Research Article

Effect of Shale Sample Particle Size on Pore Structure Obtained from High Pressure Mercury Intrusion Porosimetry

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With the rapid development of unconventional oil and gas, the pore structure characterization of shale reservoirs has attracted an increasing attention. High pressure mercury intrusion porosimetry (HPMIP) has been widely used to quantitatively characterize the pore structure of tight shales. However, the pore structure obtained from HPMIP could be significantly affected by the sample particle size used for the analyses. This study mainly investigates the influence of shale sample particle size on the pore structure obtained from HPMIP, using Mississippian-aged Barnett Shale samples. The results show that the porosity of Barnett Shale samples with different particle sizes obtained from HPMIP has an exponentially increasing relation with the particle size, which is mainly caused by the new pores or fractures created during shale crushing process as well as the increasing exposure of blind or closed pores. The amount and proportion of mercury retention during mercury extrusion process increase with the decrease of shale particle size, which is closely related to the increased ink-bottle effect in shale sample with smaller particle size. In addition, the fractal dimension of Barnett Shale is positively related to the particle size, which indicates that the heterogeneity of pore structure is stronger in shale sample with larger particle size. Furthermore, the skeletal density of shale sample increases with the decrease of particle size, which is possibly caused by the differentiation of mineral composition during shale crushing process.

1. Introduction

In recent years, more and more attention has been paid to the production of oil and gas from unconventional reservoirs, which will make a great contribution to the world's energy supply in the future [1]. The total shale gas production in the world was 670.3 billion m³ in 2018, with the top three producing countries being the USA, Canada, and China, producing 607.2 billion m³, 48.0 billion m³, and 10.8 billion m³, respectively [2].

Different from conventional hydrocarbon reservoirs, shale reservoirs with low porosity and extralow permeability contain abundant nanopores [3–6], which significantly control the storage and seepage capacity of shale reservoirs [7]. Therefore, it is quite meaningful to characterize shale pore structure, such as pore shape, pore size, and pore connectiv-

ity [8]. Many advanced technologies have been applied in shale pore structure characterization [9–11], such as imaging method (scanning electron microscopy, micro-nano CT, atomic force microscopy, etc.), nuclear magnetic resonance, gas physisorption, and high pressure mercury intrusion porosimetry (HPMIP) [7, 12–20].

HPMIP has been widely used in pore structure characterization of different porous media, such as concrete, food, metallurgy, catalyst, material science, medicine and pharmacy, and chemical and petroleum engineering [21–24]. Recently, HPMIP becomes a very useful tool to quantitatively characterize shale pore structure, and many important pore structure parameters (such as skeletal and apparent density, porosity, pore connectivity, permeability, fractal dimension, and tortuosity) could be derived from HPMIP data [25–29]. The advantages of HPMIP include simple

TABLE 1: Six particle sizes of shale sample B7191.

Mesh	Bulk	Large than 20 mesh	20-50 mesh	50-100 mesh	100-270 mesh	Less than 270 mesh
Particle size range/ μm	5000	>830	270-830	150-270	53-150	<53
Representative particle size/ μm	5000	2915	550	210	102	27

principle [30], wide pore-throat size coverage (3 nm~300 μm) [28, 31], and short experimental time (~2 hours) [32, 33]. However, HPMIP has some shortcomings. For example, mercury is toxic, and its leakage may cause a damage to human health. In addition, samples tested by HPMIP are contaminated by mercury and cannot be reused for other pore structure analyses.

One of the basic assumptions for HPMIP analysis is the cylindrical pore shape. However, the actual pore morphology of shale samples is very complex, which could cause a deviation between HPMIP results and the real pore structure [34, 35]. The contact angle used in HPMIP is usually a constant value. However, the actual contact angle could change in different compositions of shale samples due to their strong heterogeneity, which could also make the HPMIP results deviate from the actual situation [36, 37].

Furthermore, the particle size of shale sample also has a great influence on the results of pore structure measured by HPMIP, which is known as the particle size effect. HPMIP can be used to determine the pore structure of intact shale samples or crushed shale samples (such as cuttings). However, there is no standard particle size of shale sample recommended for HPMIP, and different particle sizes were used in different studies. For example, Rourke [38] used a horizontal 1 inch core plug, and Gao et al. [39] used irregular shale samples at ~1 cm in linear dimensions. This could lead to differences in pore structure information even if the same shale sample was used due to the particle size effect. During HPMIP analysis, mercury could enter larger pores through narrower pore throat, and these larger pores are counted as smaller pores. Consequently, the intact shale sample is not the ideal target used for revealing the real pore structure information by HPMIP, and smaller particle size was used in HPMIP analysis in order to obtain more reliable pore-throat size distribution [40]. However, few previous studies were conducted on the influence of sample particle size on pore structure derived from HPMIP and its causing mechanisms [41].

By comparing the pore structure parameters of Barnett Shale samples with different particle sizes obtained from HPMIP, this study investigates the influence of particle size on the HPMIP results and the influencing mechanism. The outcomes of this study will promote the application of HPMIP in the pore structure characterization of shale reservoirs. In addition, hydraulic fracturing is an important technology to extract shale petroleum [42–45]. Previous studies have shown that the pore structure of fractured shale varies with the concentration of proppant in fracturing fluid. For example, after water fracturing, the change of pores with large pore throat is very small, and the proportion of pore throat is increased. The use of clean water plus 1% ceramicsite proppant resulted in high proportion of large pore throats

and large pore sizes in fractured shales, with the highest shale permeability [46–49]. The fracturing process of shale reservoir is also one type of sample crushing process, which reduces the size of shale matrix and changes the original pore system. Shale gas production behavior is very complicated, and large amounts of fracturing fluids are commonly retained within shale reservoirs after shale gas production, both of which are significantly affected by the fractured shale pore system. Therefore, the outcomes of this study also have a great significance for the improved understanding of shale gas production mechanism and the retention mechanism of fracturing fluids.

2. Samples and Experimental Methods

2.1. The Experimental Samples. The Mississippian Barnett Shale sample B7191 at the depth of 2191.82 m (7191 ft) from Blakely #1 core in Wise County of Texas was used in this study. Barnett Shale was a marine shelf deposit, and its thickness is from 61 to 305 m across the Fort Worth Basin. Barnett Shale can be divided into three sublayers: upper Barnett Shale, Forestburg limestone, and lower Barnett Shale [50]. The upper and lower Barnett Shale is mainly composed of siliceous mudstone while interbedded lime mudstone is less developed. The Forestburg limestone is composed of argillaceous lime mudstone [51]. The mineral composition of Barnett Shale is as follows: quartz and plagioclase (45 wt%-55 wt%), carbonates (mainly calcite, some dolomite and siderite) (15 wt%-25 wt%), clay minerals (20 wt%-35 wt%), and pyrite (2 wt%-6 wt%) [51, 52]. The total organic carbon (TOC) content of Barnett Shale is about 3.5 wt%~4.5 wt%, and the kerogen is mainly type II.

The mineral composition of sample B7191 is mainly quartz, feldspar, clay minerals, and pyrite. The TOC of B7191 is about 3.8%, and its porosity is about 4.8% based on ~1.5 cm-sided cube [50, 52]. The sample B7191 was pulverized manually by hammer and then sieved through sieves with different mesh sizes. As shown in Table 1, the particle size of sample B7191 is divided into six grades to be used in this work. The representative particle size uses the average of two bounding sizes for result plotting.

2.2. The Theory of HPMIP. Micromeritics AutoPore IV 9510 was used to perform HPMIP tests in this study. This instrument could generate the highest pressure of 60,000 psia (413 MPa) and detect the pore-throat diameter down to 3 nm. All the samples were dried in a 60°C oven for more than 48 hours before the HPMIP experiment in order to remove the moisture within pore spaces.

2.2.1. The Principle of HPMIP. Mercury is a nonwetting fluid to most rocks including shale and external pressure should

FIGURE 1: Cumulative mercury intrusion volume of shale samples with different particle sizes: (a) complete mercury intrusion curves; (b) removal of mercury intrusion volume in pores larger than 10 μm ; (c) removal of mercury intrusion volume in pores larger than 20 nm; (d) cumulative mercury intrusion volume of shale with different particle sizes for different pore sizes.

be applied on mercury to push it into pore spaces. The diameter of pores that mercury could enter is inversely proportional to the applied pressure, and this relationship was presented by Washburn's equation [53] on the basis of assuming that all the pores were cylindrical [54, 55], which is shown in Equation (1):

$$D = -4\gamma \cos \frac{\theta}{P}, \quad (1)$$

where D is the pore diameter, γ is the surface tension of mercury (485 dyne/cm) [28], θ is the contact angle between mercury and pore surface (130°) [28], and P is pressure.

2.2.2. Fractal Dimension Derived from HPMIP. Fractal theory is a mathematical method to describe the irregularity and complexity of materials as well as other nonlinear problems [26, 40, 56–58]. The fractal dimension of pore structure should be between 2 and 3 [36, 55, 59], which can reflect the complexity of pore structure [36, 60]. Recently, fractal dimension has been used to quantify the heterogeneity of shale pore structure [40, 61, 62]. The larger the fractal dimension is, the stronger is the heterogeneity [61, 63, 64].

For HPMIP tests, Mandlbrot's method [4, 26, 65] was used to obtain the fractal dimension of shale pore structure, which is shown in Equation (2):

$$\ln S_{\text{Hg}} = (D - 2) \ln P_c + \ln \alpha, \quad (2)$$

FIGURE 2: Pore structure models modified from Giesche (2006): (a) before breakage; (b) after breakage.

FIGURE 3: Pores with different seepage channels in the rock: (a) before breakage; (b) after breakage.

where D is the fractal dimension, S_{Hg} is the mercury saturation, P_c is the capillary pressure, and α is a constant.

3. Results and Discussion

3.1. Effect of Sample Particle Size on the Cumulative Intrusion Volume. During the early mercury intrusion stage with low intrusion pressures, mercury entered large pores. A large proportion of these large pores were interparticle pores generated artificially due to the loose packing of powdered shale particles, which was also treated as conformance effect [50]. As a result, the mercury intrusion volume during this early stage could not reflect the actual pore volume. As shown in Figure 1(a), the relationship between mercury intrusion volume and sample particle size was weak when the pores larger than $10\mu\text{m}$ were taken into account. In order to eliminate the influence of artificial pores or conformance effect, the mercury intrusion volume of pores larger than $10\mu\text{m}$ was subtracted from the cumulative mercury intrusion volume, which was shown in Figure 1(b). In order to define the lower pore size limit that sample particle size can affect the cumulative mercury intrusion volume, mercury intrusion volume of pores larger than 20nm was also removed in Figure 1(c). As shown in Figures 1(b)–1(d), the cumulative mercury intrusion volume increased with the

decrease of sample particle size for pores less than 20nm and pores between 20nm and $10\mu\text{m}$, which indicated that the sample particle size could affect the mercury intrusion volume of both mesopores ($2\text{--}50\text{nm}$ in diameter) and macropores ($>50\text{nm}$).

For HPMIP tests, the effect of sample particle size on cumulative mercury intrusion volume is related to the pore structure of shale. According to the pore accessibility, pores in shale could be divided into connected pores, cross-linked pores, blind pores, and closed pores as shown in Figure 2(a) [66]. The connected pores and cross-linked pores have good connectivity and seepage capacity, and the mercury is easy to flow into and occupy these pores. For blind pores with poor connectivity and isolated/closed pores, it is difficult for mercury to enter these pores, and HPMIP can hardly recognize the information of such pores.

The original shale pore structure could be changed during the sample crushing process. For example, the closed pores and blind pores could be exposed to external space during crushing process, thus improving the pore connectivity of these pores (as shown in Figure 2(b)).

In addition, the crushing process is accompanied by strong external forces, which could create new pores or cause the merging and collapse of pores [67], especially on the surface and inside of brittle minerals.

FIGURE 4: Continued.

FIGURE 4: The incremental mercury intrusion volume of shale samples with different particle sizes: (a) complete curve; (b) pore size range of 20 nm–10 μm ; (c) pore size range of 3–20 nm; (d) the relationship between the incremental pore volume difference with 5000 μm particle size and pore diameter; (e) the relationship between incremental pore volume and shale particle size.

As shown in Figures 1(b) and 1(c), the increment of cumulative mercury intrusion volume with a decrease of particle size in the pore size range of 20 nm–10 μm was much higher than that under 20 nm.

Previous studies showed that the micropores (<2 nm in diameter) and some mesopores were mainly organic matter-hosted pores and intergranular pores of clay minerals, which had relatively long seepage channels [24]. The longer the seepage channel is, the more likely it is to be connected with the external space by crushing as shown in Figure 3. According to Figure 1(b), the pore volume of larger pores increased more obviously with the decrease of particle size, compared with micropores and small mesopores. It is speculated that the total volume of smaller mesopores is much lower than that of macropores, and the seepage channel of larger pores is possibly longer than smaller pores. Consequently, the crushing of the sample is more likely to increase the connectivity of macropores.

As a result, the pore volume of sample B7191 increased with the decrease of particle size, which was due to the increased pore accessibility caused by the newly generated pores and the exposure of both blind and closed pores resulting from sample crushing.

Some studies pointed out that sample crushing could result in the differentiation of mineral composition. For example, clay minerals have good elasticity and are distributed among mineral particles in shale, which are easy to break away from shale during crushing process [51]. However, brittle minerals such as quartz and feldspar, which have

larger particle size and stronger hardness, are likely to remain in shale during crushing process. The affinity of mercury to different minerals is different, and different external pressures were required for mercury to enter the pores with the same pore size associated with different minerals. Consequently, the measured pore structure information by HPMIP could also be affected by mineral differentiation caused by sample crushing process.

3.2. Effect of Sample Particle Size on the Incremental Pore Volume. As shown in Figure 4(a), the incremental pore volume of pores between 20 nm and 10 μm has a good relationship with the sample particle size of B7191 while this relationship disappeared for pores less than 20 nm.

As shown in Figure 4(b), the pore volume of a certain pore size in the range of 20 nm–10 μm generally increased with the decrease of the sample particle size. More specifically, there was an exponential relationship between pore volume and sample particle size (Figure 4(e)). Furthermore, the incremental pore volume difference between B7191 sample with 5000 μm particle size and other smaller particle sizes became more obvious with the increase of pore size in the range of 20–200 nm as shown in Figure 4(d). However, an opposite phenomenon was observed for pores larger than 200 nm.

It is speculated that in the pore-throat size range of 20–200 nm, the length of seepage channel increased with the increase of pore size, which made larger pores more easily to be connected with external surface during the sample

crushing process while the length of seepage channel became shorter as the pore size increased in the range of >200 nm.

For pores between 3 nm and 20 nm, no obvious relationship existed between the incremental pore volume and sample particle size (Figure 4(c)), which indicated the sample crushing process had a random effect on the pore volume and connectivity of pores below 20 nm.

3.3. Effect of Sample Particle Size on the Mercury Retraction Efficiency. The hysteresis phenomenon between mercury intrusion curve and extrusion curve was observed for all sample sizes in Figure 5. Several theories, such as contact angle hysteresis, the effect of ink-bottle pores, and penetration-connectivity model [25], have been proposed to interpret the hysteresis phenomenon, and the effect of ink-bottle pores was used in this study. Ink-bottle pores are the pores connected with external surface through much smaller pore throats (Figure 6). During mercury extrusion process, the flow of mercury would easily break in the narrower pore throats, which could make the mercury stuck within the shale sample and then lead to the hysteresis phenomenon.

As shown in Figure 7(a), the mercury retention volume for pores between 20 nm and $10\mu\text{m}$ and pores between 3 nm and $10\mu\text{m}$ showed a consistent trend, with increasing volume with the decrease of sample particle size. More specifically, the mercury retention volume significantly increased when the sample particle size became less than $102\mu\text{m}$. Consequently, many pore throats larger than 20 nm appeared when blind pores were connected with external surface and new pores were produced during sample crushing process, which could enhance the ink-bottle effect and lead to more mercury retention volume. However, the mercury retention volume did not increase significantly with the decrease of sample particle size for pores between 3 nm and 20 nm.

The mercury retention rate is defined as the ratio of the mercury retention volume to the mercury intrusion volume. For all the shale samples with different particle sizes, the mercury retention rate of pores between 3 nm and 20 nm was significantly higher than that of pores between 20 nm and $10\mu\text{m}$ (Figure 7(b)), which indicated that the effect of ink-bottle pores was more obvious in smaller pores. As shown in Figure 7(c), the smaller the pore-throat diameter is, the greater is the mercury retention rate.

3.4. Effect of Sample Particle Size on Fractal Dimension. The fractal curves of the six B7191 samples with different particle sizes were presented in Figure 8, which showed two or three trend lines with different slopes. The fractal dimensions (D_1 , D_2 , D_3) of six B7191 samples with different particle sizes and their corresponding pore size ranges are presented in Figures 9(a)–9(c).

D_1 corresponded to larger pores, and D_3 corresponded to smaller pores while D_2 fell between D_1 and D_2 . As shown in Figures 8(d) and 8(e), D_2 and D_3 had the same value for sample B7191 with particle sizes of $210\mu\text{m}$ and $102\mu\text{m}$. For most of the shale samples used in this study, the fractal dimensions showed the order of $D_1 > D_3 > D_2$ (Figure 9(a)).

FIGURE 5: Mercury intrusion and extrusion curves of shale samples with different particle sizes.

FIGURE 6: Schematics of ink-bottle pores.

The pore structure of larger pores was most heterogeneous, followed by the smaller pores, and the pore structure of middle range pores was less heterogeneous.

In addition, D_1 presented an S-shaped curve with the decrease of sample particle size as shown in Figure 9(a), and the effect of sample particle size on these larger pores was relatively random due to the influence of loose packing or conformance.

It can be seen that D_2 and D_3 basically showed a decreasing trend with the decrease of sample particle size, indicating

FIGURE 7: Effect of particle size and pore size on mercury retention. (a) The relationship between mercury retention volume and shale particle size. (b) The relationship between mercury retention rate and shale particle size. (c) Schematic diagram of mercury retention within different pore-throat systems.

that sample crushing process reduced the pore structure complexity of smaller pores.

Figure 9(c) showed that the corresponding pore size range of D_2 first increased with the decrease of the sample particle size, reached the maximum value for the sample with particle size of 210 μm , and then decreased continuously. The D_2 of the sample with particle size of 210 μm had the lowest value, and the corresponding pore size range of D_2 was the largest. This indicated that a certain degree of crushing greatly increased the amount and pore size range of pores with less heterogeneity, but excessive crushing could lose this effect.

One possible reason for this phenomenon is that the new pores were produced instantaneously by crushing without experiencing complicated diagenetic processes and had very smooth surfaces. However, if the particle size was too small, the newly generated pores during crushing process tended to have complex surfaces (Figure 10(b)).

3.5. Effect of Sample Particle Size on Other Pore Structure Parameters. The bulk density of shale sample B7191 decreased gradually with the decrease of sample particle size (Figure 11(a)), which was due to the new pore spaces generated during the sample crushing process. However, the skeletal density increased with the decrease of sample particle size (Figure 11(a)), which was probably caused by the differentiation of mineral compositions during the sample crushing process. The densities of clay minerals are generally lower than those of brittle minerals [68–71]. Therefore, the sample crushing process could make more clay minerals to break away from the shale sample, leading to the larger skeletal density of samples with smaller particle sizes.

As shown in Figures 11(b)–11(d), porosity, average pore size, and total mercury intrusion volume showed a roughly increasing trend with the decrease of sample particle size. The exponential relationship between porosity and sample

FIGURE 8: Fractal dimensions of shale samples with different particle sizes: (a) 5000 μm ; (b) 2915 μm ; (c) 550 μm ; (d) 210 μm ; (e) 102 μm ; (f) 27 μm .

particle size was presented by Equation (3).

$$\varnothing = 66.18e^{-0.00223L}, \quad (3)$$

where φ is the porosity (%) and L is the sample particle size (μm).

However, permeability, the median pore diameter (volume), and total pore area showed a peak value when the

FIGURE 9: Effect of particle size on fractal dimensions of shale pore structure. (a) Fractal dimensions d_1 , d_2 , and d_3 of shale samples with different particle sizes. (b) Fractal dimensions d_2 and d_3 of shale samples with different particle sizes (excluding d_1). (c) The pore size ranges of fractal dimensions d_1 , d_2 , and d_3 of shale samples with different particle sizes.

FIGURE 10: Effect of particle size on shale pore structure: (a) larger shale particle size; (b) smaller shale particle size.

FIGURE 11: The relationship between pore structure parameters and particle size: (a) skeletal density and bulk density; (b) porosity and permeability calculated according to Katz and Thompson (1986); (c) median pore diameter and average pore diameter; (d) total mercury intrusion volume and total pore area.

sample particle size is 210 μm. The pore size range of smooth pores (D_3) in the sample with particle size of 210 μm was also the largest (Figure 9(c)), which indicated the smooth pores tended to have higher permeability.

3.6. The Models for Shale Samples with Different Particle Sizes. Based on the abovementioned viewpoints, two mercury intrusion and extrusion models were established for shale samples with coarse and fine particle sizes (Figure 12). There are two parts in the shale with identical pore structure before sample crushing process, which contains ink-bottle pores, ordinary pores (throat $d_1 > d_3$) and closed pores with different seepage lengths (Figure 12(a)).

The mercury intrusion and extrusion processes of shale with coarse (before sample crushing process; Figure 12(b))

and fine particle (after sample crushing process; Figure 12(c)) are divided into 5 stages: low pressure intrusion, high pressure intrusion, higher pressure intrusion, high pressure extrusion, and low pressure extrusion.

During low pressure intrusion, mercury firstly enters pores with larger pore throat of d_1 . During high pressure mercury intrusion, mercury enters pores with smaller pore throat of d_2 . As the shale particle size decreases, closed pores with long seepage channels are connected with external surface, and some new pores with narrower pore throat of d_3 are generated. Therefore, mercury begins to fill the pores with pore throat of d_3 under higher intrusion pressure (Figure 12(c)).

During the extrusion process, mercury firstly comes out of pores with smaller pore throats under higher pressure and

FIGURE 12: Schematic of mercury intrusion and extrusion in shale with different particle sizes: (a) shale sample with two identical parts; (b) shale sample with relatively large particle size before sample crushing process; (c) shale sample with relatively small particle size after sample crushing process.

then pores with larger pore throats under low pressure. Ordinary pores with cylindrical shape show a complete mercury extrusion while some part of intruded mercury is retained within ink-bottle pores and ink-bottle pores with smaller pore throats have higher mercury retention efficiency.

4. Conclusions

- (1) New pore spaces were generated, and the pore accessibility of blind-closed pores was increased during sample crushing process, both of which increased the measured porosity and pore volume
- (2) The effect of sample particle size on pore volume measured by HPMIP varied for pores with different pore sizes. For pores less than 20 nm, the effect of sample particle size on pore volume was limited while the decrease of sample particle size significantly increased the pore volume for pores between 20 nm and 10 μm
- (3) With the decrease of shale sample particle size, the effect of ink-bottle pores was enhanced, leading to the increase of mercury retention during mercury extrusion process. Moreover, the smaller the pore throat is, the greater will be the mercury retention rate
- (4) The fractal dimensions showed the order of $D_1 > D_3 > D_2$, which indicated that the pore structure of larger pores in shale was more complex. D_2 and D_3 were positively related with the sample particle size, indicating that sample crushing process reduced the pore structure complexity. In addition, B7191 sample with particle size of 210 μm had the largest amount and pore size range of smooth pores, increasing its permeability
- (5) Sample crushing process could lead to the differentiation of mineral compositions. Clay minerals are easy to be lost while brittle minerals tend to retain during sample crushing process. Therefore, the skeletal density increased with the decrease of sample particle size

Data Availability

The data in this manuscript will be available up on the readers' request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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