2.981 | 3.912 |
| FX-2   | 40–60                | 0.15        | 30.96       | 1.917 | 2.978 | 3.85  |
| FX-3   | 60–80                | 0.15        | 30.96       | 1.891 | 2.977 | 3.73  |
| HF-1   | 20–40                | 0.14        | 17.2        | 1.892 | 2.978 | 3.94  |
| HF-2   | 40–60                | 0.14        | 24.11       | 1.734 | 2.992 | 3.912 |
| HF-3   | 60–80                | 0.1        | 24.08       | 1.956 | 2.99  | 3.928 |

The particle voids of coal subsamples are related to coal
grain size.10,29,30 With a decrease in coal grain size, $P_f$ varies
slightly (Table 1). For FX subsamples, $P_f$ ranges from 0.12 to
0.15 MPa, which is equivalent to pore sizes of 8238.2 to
10,069.5 nm. $P_f$ for HF subsamples varies from 0.1 to 0.14
MPa, with the corresponding pore sizes ranging from 9064.4 to
12,943.3 nm. When the mercury injection pressure is less than
$P_f$, $D_1$ is commonly less than 2 (Table 1), indicating that the
pore structure does not present fractal characteristics. Addi-
tionally, the pore diameter is nearly greater than 10 μm.32

The $P_f$ increases with decreasing coal grain sizes (Table 1).
Under low mercury injection pressure, the coal particles are
commonly in loose forms. With increasing mercury injection
pressure, the accumulation types range from “compact” to
“ultimative”, which reflect the accumulation modes of coal
particles.41 With decreased coal grain size, the coal particle
voids also decrease, and thus, the accumulation type of coal
gains tends to be compacted, thereby enhancing the resistance
of stress on the coal and leading to an increase of $P_c$. When the
mercury injection pressure ranges from $P_f$ to $P_c$, the $D_2$ varies
from 2 to 3, indicating that the pore structure has fractal
characteristics. Once the mercury injection pressure exceeds $P_c$,
$D_3$ is greater than 3, which equals to a pore size of 52 nm.

### 3.3.2. The Modifying Method of the Pore Volume

Previous studies on the fractal characteristics of pore structures
have indicated that an increase of mercury injection volume is
mainly due to the compressed volume of the coal matrix when
the $D$ is greater than 3.10,29,30 Therefore, it cannot reveal the
true pore volume, and it is necessary to modify the true pore
volume. For the subsamples used in this paper, when the
mercury injection pressure exceeds $P_c$ the coal matrix achieves
compressibility, and the increased mercury injection volume is
the sum of incremental pore volume and coal matrix
compressed volume. The true pore volume of the coal can
be acquired from calculating the coal matrix compressibility
coefficient.

The coal matrix compressibility can be described as follows

$$K_c = \frac{1}{V_c} \times \frac{dV}{dP}$$

(3)

where $K_c$ is the coal matrix compressibility (m$^2$/N), and $V_c$ is the volume of the coal matrix (cm$^3$/g).

The coal matrix is composed of organic matter and micro pores (<3 nm). The tested floor pore diameter of MIP
is 7.5 nm. However, when the pore diameter is less than 52
nm, this pore volume is not the true pore volume though it can
be acquired from LP-N$_2$A. The LP-N$_2$A can only acquire pore
departure that is greater than 2 nm. In regard to lesser pore
diameters (<2 nm), the LP-CO$_2$A is instead required.22 For
certain reasons, the LP-CO$_2$A did not operate in this study,
and the pores <2 nm in size are thought to exist in the coal
matrix.

$$V_c = \frac{1}{\rho} + V_{N_2}$$

(4)

where $\rho$ is the true density of coal (g/cm$^3$), and $V_{N_2}$ is the pore volume of low-temperature nitrogen sorption (<52 nm) (cm$^3$/
g).

For porous materials, the mercury injection volume is
composed of two parts

$$\Delta V_{obs} = \Delta V_p + \Delta V_c$$

(5)

where $\Delta V_{obs}$ is the mercury injection volume (cm$^3$/g), $\Delta V_p$ is the pore volume in the coal (cm$^3$/g), and $\Delta V_c$ is the volume of the
coal matrix compressed (cm$^3$/g).

When the mercury injection pressure is higher than $P_c$, the
coal matrix compressibility effect generally occurs. It is found
that the relationship between the cumulative pore volume and
mercury injection pressure is linear (Figure 8), and eq 5 can be
rewritten as

![Figure 8. Linear relationship between the cumulative pore volume and mercury injection pressure.](https://dx.doi.org/10.1021/acsomega.0c02569)
Coal matrix compressibility has a strong relationship with coalification. In 17 coal samples (with carbon content of 72.7–93.2%), it was found that there is an M-shaped relationship between coal compressibility and carbon content. For a group of 21 low and medium rank coals, the relationship between the coal compressibility and carbon content is U-shaped. Because of the compressibility of the pores in the coal, the coal affects the compressibility. The low rank coal develops seepage spaces, and the high and medium rank coals contain large amounts of adsorption pores (mainly micropores). The higher the micropore volume, the higher the coal compressibility will be. In addition, the compressibility of coal is also influenced by the macerals, mineral content, moisture content, and so on. Inertinite within the coal may have large amounts of open pores and has a laminated structure, so it is easily compressed. For moisture, the content of moisture in a coal influences its mechanical properties. As pertaining to the FX and HF subsamples in this paper, the \( R_{\text{max}} \) of HF subsamples is higher than that of FX subsamples (Table 2), and the volumes of micro- and transition pores of HF subsamples are also higher (Figure 4); this may be the reason why the coal matrix compressibility coefficients of HF subsamples are higher (Figure 9).

### 3.3.4. The Modified Pore Volume

According to the calculated coal matrix compressibility coefficients, the true pore volume of the subsamples was modified. Under high mercury injection pressure, the increased incremental pore volume is primarily derived from the compressed volume of the coal matrix. Therefore, when the mercury injection pressure is higher than \( P_0 \), the pore volume is mainly modified. Due to the maximum mercury injection pressure of the used mercury porosimeter, micropores with apertures of 7.5–10 nm were not modified, and the total pore volume is the sum of macropores (1000–10,000 nm), mesopores (100–1000 nm), and transition pores (10–100 nm). It can be observed that the volume of macropores is almost unchanged, while the volumes of meso- and transition pores clearly decrease, especially transition pores (Figure 10). The total pore volume increased with decreasing coal grain sizes. The total pore volume of FX subsamples has increased 5.45% while that for HF subsamples approximately 12.41% (Figure 10).

The subsamples in this paper were crushed and sieved before the measurements. In this process, the primary macro- and mesopores in the coal may have been destroyed to microfractures, which leads to a change in the volume of macro- and mesopores. In addition, there are large amounts of closed pores in the coal, and the volume of closed pores provides a significant contribution to the total pore volume. With a continuous decrease in coal grain sizes, closed pores may be exposed, and gas pores that are hidden into the coal matrix may also be exposed, resulting in the increasing volume of micro- and transition pores. As shown in Figure 11, the pores of the FX and HF coal samples are filled with pyrite and clay minerals. These minerals may have been removed during the sample preparation process, also leading to a change in pore volume.

### 3.4. Pore Fractal Characteristics with the Modified Pore Volume

Combining the modified pore volume, \( P_i \) and \( P_0 \), the pore structure fractal characteristics with the modified pore volume were also studied. As shown in Figure 12, when the mercury injection pressure is less than \( P_0 \), the pore

\[
\frac{\Delta V_i}{\Delta P} = \frac{\Delta V_p}{\Delta P} + \frac{\Delta V_c}{\Delta P}
\]

\[
\frac{\Delta V_c}{\Delta P} = \beta - \frac{\Delta V_p}{\Delta P}
\]

where \( \Delta V_c \) can be acquired from the low-temperature nitrogen sorption porosimetry. Finally, \( K_c \) can also be calculated.

Supposing \( K_c \) is constant during the increasing mercury injection pressure, the volume of the coal matrix under various pressures can be calculated as follows

\[
V_i = V_c - K \times V_c \times (P - P_0)
\]

where \( V_i \) is the volume of the coal matrix under \( P_i \) (cm³/g). Using eqs 3 and 9, the true pore volume under various mercury injection pressures can be acquired as follows

\[
V_{p_i} = V_{obs} - (V_i - V_c)
\]

where \( V_{p_i} \) is the true pore volume of coal under \( P_i \) (cm³/g), and \( V_{obs} \) is the mercury injection volume under \( P_i \) (cm³/g).

**Figure 9.** Histogram of coal matrix compressibility coefficients of HF and FX subsamples.
structure does not display fractal characteristics. However, the pore (<10,000 nm) shows the fractal characteristics with increasing mercury injection pressure. Due to the manually crushed nature of the subsamples, the pores (<52 nm) of subsamples FX-1 and HF-3 still do not display the fractal characteristics (Figure 12).

4. CONCLUSIONS

(1) \( P_f \) shows a faint increase with decreasing coal grain sizes, which correspond to pore diameters between 8238.2 and 12943.3 nm. \( P_c \) shows a continuous increase with decreasing coal grain size, mainly because decreased coal grain size increases the compactness of the coal particles, thereby enhancing resistance to stress of the coal.

(2) There is a clear decrease in the true pore volume of meso- and transition pores, indicating the significant compressibility of coal under high mercury injection pressure. The total pore volume reveals a continuous increase with decreasing coal grain sizes. When the test pressure exceeds the \( P_f \), the pore structure shows fractal characteristics with the modified pore volume.

5. EXPERIMENTAL SECTION

5.1. Sample Collection. The fresh coal samples were collected from the working face of the Hongfa coal mine (HF, no. 16 coal seam) and Fuxiang coal mine (FX, no. 23 coal mine) (Figure 13), and the vitrinite reflectance, coal quality analysis, and whole rock analysis of coal samples are shown in Table 2. The collected coal sample size was approximately 20 cm × 20 cm × 10 cm. To avoid oxidation, the coal samples were packed into plastic bags rapidly, which were immediately sealed, and then conveyed and stored in laboratory desiccators.

5.2. Sample Preparation. Although the coal samples were packed, the coal surfaces may have become oxidized; so, to minimize any potential error, the coal surfaces were removed. Subsequently, the coal samples were crushed in an agate mortar and sieved into three different grain sizes using standard laboratory test sieves (Table 3).

5.3. Sample Experimental Tests. Coal is an anisotropic substance. To minimize errors induced by the pore structures of the subsamples, subsamples of the same grain sizes were divided into two groups. One group was set aside for MIP, and the other group for LP-N₂A analysis.

The MIP analysis was launched in the Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process of the Ministry of Education (China University of Mining and Technology) with the IV9510 automatic mercury porosimeter.
(Micromeritics Instrument Corp.). The maximum mercury injection pressure can reach to 175 MPa, which can detect the pore diameters as small as 7.5 nm. The contact angle of the Hg in the test is 130°, and the surface tension of the Hg is 485 dyn/cm. (1) The subsample was dried in the drying oven for 24 h at 85 °C. (2) The subsample was put into the cell under low pressure in order to evacuate the air in the cell and adsorbed gas on the surface of the subsample. (3) The equilibration method was used under high test pressure with an equilibration time of 90 s. The test results were automatically recorded by the computer.

Figure 12. Pore structure fractal characteristics with the modified pore volume.
Figure 13. Detailed stratigraphic column of the Upper Permian Longtan coal-bearing formation in the Zhucang syncline.

Table 3. The Grain Sizes of the Subsamples in the Measurements

| coal mine | subsamples | coal particle size range (mesh) | coal particle size range (μm) |
|-----------|------------|--------------------------------|------------------------------|
| FX        | FX-1       | 20−40                          | 350−833                      |
|           | FX-2       | 40−60                          | 245−350                      |
|           | FX-3       | 60−80                          | 198−245                      |
| HF        | HF-1       | 20−40                          | 350−833                      |
|           | HF-2       | 40−60                          | 245−350                      |
|           | HF-3       | 60−80                          | 198−245                      |

The LP-N₂A analysis of subsamples was carried out at the SGS Unconventional Hydrocarbon Technology Detection (Beijing) Company Limited with the TriStar II 3020 specific surface area analyzer (Micromeritics Instrument Corp.). (1) The sample was initially dried for 12 h at 105 °C to discharge the moisture. (2) Approximately 2 g of the subsample was heated at 105 °C under vacuum to evacuate the adsorbed gas on the surface of the subsample. Pure nitrogen was used as the adsorbate, and the whole adsorption process was launched with a relative pressure varying from 0.01 to 0.995, under 77 K. The BJH model was utilized to acquire the pore volume.

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Notes
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