Accurate characterization of full pore size distribution of tight sandstones by low-temperature nitrogen gas adsorption and high-pressure mercury intrusion combination method

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Abstract

The full pore size distribution represents the integrated characteristics of micro-nano pore-throat systems in tight reservoirs. And it involves experiments of different scales to fully analyze the microscope properties. In this paper, we established a new approach for full pore size characterization through conducting the high-pressure mercury intrusion (HPMI) experiments and low-temperature nitrogen gas adsorption (LTN2GA) experiments. Meanwhile, we studied the petrology feature of the tight sandstones through X-ray diffraction (X-rD) and TESCAN Integrated Mineral Analyzer (TIMA). Then, we investigated the HPMI capillary pressure curves and pore size distribution characteristics, as well as the adsorption-desorption isotherms features and BET-specific surface area. Finally, the BJH, non-local density functional theory (NLDFT) and the quenched solid density functional theory (QSDFT) are contrasted for analyzing the adsorption and pore size distribution characteristics. The HPMI method characterizes the macropores distribution accurately, and the micro/mesopores take up of 14.47% of the total pore spaces. The physisorption isotherms take on the combining shape of type II and IV(a), and the hysteresis loops are like type H3 combined with H4. The BET-specific surface area is inversely proportional to permeability, and the constant of adsorption heat shows consistence with the analysis results of mineral content. QSDFT can characterize the pore size distribution of micro/mesopores more accurately than the BJH, HPMI, and NLDFT method. By combining the pores narrower than 34 nm calculated from QSDFT method and pores larger than 34 nm calculated from HPMI data with mercury intrusion pressure lower than 42.65 MPa, the full pore size distribution features of tight sandstones are accurately characterized. The micro/mesopores from the new combination method are 3.72% more than that calculated from the HPMI data, and it is of great significance for the accurate pore distribution evaluation and development of tight reservoirs.
1 | INTRODUCTION

With the huge increasing demand of energy, tight oil and gas resources have been playing critical roles in the petroleum industry, especially in China where the tight oil and gas reservoirs make up of more than two thirds of the newly proved reserves. The general definition for tight oil is the petroleum reserved in tight sandstones or carbonates with gas permeability less than $1 \times 10^{-3}$ $\mu m^2$ (or in situ matrix permeability less than 0.1 $\times 10^{-3}$ $\mu m^2$). The pores and throats in the tight reservoir rocks are small and complex, which causes strong heterogeneity. The pore structure characteristic is the key parameter for reservoir evaluation, which also affects the hydrocarbon accumulation, fluid flow in the reservoir and production significantly. According to the IUPAC classification, pores are small and complex, which causes strong heterogeneity. The pore structure characteristic is the key parameter for reservoir evaluation, which also affects the hydrocarbon accumulation, fluid flow in the reservoir and production significantly. The micropores and mesopores volume in the tight reservoir rocks have an important influence on the reservoir storage performance, oil and gas distribution, and fluid flow characteristics. There are several commonly used methods to determine the pore size distribution of reservoir rocks, such as high-pressure mercury intrusion method (HPMI), constant-speed mercury intrusion (CSMI) nuclear magnetic resonance (NMR), and low-temperature nitrogen gas adsorption (LTN$_2$GA). The pore sizes obtained by different methods are different. It is impossible to fully characterize the pore structure of tight reservoirs just by one single method.

The pore/throat structures of the cores are complex and can be seen as a series of interconnected capillary networks. The relationship between the mercury intrusion pressure and the mercury saturation in the core is the capillary pressure curve. The HPMI capillary pressure curve and the pore size distribution curve can reflect three types of parameters which represent the pore structure characteristics, such as parameters that reflect the pore/throat size types, pore/throat connectivity, and the pore/throat sorting degree. The high-pressure mercury intrusion method (HPMI) can measure a core pore size range from 3 nm to 1000 $\mu m$; however, it cannot determine the nanoscale pore distribution accurately. When the mercury intrusion pressure exceeds 200 MPa, mercury can enter pores with a diameter of less than 7 nm. At this time, the core pores are at risk of being destroyed, so the mesopores volume obtained from HPMI experiment has potential pitfalls, which means the HPMI method cannot characterize the mesopores and micropores accurately. The constant-speed mercury intrusion (CSMI) can quantitatively characterize the microscopic pore/throat structure characteristics of reservoir stones, with subtle features of pores, throats, pore/throat ratio, etc. However, the maximum mercury intrusion pressure of most CSMI instruments is less than 10 MPa, and the corresponding minimum detectable pore width is around 0.15 $\mu m$. So the CSMI method itself is also inadequate to characterize the micro/mesopore structures of tight reservoirs.

The low-temperature nitrogen gas adsorption (LTN$_2$GA) experiment is based on physical adsorption caused by intermolecular forces, and it measures the nitrogen adsorption-desorption curves. Nitrogen is used as the adsorbate, and the core samples act as adsorbent. Single-layer adsorption, multi-layer adsorption, and capillary condensation occur in the pores of porous media during the low-temperature nitrogen adsorption experiments. The adsorption/desorption process can effectively reflect the distribution of micropores and mesopores in the material without destroying the pore structure of it, but this method cannot measure macro pores distribution. Since the low-temperature nitrogen adsorption method can accurately characterize the micropores and mesopores of the reservoir rock, some scholars therefore proposed that low-temperature adsorption method should be combined with high-pressure mercury intrusion for the quantitative characterization of reservoir rocks pore characteristics.

The commonly used methods for LTN$_2$GA data processing are BJH method and DFT method. By processing the LTN$_2$GA data via classical macroscopic thermodynamic methods, the pore size distribution can be obtained. However, different processing methods have different application scopes. For example, the Dubinin-Radushkevich (DR) method and the semi-empirical processing method (HK method and SF method) are only applicable to the micropore filling stage. The BJH method is suitable for the treatment of cylindrical pore models with a pore diameter larger than 5 nm. When calculating pores with a diameter of less than 5 nm by BJH method, a 20% error is generated. While for a diameter less than 10 nm, the pore size can be underestimated. Therefore, it is not suitable to use the BJH method when analyzing mesopores and fine micropores. In recent years, density functional theory (DFT) combing computational simulation methods are widely used to study the pore size distribution of materials. They establish an actual fluid model and rely on the interaction parameters between...
actual fluid molecules. Among which, non-localized density functional theory (NLDFT) and Monte Carlo simulation method (GCMC) not only provide a microscopic model of adsorption, but also reflect the thermodynamic properties and structural properties of fluids in pores more realistically. These two methods can analyze micropores and mesopores more accurately and have a good correspondence. Later on, Ravikovitch et al. proposed the quenched solid density function theory (QSDFT), and it adds the influence of surface roughness and anisotropy on the calculation results into consideration. The adsorption experiment based on the standard molecular sieve model of known pore types and comparison calculations show that QSDFT further improves the accuracy of the pore size calculation and analysis results.

In this paper, LTN₂GA, HPMI, and X-rD experiments were carried out on different real ultra-low permeability/ tight sandstone reservoir core samples. According to the HPMI data, the capillary pressure curves and relating structure parameters are calculated. Basing on the LTN₂GA experiments, the adsorption-desorption isotherms characteristics and the BET-specific surface areas for cores of different permeability were calculated and analyzed. Then the compatibility and accuracy of the calculated pore size distributions of NLDFT and QSDFT were compared and analyzed. The pore size distributions of micropores and mesopores were calculated and analyzed by QSDFT, BJH, and HPMI method respectively afterward. Finally, the full pore size distribution characteristics of ultra-low permeability/ tight sandstones were characterized by the combination of QSDFT method from LTN₂GA and HPMI.

2 | MATERIALS AND METHODOLOGY

2.1 | Geological background and sample preparation

A total of 6 tight natural core samples were collected from the Chang 6 reservoir of Changqing oilfield. This area is a superimposed development zone of two oil-bearing strata group, which are the Triassic Yanchang Formation and the Jurassic Yan’an Formation. The lithologic characteristics of which are mainly gray and gray-black siltstone. The core samples were cleaned and dried, and then the gas permeability and porosity were measured by the pulse-decay permeability measurement apparatus and helium porosimeter, respectively. Table 1 shows the basic data of the core samples.

The six samples were cut to three parts of appropriate lengths by a cutting machine for subsequent experiments respectively. The HPMI experiment requires a sample length of 2 cm. The low-temperature nitrogen adsorption experiment requires a sample of 3 cm for sample preparation. The X-ray diffraction experiment requires a small amount of samples, and the remaining parts of the sample are sufficient for X-rD analysis.

2.2 | Mineralogy and morphology analysis

The remaining parts of samples were ground into powders, and the whole rock minerals and clay minerals were analyzed by X’Pert Pro MPD polycrystalline X-ray diffractometer manufactured by PANalytical BV.

The pore type and morphology were also studied on crushed grain samples from LTN₂GA using the TSCAN Integrated Mineral Analyzer (TIMA). TESCAN TIMA uses a fully integrated quantitative energy-dispersive X-ray spectrometry (EDS) and an advanced statistical approach to automated scanning electron microscopy (ASEM) systems.

2.3 | High-pressure mercury intrusion (HPMI)

The HPMI experiments were carried out on 6 core samples respectively using the fully automatic HPMI apparatus PoreMaster 60 produced by Quantachrome (Figure 1). PoreMaster 60 can test a pore size range of 0.0036-1100 μm in diameter and has a working pressure range of 0.2-60 000 psi. 2 centimeters of each samples cut from the original cores are cleaned and dried to perform the HPMI experiments.

The HPMI measurement procedures are as follows. A core sample of about 2 cm in length and 2.5 cm in diameter was put in a sample cell. The vacuum filling apparatus was used to remove air from the cell and pores within the

| Core No. | Length/cm | Diameter/cm | Permeability/10⁻³ μm² | Porosity/% |
|---------|------------|-------------|-----------------------|------------|
| 1       | 7.076      | 2.527       | 0.019                 | 9.68       |
| 2       | 6.931      | 2.533       | 0.031                 | 9.59       |
| 3       | 7.013      | 2.522       | 0.127                 | 16.31      |
| 4       | 7.211      | 2.535       | 0.257                 | 13.04      |
| 5       | 6.523      | 2.529       | 0.317                 | 12.45      |
| 6       | 6.307      | 2.516       | 0.390                 | 13.06      |

**TABLE 1** Physical property data of core samples
sample, and mercury was transferred in the sample sell by operation in the low-pressure vessel. The sample cell was put into a protection cell and together they were assembled in the high-pressure vessel. Then the pressure generator was used to transmit pressure into the high-pressure vessel by hydraulic fluid. The mercury intrusion process finished until the pressure reached 400 MPa and then the extrusion measurement started as the pressure declined to zero gradually. Meanwhile, the change of mercury volume as a function of applied pressure was monitored through the measuring circuits.

2.4 Low-temperature nitrogen adsorption

The low-temperature nitrogen adsorption experiments were performed on 6 core samples respectively using the KUBO-X1000 pore size and specific surface area analyzer (Figure 2) produced by Beijing Biotech Electronic Technology Co., Ltd. The flow chart for the gas adsorption measurement is shown in Figure 3. The pore diameter analysis range of the device is 0.35-500 nm. About 3 cm of each samples were cut from the original cores to prepare for the measurement. The samples were cleaned and dried, and then crushed into particles of 2-3 mm as the adsorbent. The samples were vacuumized for 6 hours under a temperature of 120°C for pretreatment to remove moist before adsorption measurement. High-purity nitrogen with a purity over 99.99% was used as the adsorbate, and the nitrogen adsorption amounts under different relative pressures were measured at 77.35 K (−195.8°C). Taking the relative pressure as the abscissa and the adsorption amount per unit mass sample as the ordinate, the nitrogen adsorption-desorption isotherms were obtained (ISO 15901).

The LTN$_2$GA measurement procedures are as follows. The rock particle samples were dried and weighed, and then put into the sample tube. Together with which they were assembled into the device. The liquid nitrogen cup was filled with liquid nitrogen. The system was then vacuumized via molecular vacuum pump and helium gas was used to calibrate the free space volume in the sample tube. A certain amount of nitrogen gas was injected into the manifold tube. The initial pressure and temperature in the manifold ($P_{r1}$, $T_{r1}$) were recorded respectively. At the same time, the initial pressure and temperature in the sample tube ($P_{s1}$, $T_{s1}$) were also recorded. The initial gas weight in the manifold ($m_{r1}$) and the sample tube ($m_{s1}$) was calculated. Then a certain amount of N$_2$ was injected into the sample tube from the manifold, and when the equilibrium state was reached, the pressure and temperature in the manifold ($P_{r2}$, $T_{r2}$) and sample tube ($P_{s2}$, $T_{s2}$) were recorded, and then the gas weight in the manifold ($m_{r2}$) and sample tube ($m_{s2}$) was calculated, respectively. Then, the adsorption volume ($V$) in the sample can be calculated.
3 RESULTS

3.1 Mineral contents and morphology characteristics

Figure 4 shows the mineral components in the samples. It can be seen from the stacked histogram that the samples mainly consist of quartz (27%-60%), plagioclase (21%-37%), and orthoclase (8%-31%). The clay mineral content of the samples is relatively low (3%-5%), and mainly composed by chlorite, illite, and illite/smectite interlayer, with zero kaolinite content and a 20% of montmorillonite in the I/S interlayer. The overall content of montmorillonite is low, so the core samples are not susceptible to water sensitivity and rapid sensitivity.

Figure 5 shows the color-enhanced mineral distribution characteristics of several sample areas. The results show that the oil storage spaces are mainly composed of dissolution pores and micropores, with poor pore-throat connectivity.

3.2 HPMI capillary pressure curve and pore structure characteristic

Figure 6 shows the HPMI capillary pressure curves of ultra-low permeability/tight core samples, and Figure 7 represents the corresponding pore size distribution curves basing on HPMI data (hereinafter referred to as the HPMI pore size distribution). It can be seen that the curves have a relatively flat platform in the mercury intrusion stage for all of the 6 core samples, reflecting a good sorting of the cores. With the increase of core permeability, the HPMI capillary pressure curves move to the lower left, and the maximum mercury saturation and mercury extrusion efficiency increase gradually. Also, the maximum pore-throat diameter increases, and the peak value of pore-throat distribution curve moves to the right, while the size of pore throat with higher distribution frequency increases.

Table 2 summarizes the characteristic values of the HPMI capillary pressure curves and the pore size distribution curves. The threshold displacement pressure of the tight core samples is between 0.707-6.430 MPa, and the corresponding maximum pore radiuses are from 0.114 to 1.040 μm, which indicates a relatively good storage performance. The median pressures are between 3.531-18.209 MPa and the corresponding median pore radiuses being 0.040-0.208 μm. The production capacities of different cores are different, with some of which being tight. The maximum mercury saturations are between 75.535%-81.326%, and the mercury extrusion efficiency between 13.0%-22.7%. Because of the mercury, intrusion pressure can reach as high as 400 MPa, mercury can enter the pores with a diameter of 3 nm. According to the HPMI pore size distribution data, the micro/mesopores take up of 9.71%-18.3% of the total pore volumes, with an average value of 14.47%. Macropores (>50 nm) take up most of the pore spaces in the core samples, with an average value of 85.53%.

Figure 8 shows the HPMI characteristic parameters' relationship between permeability. The threshold displacement pressure decreases rapidly with permeability increase. The average pore radius and mercury extrusion efficiency show increasing trend when permeability increases. The micro/mesopore spaces proportion in the tight samples show a decreasing trend when permeability increases.

3.3 Adsorption-desorption isotherms

According to IUPAC 2015,36 the updated classification standards of adsorption-desorption isotherms and hysteresis loops, the types of physisorption and isotherms hysteresis loops are
shown in Figures 9 and 10 respectively. Figure 11 shows the absorption/desorption (physisorption) isotherms of the measured core samples. It can be seen from the figure that the isotherms and hysteresis loops measured in the experiment cannot be simply attributed to a certain classification. Due to the complex pore structure inside the sandstone, it is needed to combine the different isotherms and hysteresis loops to characterize the internal pore structure characteristics. By comparing and analyzing the measured and standard isotherms and hysteresis loops, it can be seen that the adsorption-desorption
isotherms of the six samples are alike, which are the combination of type II and type IV(a). The adsorption isotherm curve is mainly divided into the following three stages.

1. Single-layer adsorption stage: At a lower relative pressure, the adsorption amount rises rapidly and the curve is convex, which is consistent with the first stage of type II and type IV(a) curves. This is caused by the combination of micropore filling and single-layer adsorption. When microporous filling occurs in the micropores of the core where the micropore diameter is close to the diameter of the adsorbate molecules, the potential fields on adsorbed molecules of two opposing pore walls in the micropores overlap. Also, the adsorption potential energy of gas molecules is relatively large and the Kelvin formula is not valid.\(^{37,38}\) At the relative pressure \(P/P_0 \approx 0.01\), single-layer adsorption is basically completed, and the inflection point (point B) of isotherm usually appears here. It can be determined by the saturated adsorption capacity of the single-layer calculated in the following part.

2. Multi-layer adsorption stage: The relative pressure \(P/P_0\) continues to increase and the multi-layer adsorption gradually forms. This is consistent with the second stage of the Type II and IV(a) curves.

3. Capillary condensation stage: When the relative pressure \(P/P_0 \approx 0.46\) to 0.48, the saturated vapor pressure of the liquid at the bending liquid level in the mesoporous capillary is smaller than that at the plain liquid level, so the liquid level in the capillary rises and the vapor condensates (capillary condensation).\(^{34}\) When the relative pressure \(P/P_0\) is close to 1, the adsorption does not reach saturation, which is due to the presence of macropores in the sample. It is

### Table 2: High-pressure mercury intrusion characteristic data

| Core No. | Permeability/10\(^{-3}\) \(\mu m^2\) | Threshold displacement pressure/MPa | Maximum pore radius/\(\mu m\) | Median pressure/MPa | Median pore radius/\(\mu m\) | Maximum \(S_{Hg}\)% |
|----------|----------------------------------|----------------------------------|-----------------------------|---------------------|-----------------------------|------------------|
| 1        | 0.019                            | 6.430                            | 0.114                       | 18.209              | 0.040                       | 75.535           |
| 2        | 0.031                            | 4.691                            | 0.157                       | 11.708              | 0.063                       | 76.017           |
| 3        | 0.127                            | 2.132                            | 0.345                       | 16.050              | 0.046                       | 77.362           |
| 4        | 0.257                            | 0.910                            | 0.808                       | 3.531               | 0.208                       | 79.622           |
| 5        | 0.317                            | 0.802                            | 0.916                       | 2.058               | 0.357                       | 83.302           |
| 6        | 0.390                            | 0.707                            | 1.040                       | 2.583               | 0.285                       | 82.093           |

| Core No. | Hg extrusion efficiency/%       | Average pore radius/\(\mu m\) | Main throat radius/\(\mu m\) | Homogeneity coefficient | Sorting coefficient | Micro/mesopore proportion/% |
|----------|---------------------------------|------------------------------|----------------------------|-------------------------|---------------------|---------------------------|
| 1        | 13.024                          | 0.057                        | 0.074                      | 0.499                   | 0.031               | 16.55                     |
| 2        | 14.496                          | 0.072                        | 0.092                      | 0.457                   | 0.028               | 15.62                     |
| 3        | 16.640                          | 0.092                        | 0.135                      | 0.267                   | 0.040               | 18.30                     |
| 4        | 18.565                          | 0.360                        | 0.546                      | 0.446                   | 0.233               | 11.79                     |
| 5        | 22.717                          | 0.340                        | 0.637                      | 0.371                   | 0.214               | 9.71                      |
| 6        | 18.739                          | 0.392                        | 0.628                      | 0.377                   | 0.203               | 14.86                     |
difficult to determine the accurate equilibrium adsorption value, which is consistent with the trend of type II curve. While the IV (a) type curve at a higher relative pressure peaks and mesoporous adsorption ends when mesopores fill up with capillary condensation. This indicates that the sample pore structure is very irregular.

When the relative pressure \( P/P_0 > 0.4 \), it can be found that the desorption isotherm of the middle section and the absorption isotherm do not coincide, and the adsorption hysteresis loop appears, which is consistent with the IV(a) type curve. This means that mesopores exist in the sandstone and capillary condensation phenomenon occurs. The type of hysteresis loop reflects the pore structure present in the adsorbent. The types of hysteresis loop of sandstones in low-temperature nitrogen adsorption experiments are combination of H3 and H4. H3-type hysteresis loops (sample 3, 5, 6) reflect pores including plate slit structure, crack, and wedge structure. H4-type hysteresis loops (sample 1, 2, 4) often occur on adsorbents mixed with micropores and mesopores, and in solids containing narrow crack pores.
Therefore, it can be concluded from the analysis that the pores in the core samples are mainly of the flat slit structure with open all around, and the pores in each pore size segment from the micropores to the macropores are relatively well developed and have good connectivity, which is beneficial to the flow of oil and gas.28,34

**FIGURE 11** Experimental adsorption-desorption isotherms (SLA—Single-layer adsorption; MLA—Multi-layer adsorption; CC-Capillary condensation)

3.4 | Specific surface area

Brunauer, Emmett, and Telle (BET) extended the Langmuir single-molecule adsorption theory to the multi-layer adsorption type II isotherm, also known as the BET-type isotherm, and derived the multi-molecular layer adsorption formula.39
The “ratio” in the specific surface area of sandstone refers to the relative area ratio occupied by the adsorbate molecules (nitrogen molecules). The relationship between the adsorption amount of the multi-layer stage and the relative pressure in the adsorption isotherm can be characterized by the BET equation, as shown in Equation (1):

\[
\frac{P}{V(P_0 - P)} = \frac{C - 1}{V_mC} \frac{P}{P_0} + \frac{1}{V_mC}
\]

where \( P \) is the equilibrium pressure of the adsorbed gas; \( P_0 \) is the saturated vapor pressure of the adsorbed gas; \( V \) is the actual (multi-layer) adsorption amount of the sample, \( \text{cm}^3/\text{g} \); \( V_m \) is the single-layer saturated adsorption amount per unit sandstone mass, \( \text{cm}^3/\text{g} \); \( C \) is the constant reflecting the adsorption heat.

The data on the adsorption isotherm in the range of relative pressure \( P/P_0 \) from 0.05 to 0.3 were selected for processing. Then plotted using the \( P/P_0 \) as abscissa and \( P/V(P_0 - P) \) as the vertical coordinate. After that, slope and intercept were obtained through linear fitting, and single-layer saturated adsorption capacity was obtained, so as to calculate the specific surface area of the sandstone sample. The formula for calculating the specific surface area is shown in the following Equation (2):

\[
A_s = \left( \frac{V_m N a_m}{22 400} \right) \times 10^{-18}
\]

where \( A_s \) is the multi-point BET-specific surface area, \( \text{m}^2/\text{g} \); \( V_m \) is the single-layer saturated adsorption capacity per unit mass of sandstone, \( \text{cm}^3/\text{g} \), standard condition; \( N \) is Avogadro’s constant, \( 6.022 \times 10^{23} \); \( a_m \) is the cross-sectional area of a single nitrogen molecule, the adsorption layer is a hexagonal close-packed structure;\(^{34} \) the nitrogen molecules are considered spherical, at 77.3 K, \( a_m = 0.162 \text{ nm}^2 \).

Figure 12 shows the calculation results of sandstone BET-specific surface area, and \( C \) value. The specific surface area of the six samples shows a decreasing trend with permeability increase, ranging from 1.6 to 4.1 \( \text{m}^2/\text{g} \). The range of \( C \) value is 60-132, which reflects that the main adsorbed materials in sandstone are oxides and silica.\(^{28} \) The \( C \) value shows consistence with the whole rock mineral composition analysis result that quartz and plagioclase are the main components of sandstone (Figure 4).

4 | DISCUSSION

4.1 | BJH method and pore size distribution by BJH model

The pore size distribution of the low-temperature nitrogen adsorption method is usually calculated by the BJH method based on the Kelvin equation (Equation 3).\(^{40} \) This method combines the Wheeler theory with physical adsorption and capillary condensation and directly calculate the pore size distribution from the desorption isotherm in the absorption/desorption isotherm curve. However, the following three assumptions should be satisfied: (a) The pore passage is rigid and suitable for cylindrical pores, (b) no micropores exist, (c) at the highest relative pressure, all the pores to be determined have been filled.\(^{34} \) Basing on the Kelvin equation, the capillary radius \( (r_k) \) could be calculated when capillary condensation occurs. Then the relationship curve of liquid nitrogen volume \( (V) \) and capillary radius \( (r_k) \) can be drawn, which as well is the cumulative pore volume distribution curve.

\[
\ln \frac{P}{P_0} = -\frac{2\gamma \bar{v} \cos \theta}{r_k RT}
\]

where \( P/P_0 \) is the equilibrium pressure over the saturated vapor pressure of the adsorbed gas; \( \bar{v} \) is the mole volume of the liquid nitrogen; \( \gamma \) is the interfacial tension of the liquid nitrogen.

The pore size distributions of the sandstones calculated by the BJH method (hereinafter referred to as BJH pore size distribution for the absorption and desorption curves from the absorption/desorption isotherm curves are shown in Figure 13). The vertical coordinate \( dV/dD \) in the figure is the differential of pore volume with respect to pore diameter,
which is the change in pore volume per unit pore diameter, also expressed as $dV/dD$. The $dV/dD$ would amplify the varying detail for the micro and meso parts on the distribution curve. According to the absorption and desorption curves, the pore diameter distribution of samples was calculated and compared. It can be seen that the data points of pore size distribution are inadequate to accurately characterize the distribution of mesopores in the core samples. Since the BJH
pore size distribution is mainly for the type IV isotherm and H1 type hysteresis loop, and because of other reasons like the internal tension strength effect of the sample, the connectivity of the pores, the diversity of the pore types, and the dispersion of the pore size, etc, a false peak appears at the pore diameter of 3-4 nm.

However, there are micropores in the real core samples.

**Figure 14** Experimental isotherm together with the NLDFT and QSDFT theoretical isotherms (SLA—Single-layer adsorption; MLA—Multi-layer adsorption; CC—Capillary condensation)
4.2 | Comparison of NLDFT and QSDFT desorption isotherms

Density functional theory (DFT) can select the appropriate model parameters to fit the desorption curve for different types of isotherms and hysteresis loops of different types of samples. Therefore, the mathematical model matching the pore structure type in the actual sample is selected to solve the problem. The DFT method can truly reflect the mechanism of absorption and desorption in the micropores and mesopores in the sample, thereby avoiding the occurrence of false peaks in the pore size distribution and make the pore size distribution more accurate. The non-localized density functional theory (NLDFT) uses molecular dynamics to describe the fluid in the pores of the adsorbent, and it is based on the assumption that the pore wall of the sample is isotropic and smooth. Quenched solid density function theory (QSDFT) incorporates pore surface roughness and the influence of anisotropy and constructs a two-component density functional to separate the fluid density from the solid density. The calculation method of NLDFT and QSDFT is shown in the Appendix 1.

Since the desorption curve can truly reflect the pores of the sample, the isothermal desorption curves measured by the experiments were compared with the desorption curves calculated by the NLDFT and QSDFT methods, and the root mean square error (RMSE) was calculated to characterize the accuracy of the two methods. The results of the calculated and measured desorption curves comparison are shown in Figure 14. The fitting errors of the adsorption volumes of the two methods at different stages are shown in Table 3. It can be seen from the figure that the fitting accuracy of the two methods in the single-layer adsorption stage and the multi-layer adsorption stage is high. However, according to the RMSE table, it is clear that the QSDFT method fits better with the experimental data and the accuracy is better throughout the isothermal desorption process. Therefore, the QSDFT method was used to characterize the pore size distribution of micropores and mesopores in the core samples.

4.3 | Comparison of micro/mesopore size distribution of different method

Basing on the desorption isotherms of the LTN2GA data, the micropores and mesopores pore size distribution for the ultra-low permeability and tight sandstone samples were obtained by QSDFT method (hereinafter referred to as QSDFT pore size distribution). The dashed lines in Figure 15 represent the QSDFT pore size distribution curves. The red lines represent the BJH pore size distribution curves. Since the HPMI pore size distribution can characterize the pore structure of macropores and mesopores in the core samples, the mesoporous portions from HPMI pore size distribution data (blue lines) were selected, which were treated to be consistent at the same radius range with the BJH pore size distribution and the QSDFT pore size distribution. Figure 8 shows comparison of pore size distribution in different methods.

The ordinate Dv(d) in the comparison of the pore size distribution refers to the rate of change of the pore volume per unit pore diameter, that is, the differential of the pore volume to the pore size, which can accurately characterize the distribution characteristics of the micropores and mesopores. According to comparison results, it is clear that the BJH curves are less accurate. Due to the limitations of the BJH method and its assumption conditions, the BJH method has a relatively bigger error in charactering the pore size distribution and cannot depict the mesopores accurately. However, the mesopores distribution trend of BJH method is the same with the other two methods.

Both of the HPMI and BJH pore size distribution cannot obtain the micropores characteristics of the core samples.

### Table 3 DFT method error analysis

| Core No. | QSDFT-RMSE | NLDFT-RMSE |
|----------|------------|------------|
|          | Single-layer adsorption | Multi-layer adsorption | Capillary condensation | Whole process | Single-layer adsorption | Multi-layer adsorption | Capillary condensation | Whole process |
| 1        | 0.285      | 0.099      | 0.816      | 1.389          | 0.309      | 0.088      | 0.862      | 1.477          |
| 2        | 0.335      | 0.109      | 0.919      | 1.691          | 0.360      | 0.116      | 0.951      | 1.795          |
| 3        | 0.309      | 0.124      | 1.855      | 2.324          | 0.346      | 0.119      | 1.903      | 2.340          |
| 4        | 0.131      | 0.047      | 0.902      | 1.074          | 0.148      | 0.045      | 0.928      | 1.074          |
| 5        | 0.205      | 0.076      | 0.744      | 1.157          | 0.220      | 0.072      | 0.767      | 1.209          |
| 6        | 0.139      | 0.051      | 1.236      | 1.327          | 0.157      | 0.048      | 1.266      | 1.352          |
However, compared with the BJH method, the HPMI method can measure a wider range of pore data corresponding to different pore sizes. The HPMI pore size distribution is more comprehensive than the BJH pore size distribution and can much more accurately reflect the internal pore structure of the core samples.
Comparing the HPMI pore size distribution with the QSDFT pore size distribution, the two pore size distributions have high accuracy and consistency in the same pore size range. However, the HPMI pore volume changes with the pore diameter at certain pore diameter in the mesopores range. That is, $Dv(d)$ is zero, and this is an obvious error. This occurs when the pore diameter is less than 0.01 μm. The comparison results show that the QSDFT pore size distribution can accurately characterize the pore volume and pore size distribution of micropores and mesopores in the sample.
4.4 | Accurate characterization of full pore size distribution by combination method

Through the combination of HPMI and LTN₂GA QSDFT pore size distribution, the pore characteristics of tight sandstones were comprehensively and quantitatively characterized. The results are shown in Figure 16. For the core samples measured in the experiment, the pore diameter corresponding to the connection point of HPMI and QSDFT data is 0.034 μm. That diameter is calculated from largest value of the adsorption isotherms data ($P/P_0 = 1$) via QSDFT method. The pores smaller than 0.034 μm in the combination distribution curve are calculated from LTN₂GA QSDFT method. The pores larger than 0.034 μm were obtained from HPMI data (the red solid line in the figure, obtained from HPMI capillary pressure data from 0-42.65 MPa). The HPMI and QSDFT pore size distribution data showed perfect consistency.

The pore-throat distribution frequency refers to the percentage of the pore volume corresponding to each pore diameter over the total pore volume, which can objectively and truly reflect the characteristics of the full-size pore distribution. It can be seen from the pore-throat distribution frequency curve (the black solid line in the Figure 16) that the sandstones contain small amount of micropores and mesopores, and mainly macropores. The pore-throat distribution frequency diagram can clearly reflect the distribution characteristics of large pores.

The pore volume differential $Dv(d)$ amplifies the variation characteristics of pore volume for micropores and mesopores and reduces the variation characteristics in macropores. Therefore, it is more suitable to characterize the pore size distribution and regularity of micropores and mesopores in the core. The two distribution functions curves are combined to analyze the pore size distribution and the pore development characteristics of the sample. It is clear that pores develop around the pore diameters of 1 nm, 3 nm, and 0.1 μm, and the wave peak presents multi-peak characteristics.

4.5 | Relationship between pore size distribution and physical properties

The full pore size composition of the samples is listed in Table 4. The average proportion of micropores in the samples is just 0.64%, and 17.55% for mesopores and 81.81% for macropores (>50 nm). The average content of micro/mesopores from the combining method's full-size distribution is 18.19%, which is averagely 3.72% higher than that from the HPMI
pore size distribution data. This clearly shows that the HPMI method underestimates the micro/mesopores content, and the QSDFT and HPMI combing method recognizes the microstructures more specifically.

The relationship between the permeability and pore proportions from full pore size distribution is shown in Figure 17. It shows that the permeability of the cores is in a negative correlation with the micro/mesopores proportion. However, the permeability of the cores is in a positive correlation with the macropores proportion.

According to the current internationally recognized pore size scale classification for oil and gas reservoir rock, the pore size composition data are shown in Table 5. Submicron pores (0.1-1 μm) in the measured ultra-low permeability sandstones account for 50.32%, micron pores (1-5 μm) account for 27.80%, and nanoscale pores (0.1 nm-0.1 μm) account for 21.88%. While, the pores in the tight sandstones are mainly composed of submicron pores (67.72%) and nanopores (37.28%). Figure 18 shows the relationship of physical properties and submicron pores proportion. The permeability shows a better negative relationship with submicron pores proportion. But the porosity relationship with submicron pores proportion shows no obvious pattern.

Due to the small pores distributed in the tight reservoir, they are close to the lower limit of the effective fluid flow and almost no natural production capacity occurs in the tight reservoir. It is difficult to develop tight reservoir by water injection because of the high additional flow resistance caused by the strong Jamin effect and extremely narrow pores and throats. And large-scale fracturing transformation is required for this kind of reservoir to be put into production. Further consideration should be given to the development of tight reservoirs using new methods and advanced technologies.

5 | CONCLUSIONS

The physical properties and full pore size distribution characteristics of tight sandstones from Chang 6 reservoir of Changqing oilfield were studied through HPMI, LTN2GA, X-rD, and TIMA experiments. By analyzing pore structural features and comparing different characterizing method for pore size distribution, the conclusions drawn from this study are as follows:

1. The porous spaces in the researched tight sandstones are mainly composed of dissolution pores and micropores, with poor pore-throat connectivity. The HPMI method characterizes the macropores distribution accurately, and

| TABLE 5 | Pore size composition according to scale classification in reservoir rock |
|---|---|---|---|---|
| Core No. | Permeability/10^{-3} μm^2 | Porosity/% | Nanoscale pores (0.1 nm-0.1 μm)/% | Submicron pores (0.1-1 μm)/% | Microscale pores (1-5 μm)/% |
| 1 | 0.019 | 9.68 | 36.25 | 63.75 | 0 |
| 2 | 0.031 | 9.59 | 28.17 | 71.83 | 0 |
| 3 | 0.127 | 16.31 | 30.48 | 69.52 | 0 |
| 4 | 0.257 | 13.04 | 19.2 | 55.15 | 25.64 |
| 5 | 0.317 | 12.45 | 21.7 | 48.97 | 29.33 |
| 6 | 0.39 | 13.06 | 24.72 | 46.85 | 28.43 |

FIGURE 17 Relationship between the permeability and submicron pores proportion

FIGURE 18 Relationship between the physical properties and submicron pores proportion

\[ y = -0.789 \ln(x) + 3.4008 \quad R^2 = 0.8554 \]

\[ y = 15.681 e^{0.004x} \quad R^2 = 0.0506 \]
the micro/mesopores take up of 14.47% of the total pore spaces.

2. The physisorption isotherms of the researched samples take on the combining shape of type II and IV(a), and the hysteresis loops are like type H3 combined with H4. The BET-specific surface area is inversely proportional to the core permeability. The material component corresponding to the adsorption heat constant verified to be quartz and plagioclase, which shows consistence with the petrology analysis.

3. The BJH method has deficiencies in calculating the pore size distribution. Due to the tensile strength effect, the pore size distribution calculated by the desorption curve has a false peak at 3-4 nm. QSDFT method has higher accuracy and can characterize the pore size distribution of micro/mesopores more accurately than the BJH, HPMI, and NLDFT methods.

4. By combining the pores narrower than 34 nm calculated from QSDFT method and pores larger than 34 nm calculated from HPMI data with mercury intrusion pressure lower than 42.65 MPa, the full pore size distribution features of tight sandstones are accurately characterized. The new characterization approach is an effective and precise way to study the pore structure characteristic. And the micro/mesopores from the new combination method are 3.72% more than that calculated from the HPMI data.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section.
APPENDIX 1

NLDFT model
The non-localized density functional theory (NLDFT) in density functional theory (DFT) uses molecular dynamics to describe the fluid in the pores of the adsorbent, which influences the flow behavior in the adsorption experiments. Accurate pore size distribution of micropores and mesopores can be obtained for the samples. NLDFT is based on the assumption that the pore wall of the sample is isotropic and smooth. Given a chemical potential \( \mu \) and a temperature \( T \), the adsorbed fluid in the pores is in equilibrium with the bulk gas, and the adsorption process is usually calculated in the following Grand Canonical Monte Carlo:

\[
\Omega[\rho(r)] = F[\rho(r)] - \int dr \rho(r) (\mu - V_{ext}(r))
\]

\[
= \frac{1}{2} \int dr dr' \rho(r) \rho(r') \phi_{att}(|r-r'|) + k_B T \int dr \rho(r) \ln (\Lambda^3) \tag{41}
\]

\[
+ k_B T \int dr dr' f_{ext}(\rho(r)) - \int dr \rho(r) (\mu - V_{ext}(r))
\]

where \( V_{ext}(r) \) is the external potential energy caused by the pore walls; \( \mu \) is the chemical potential; \( \rho(r) \) is the density distribution curve of the fluid along the vertical direction of the wall surface; \( F[\rho(r)] \) is the Helmholtz free energy and consists of the ideal gas free energy \( F_{id} \) and the excess Helmholtz free energy \( F_{ex} \). \( k_B \) is the Boltzmann constant; \( \eta \) is the stacking factor; \( \Lambda \) is the de Broglie wavelength of the gas; \( \phi_{att}(r) \) is the smooth approximation of \( \rho(r) \) processing (SDA), obtained by the weight function proposed by Tarazona.

The external potential energy \( V_{ext}(r) \) is related to the pore model. When the pore model is a slit pore, the equation is as follows:

\[
V_{ext}(r) = \phi_{CN}(z) + \phi_{CN}(W-z)
\]

where \( W \) is the pore diameter; \( z \) is the distance from the pore wall; \( \phi_{CN} \) is the interaction potential energy between the molecule and the pore wall, which is usually determined by the Steele potential equation. Its equation is as follows:

\[
\phi_{CN}(z) = 2 \varepsilon_{CN} \rho_c \sigma_{CN}^2 \Delta \left[ \frac{2}{3} \left( \frac{\sigma_{CN}}{z} \right)^{10} - \left( \frac{\sigma_{CN}}{z} \right)^{4} - \frac{\sigma_{CN}^4}{3 \Delta (z+0.61 \Delta)} \right] \tag{6}
\]

where \( \varepsilon_{CN} \) is the interaction potential energy parameter between gas and pore wall; \( \sigma_{CN} \) is the effective distance between gas and pore wall; \( \rho_c \) is graphite density; \( \Delta \) is graphite layer spacing.

At equilibrium state, the minimum value of \( \Omega[\rho(r)] \) is obtained using Euler-Lagrange equation or ILM method. The density distribution \( \rho(r) \) expression is as shown in the following Equation (4):

\[
\rho(r) = \Lambda^{-3} \exp \left\{ \varepsilon^{(1)}(r;[\rho_0, \rho_f]) - \beta \int dr' \rho_f(r') \right\} \tag{7}
\]

\[
... \phi_{att}(|r-r'|) + \beta \mu_f - \beta V_{ex}(r) \right\}
\]

where, \( \beta = 1/k_B T \), \( \varepsilon^{(1)}(r;[\rho_0, \rho_f]) = -\beta(\delta F_{ex}[\rho_f(r), \rho_f(r')]/(\delta \rho_f(r)) \).

QSDFT model
In order to improve the analysis accuracy of density functional theory (DFT) on pore size of carbon materials containing micropores and mesopores in low-temperature nitrogen adsorption experiments, Ravikovitch et al. proposed quenching solid density function theory (QSDFT). QSDFT incorporates pore surface roughness and the influence of anisotropy, and constructs a two-component density functional to separate the fluid density from the solid density. Therefore, \( \Omega[\rho(r)] \) of Equation (4) can be rewritten as:

\[
\Omega[\rho_s(r), \rho_f(r)] = F_{id}[\rho_s(r)] + F_{id}[\rho_f(r)] + F_{ex}[\rho_s(r), \rho_f(r)]
\]

\[
+ \frac{1}{2} \int dr dr' \rho_s(r) \rho_s(r') \chi' \left( \frac{|r-r'|}{\eta} \right)
\]

\[
+ \frac{1}{2} \int dr dr' \rho_f(r) \rho_f(r') \chi' \left( \frac{|r-r'|}{\eta} \right)
\]

\[
+ \int dr dr' \rho_s(r) \rho_s(r') \chi' \left( \frac{|r-r'|}{\eta} \right) - \mu_f \int dr \rho_f(r) - \mu_s \int dr \rho_s(r)
\]

where \( \rho_s(r) \) is the density of the solid component; \( F_{id}[\rho_s(r)] \) is the free energy of the hard sphere model solid; \( u_{ss}(r) \) and \( u_{sf}(r) \) are the potential parameter of mutually attraction between the solid solids, and the fluid and the solid respectively; \( \mu_f \) is the chemical potential of solid; \( F_{ex}[\rho_s(r), \rho_f(r)] \) is a mixture of fluid-solid excess free energy in the hard sphere model, which can be approximated by basic metric theory FMT and RLST approximation.

The density distribution of the QSDFT method at equilibrium satisfies the following formula:

\[
\frac{\partial \Omega[\rho_s(r), \rho_f(r)]}{\partial \rho_f(r)} \bigg|_{\rho_s(r)} = 0 \tag{9}
\]

Solving by the Euler-Lagrange equation, the \( \rho(r) \) is shown as follows:

\[
\rho(r) = \Lambda^{-3} \exp \left\{ \varepsilon^{(1)}(r;[\rho_0, \rho_f]) - \beta \int dr' \rho_f(r') \right\} \tag{10}
\]

\[
... \phi_{att}(|r-r'|) + \beta \mu_f - \beta V_{ex}(r) \right\}
\]

where \( \varepsilon^{(1)}(r;[\rho_0, \rho_f]) = -\beta(\delta F_{ex}[\rho_f(r), \rho_f(r')]/(\delta \rho_f(r)) \).
The pore size distribution $f(D)$ is obtained by solving the integral adsorption isotherm equation (IAE), wherein the experimentally measured absorption/desorption isotherm $N_{\text{exp}}(P/P_0)$ is the core model of QSDFT $N_{\text{QSDFT}}(P/P_0)$ is the convolution of the calculated adsorption isotherms set of a certain pore range $N_{\text{QSDFT}}(P/P_0, D)$ and the pore size distribution $f(D)$.

$$N_{\text{exp}}(P/P_0) = \int_{D_{\text{min}}}^{D_{\text{max}}} N_{\text{QSDFT}}(P/P_0, D) f(D) dD \quad (11)$$

where $D_{\text{max}}$ and $D_{\text{min}}$ are the maximum and minimum pore diameter.