Influence of particle size on gas-adsorption experiments of shales: an example from a Longmaxi Shale sample from the Sichuan Basin, China

Hui Han,^{*, a, b} Yan Cao,^a Shi-jia Chen,^a Jun-gang Lu,^a Cai-xia Huang,^a Hai-hua Zhu,^a Pan Zhan,^a Yuan Gao^c

^aSchool of Geoscience and Technology, Southwest Petroleum University, Chengdu, Sichuan 610500, P. R. China

^bKey Laboratory of Tectonics and Petroleum Resource (China University of Geosciences), Ministry of Education, Wuhan 430074, P. R. China

^cBeijing Center for Physical and Chemical Analysis, Beijing 100089, P. R. China

ABSTRACT: To explore the optimum particle size range for low-pressure gas adsorption experiments of shales, a sample of the Longmaxi shale from the Sichuan Basin, China, was crushed into various particle sizes between 4 and 0.058 mm. Low-pressure CO₂ and N₂ adsorption experiments were then performed on these crushed samples, and the pore volume, surface area, and pore size distribution (PSD) were determined from isotherms of gas adsorption. Variations in the volume of sorbed gas, pore volume, surface area, and PSD were recorded across the two series of experiments. In the CO₂ adsorption experiments, in which

particle size ranged from 4 to 0.83 mm, sorbed gas volume, pore volume, and surface area increased with decreasing particle size. No obvious changes were found in sorbed volume, pore volume, surface area, or PSD for the samples with particle sizes from 0.83 to 0.058 mm. In the N₂ adsorption experiments, the sorbed gas volume and surface area increased with decreasing particle size in samples from 4 to 0.113 mm, whereas no obvious variations were observed in the 0.113 to 0.058 mm samples. Similarly, pore volume and PSD showed clear changes with decreasing particle size for the 4 to 0.113 mm samples. The results show that 0.113 mm (130 mesh) is the optimum particle size for low-pressure CO₂ and N₂ adsorption experiments that seek to analyze the characteristics of shale reservoirs.

Key Words: Sichuan Basin; Longmaxi Shale; low-pressure gas adsorption; particle size; pore structure.

1 INTRODUCTION

Shale gas is an important unconventional gas resource that has been developed commercially in North America and China [1, 2]. Due to its potential impact on gas storage and production, shale reservoir properties have been extensively studied. Scanning electric microscopy (SEM) [3-6], atomic-force microscopy (AFM) [7], mercury intrusion porosimetry (MIP) [8], computed tomography (CT) scanning ([9, 10], nuclear magnetic resonance (NMR) [11], low-pressure gas adsorption (LPGA) [12], and small angle X-ray and neutron scattering are all used to evaluate the reservoir potential of shales [13, 14]. Compared with other methods, LPGA experiments are cost-effective and can provide quantitative information on the pore system in shale. Therefore, LPGA measurements are used extensively when studying the reservoir potential of shale.

In LPGA experiments, shale samples need to be crushed before measurement; however, there is no standard particle size for the crushed shale. Although 0.25 mm (60 mesh) is most widely used [15-18], previous studies have also used 8 mm [19], 0.25–1.4mm [20], 0.38 mm [21], and 0.15 mm [22]. Given that particle size can influence the pore volume, surface area, and PSD results obtained from LPGA experiments [23], it is important that a consistent particle size range be used to obtain reliable and comparable results of pore characteristics. Chen et al. [23] performed CO₂ and N₂ LPGA experiments on New Albany Shale samples with particle sizes of 4.75, 0.83, and 0.25 mm, revealing that pore volume increases with decreasing particle size. This trend is ascribed to incomplete equilibration of the interior of larger shale particles during LPGA experiments [24]. Accordingly, Chen et al. [23] suggested a particle size below 0.83 mm for LPGA experiments. However, the particle size range used in their experiments was relatively narrow, and the trend of pore volume in shale samples with smaller particle sizes may be different from that observed for sizes of between 4.75 and 0.25 mm. Therefore, the influence of particle size on LPGA experiments across a wider range of particle sizes needs to be explored.

In this study, a sample of Longmaxi Shale from the Sichuan Basin was crushed to particle sizes ranging from 4 to 0.058 mm. Low-pressure gas adsorption experiments (CO₂ and N₂) were then conducted with the aim of assessing the influence of particle size on shale micro- and meso-pore parameters such as pore volume, specific surface area, PSD, and sorbed gas volume. Finally, the optimal particle size ranges for shale samples used in low-pressure CO₂ and N₂ adsorption experiments are suggested.

2 SAMPLE AND METHODS

2.1 Shale sample

The Longmaxi Shale is the most important shale gas target in China [25]. In this study, a sample of the Lower Silurian Longmaxi Formation was collected from a shale gas well in the Sichuan Basin, Southwestern China. A CS-230 elemental analyzer (Leco Corporation, USA) was used to determine total organic carbon (TOC) content and a D/MAX 2500 X-ray diffractometer was used to measure mineral compositions. The reflectances of the solid bitumen were measured using a MPV-III microphotometer.

The results of the TOC measurements show that the selected sample is organic-rich and has a TOC content of 5.36 wt.% and a eqR_o value [26] of 1.59% (Table 1). Mineralogical analyses indicate the sample consists mainly of clay minerals (38.5 wt.%) and quartz (35.3 wt.%) with minor feldspar (9.1 wt.%), dolomite (8.6 wt.%), pyrite (7.4 wt.%) and calcite (1.1 wt.%). Mixed-layer illite/smectite and illite form the dominant clay minerals in the studied sample (Table 1).

2.2 Low-pressure gas adsorption experiments

The studied sample was crushed to 4, 0.83, 0.38, 0.25, 0.15, 0.113, 0.106, 0.075 and 0.058 mm (corresponding to 5, 20, 40, 60, 100, 130, 150, 200 and 250 mesh, respectively) with a pestle and mortar. The samples were then dried in an oven overnight at 110 °C and degassed under high vacuum (<10 mmHg) for 12 h at 110 °C [27].

Low-pressure CO₂ and N₂ adsorption experiments were performed using a Micromeritics^R ASAP 2020 surface area analyzer. One to two grams of each of the crushed and degassed samples were exposed to CO₂ and N₂ at the temperatures of 0 °C and −196.15 °C, respectively. CO₂ and N₂ adsorption volumes were measured over the relative equilibrium adsorption pressure (P/P_o) ranges of 0.0005–0.0300 and 0.050–0.995, respectively, where P_o is the condensation pressure of CO₂ or N₂ under laboratory conditions, and P is the actual gas pressure. CO₂ molecule can access pores with diameter from 0.35 to 1.5 nm, while N₂

adsorption can reflect the pores with diameter between 1.2 and 100 nm. Although the molecule diameter of CO₂ (0.387 nm) is larger than the N₂ (0.315 nm) [28], CO₂ adsorption experiment was performed at 0 °C, the corresponding temperature for N₂ adsorption was −196.15 °C. At the experimental temperatures, the thermal energy of CO₂ molecule is greater than N₂, which makes CO₂ molecule can penetrate smaller pores [29]. Therefore, the pores measured using low-pressure CO₂ adsorption experiment are smaller than low-pressure N₂ adsorption experiment.

The pore volume, surface area, and pore size distribution (PSD) of each sample were then calculated using the density functional theory method (DFT) [30, 31]. This method was chosen because it provides a more accurate description of the thermodynamic properties of the gas in the pores [32]. For N₂ adsorption, the adsorption branches of the isotherms were used.

3 RESULTS AND DISCUSSION

3.1 Low-pressure CO₂ adsorption

3.1.1 Isotherms

Figure 1 shows the low-pressure CO₂ adsorption (LPGA-CO₂) isotherms for each of the studied size grades. The isotherms are Type I, which indicates the studied sample is a microporous solid. The volume of sorbed CO₂ increases with decreasing particle size from 4 to 0.83 mm (Figure 1a, b); however, no discernable variation in the volume of sorbed CO₂ is observed in the 0.83 to 0.058 mm samples (Figure 1b–i). Higher sorbed CO₂ volumes in the 0.83 to 0.058 mm samples can be attributed to the higher degree of crushing of these samples. Figure 2 shows how crushing can expose pores trapped in larger particles. In the larger particle shown in Figure 2 (diameter = 4 mm) there is an open pore and a closed pore. The

CO₂ can pass through the open pore but not the closed pore. In the smaller particle (diameter = 0.83 mm), CO₂ can pass through both pores, which are both open. The sorbed CO₂ volume recorded for samples with a higher abundance of smaller particles (≤ 0.83 mm) is therefore greater than for the sample containing larger particles (≥ 4 mm).

3.1.2 Pore volume and surface area

The pore volumes obtained from the LPGA-CO₂ experiments vary from 0.0034 to 0.0055 cm³/g (Table 2). Surface area results calculated from the LPGA-CO₂ data vary from 9.99 to 16.85 m²/g (Table 2).

The relationship between particle size and each of calculated pore volume and surface area in the studied shale samples are shown in Figures 3. The patterns observed in pore volume and surface area across the particle size range considered here match those of the volume of sorbed CO₂ recorded. LPGA-CO₂ measurements show an increase in pore volume with decreasing particle size from 4 to 0.83 mm, and only minor differences in pore volume between the 0.83 and 0.058 mm samples (Figure 3a).

The pattern for LPGA-CO₂-calculated surface area follows that of LPGA-CO₂-calculated pore volume. Minor fluctuations in the volume of CO₂ are seen for the 0.83 to 0.058 mm samples, which all appear to contain a higher surface area than the 4 mm sample (Figure 3b).

3.1.3 Pore size distribution

The pore size distribution (PSD) calculated for each sample using the LPGA-CO₂ data is shown in Figure 4. For the 4 mm sample there are two major peaks at pore size diameters of 0.6 and 0.8 nm (Figure 4a), whereas the 0.83–0.058 mm samples show three major peaks at pore diameters of 0.4, 0.6, and 0.8 nm (Figure 4b–i). Note that the relative heights of these three major peaks are similar in all samples finer than 4 mm, with the exception of the 0.83

mm sample which appears to contain a more significant 0.6 nm peak. Analysis of the pore size distribution in these Longmaxi Shale samples indicates that as particle size decreases from 4 to 0.83 mm, a peak representing a pore diameter 0.4 nm appears in all samples from 0.83 to 0.058 mm. The magnitude of this peak increases as particle size decreases from 0.83 to 0.25 mm, then remains relatively constant in samples with a particle size from 0.15 to 0.058 mm (Figure 4). The increase in the magnitude of this peak with decreasing particle size from 0.83 to 0.25 mm may result from the exposure of trapped pores as a consequence of intense crushing (Figure 2).

3.1.4 Influence of particle size

According to the results above, there are no significant changes in the volume of sorbed CO₂, pore volume, surface area, or PSD in samples with particle sizes of 0.83 to 0.058 mm. Our results indicate that for the Longmaxi Shale a particle size no coarser than 0.83 mm is adequate for LPGA-CO₂ experiment.

3.2 Low-pressure N₂ adsorption

3.2.1 Isotherms

The low-pressure N₂ adsorption (LPGA-N₂) isotherms of the studied samples are shown in Figure 5. According to the Brunauer, Deming, Deming, and Teller classification [33], the LPGA-N₂ isotherms are Type II, indicating that multi-layer adsorption has occurred in the studied samples. The volume of sorbed N₂ increases with decreasing particle size from 4 to 0.113 mm (Figure 5a–f). The 0.106 mm sample has lower adsorption than the 0.113 mm sample. And the 0.075 mm sample has higher adsorption than the 0.106 and 0.058 mm samples. There is no obvious variation in the volume of sorbed N₂ for samples with a particle size between 0.113 and 0.058 mm. All the studied samples show hysteresis loops of type H₄ [34, 35], indicating the pores are slit-type. Note that the hysteresis loop of the 4 mm sample

(Figure 5a) can be attributed to the adsorption of nitrogen in micropores [34]. The hysteresis loops in the LPGA-N₂ experiments become tighter as particle size decreases from 4 to 0.058 mm (Figure 5). This trend is similar to that reported by Chen et al. [23], who attributed this phenomenon to the shorter distance needed for desorption to occur in samples containing smaller particles. Consequently, less gas is trapped in pores during desorption.

Noticeably, both the N₂ and CO₂ adsorption measurements show the same initial trend, with the volume of sorbed gas increasing as particle size decreases; however, this trend is observed over a boarder particle size range in the N₂ experiments (4–0.113 mm) compared than in the CO₂ analyses (4–0.83 mm). This difference may relate to the detection limits of the LPGA-CO₂ and LPGA-N₂ experiments. Carbon dioxide adsorption has a lower detection limit (0.35 nm) than nitrogen adsorption (1.2 nm) [36, 37]; in effect, CO₂ can enter into smaller pore throats than N₂. This is illustrated in Figure 6. For samples with a particle size of 4 mm, the pore throat labeled ‘a’ in Figure 6 is open to both CO₂ and N₂, whereas that labeled ‘b’ is closed. When the particle size decreases to 0.83 mm, pore throat ‘a’ is still open to CO₂ and N₂; however, pore throat ‘b’ is now wide enough for CO₂ to enter but not N₂. For a particle size of 0.38 mm, pore throats ‘a’ and ‘b’ are wide enough to be detected during LPGA-CO₂ and LPGA-N₂ experiments.

3.2.2 Pore volume and surface area

Pore volume calculations from the LPGA-N₂ measurements range from 0.0076 and 0.0258 cm³/g (Table 2). The surface areas obtained from the LPGA-N₂ data range from 10.43 to 22.52 m²/g (Table 2).

LPGA-N₂ measurements indicate an increase in pore volume with decreasing particle size from 4 to 0.113 mm, there is no obvious variation in LPGA-N₂-calculated pore volume for samples with a particle size between 0.113 and 0.058 mm (Figure 7a). LPGA-N₂

measurements show an increase in surface area as particle size decreases from 4 to 0.113 mm, but then a slight decrease in surface area from 0.113 to 0.058 mm (Figure 7b).

The surface area is calculated by dividing the area by the mass of the sample. It is assumed that the total pore volume is constant; consequently, the smaller the pore size, the larger the surface area. The observed trend in the LPGA-N₂ surface area values for the 4 to 0.113 mm samples therefore represents an increase in the number of open pores contributing to the overall pore volume as particle size decreases. In contrast, more big pores are open for detection in samples with particle sizes from 0.113 to 0.058 mm. This explanation is supported by the relationships between surface area and pore volume (Figure 8). Initially, the surface area increases as pore volume increases, but then remains constant as pore volume continues to increase. This suggests that the increase in pore volume results from contributions from bigger pores that would have little impact on surface area.

3.2.3 Pore size distribution

The PSD calculated for each sample using the LPGA-N₂ data is shown in Figure 9. The 4 mm sample has a wide peak at 2–5 nm (Figure 9a). The 0.83 to 0.058 mm samples show two major peaks at 2 and 3–5 nm (Figure 6b–i). In these finer samples the magnitude of the 2 nm peak appears to decrease with decreasing particle size from 0.38 to 0.058 mm.

The pore size distribution shows a peak at 2 nm and another between 3 and 5 nm, both of which increase as the particle size decreases from 4 to 0.38 mm (Figure 9). This increase is likely to be related to the size of pores that can be detected in N₂ adsorption (Figure 6). The height of the 2 nm peak decreases as particle size decreases from 0.38 to 0.058 mm, indicating a decrease in the abundance of pores of <2 nm in size.

3.2.4 Influence of particle size

According to the results in section 3.2, LPGA-N₂-obtained sorbed gas volume, pore volume, surface area, and PSD show no significant differences between the 0.113 and 0.058 mm samples. For the shale samples with particle sizes coarser than 0.113 mm, these parameters mentioned above varied significantly. It can be attributed to that the N₂ can't penetrate all the pores in the shale samples. The abundance of pores that N₂ penetrate increased with the decreasing particle size in samples from 4 to 0.113 mm. When the particle size decreased to 0.113 mm, the N₂ can detect almost all pores in samples. For the samples with sizes from 0.113 to 0.058 mm, the abundance of pores detected using N₂ adsorption experiments have no obvious variation, the corresponding parameters of pore characteristics are close to in-situ shales. These findings indicate that for the examination of pore systems in shale material using LPGA-N₂, a particle size of <0.113 mm is most suitable. Of course, only the pores connected with each other can be detected by low-pressure gas adsorption experiments. Some researchers argued that artificial pores and fractures in shale samples may be created during grounding [38]. However, the adsorption equilibration time of crushed samples is much less than bulk samples [24, 39]. Crushing and sieving have no significant influence on the microporosity (<100 nm) of shales [23].

Overall, as N₂ adsorption experiments are typically used in conjunction with CO₂ experiments, a particle size of 0.113 mm (130 mesh) is suggested for shale samples used in both low-pressure CO₂ and N₂ adsorption experiments.

3.3 Uncertainties

The present results suggest that shale samples with a particle size of <0.83 mm (20 mm) and <0.113 mm (0.113 mm) are used for LPGA-CO₂ and LPGA-N₂ experiments, respectively. However, some small variations in the pore volume, surface area, and PSD have been observed in samples that match the above criteria. These small variations may relate to the

heterogeneity of the Longmaxi Shale used in this study. It is probable that different samples, each with its own particle size, also had different organic matter and mineral compositions, and different pore structure. For example, Tinni et al. [40] reported different surface areas measured in samples with particle sizes of 0.07 mm (~200 mesh) and 0.7 mm (~24 mesh) from the same shale. This variation was attributed to differences in the abundance of organic matter. In addition, crushing may induce fractures and experimental error may arise when using the LPGA procedure [41]. It is emphasized that the particle size range suggested in this study for both LPGA-CO₂ and LPGA-N₂ experiments was attained from an investigation involving just one shale sample (i.e., a sample of the Longmaxi Formation). Therefore, the applicability of the suggested particle sizes for other shales needs to be verified.

4 CONCLUSIONS

To assess the optimum particle size for shale samples used in low-pressure gas (CO₂ and N₂) adsorption experiments, a Longmaxi Shale sample was ground into a range of particle sizes from 4 to 0.058 mm. LPGA-CO₂ and LPGA-N₂ experiments were then performed on the crushed samples.

In the LPGA-CO₂ experiments, the volume of sorbed CO₂, pore volume, and surface area increased as particle size decreased from 4 to 0.83 mm. Noticeably, PSD data show a larger peak at a pore diameter of 0.4 nm in samples with a particle size smaller than 0.83 mm. For the 0.38 to 0.058 mm samples, no significant changes in sorbed volume, pore volume, surface area, or PSD were observed. Accordingly, it is suggested that shale samples with a particle size below 0.83 mm are most suitable for LPGA-CO₂ experiments.

In the LPGA-N₂ experiments the volume of sorbed N₂ and calculated surface area increased as particle size decreased from 4 to 0.113 mm; however, no obvious differences were observed in the 0.113 to 0.058 mm samples. Pore volume and PSD show a noticeable change

as particle size decreases from 4 to 0.113 mm; however, the change observed between the 0.113 and 0.058 mm samples is much less pronounced. Therefore, we suggest that shale samples with a particle size of <0.113 mm are most suitable for LPGA-N₂ experiments. As the reservoir potential of shale samples is usually measured using both low-pressure CO₂ and N₂ adsorption experiments, a particle size of 0.113 mm (130 mesh) is suggested for all low-pressure adsorption experiments. However, it is worth noting that the heterogeneity typically exhibited by any given shale could result in error being introduced during sample preparation and analysis, and this would influence the reproducibility of LPGA results.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86 18302815786. E-mail: hanhuigeology@163.com.

ACKNOWLEDGMENTS

This project was funded by the National Science Foundation of China (41502144), the Young Scholars Development Fund of Southwest Petroleum University (SWPU) (201499010088), the Fund of Education Department of Sichuan Province (16ZA0075), the Fund of Key Laboratory of Tectonics and Petroleum Resources (TPR-2015-06), and the Sichuan Province University Scientific Innovation Team Construction Project (USITCP).

REFERENCES

- [1] Jarvie D. M., Hill R. J., Ruble T. E., Pollastro R. M. Unconventional shale-gas systems: the Mississippian Barnett shale of north-central Texas as one model for thermogenic shale-gas assessment. AAPG Bull. 2007; 91(4) : 475-99.
- [2] Guo T. L., Zhang H. R. Formation and enrichment mode of Jiaoshiba shale gas field, Sichuan basin. Petrol. Explor. Dev. 2014; 41(1): 31-40.

- [3] Loucks R. G., Reed R. M., Ruppel S. C., Jarvie D. M. Morphology, genesis, and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett Shale. *J. Sediment. Res.* 2009; 79: 848-61.
- [4] Milliken K. L., Rudnicki M., Awwiller D. N., Zhang T. Organic matter-hosted pore system, Marcellus Formation (Devonian), Pennsylvania. *AAPG Bull.* 2013; 97(2):177-200.
- [5] Wang M., Wilkins R. W. T., Song G. Q., Zhang L. Y., Xu X. Y., Li Z., Chen G. H. Geochemical and geological characteristics of the Es₃^L lacustrine shale in the Bonan sag, Bohai Bay basin, China. *Int. J. Coal Geol.* 2015; 138: 16—29.
- [6] Wang M., Sherwood N., Li Z. S., Lu S. F., Wang W. G., Huang A. H., Peng J., Lu K. Shale oil occurring between salt intervals in the Dongpu Depression, Bohai Bay basin, China. *Int. J. Coal Geol.* 2015; 152: 100—12.
- [7] Javadpour F., Farshi M. M., Amrein M. Atomic-force microscopy: a new tool for gas-shale characterization. *J. Can. Pet. Technol.* 2012; 7: 236-43.
- [8] Sondergeld C. H., Ambrose R. J., Rai C. S., Moncrieff J. Micro-structural studies of gas shales. *SPE Unconventional Gas Conference*, Pittsburgh, PA, 23-25 February, 2010.
- [9] Sisk C., Walls J., Suhrer M. 3D visualization and classification of pore structure and pore filling in gas shales. *SPE Annual Technical Conference and Exhibition*, Florence, Italy, 19-22 September, 2010.
- [10] Walls J. D., Diaz E., Cavanaugh T. Shale reservoir properties from digital rock physics. *SPE/EAGE European Unconventional Resources Conference and Exhibition*, Vienna, Austria, 20-22 March, 2012.

- [11] Tinni A., Odusina E., Hughes B., Sulucamain I., Sondergeld C., Rai C. NMR response of brine, oil, and methane in organic rich shales. SPE Unconventional Resources Conference, Woodlands, Texas; April 1-3, 2014.
- [12] Clarkson C. R., Jensen J. L., Blasingame T. A. Reservoir engineering for unconventional gas reservoirs: what do we have to consider?. The society of petroleum engineers North American unconventional gas conference and exhibition, Woodlands, Texas; June 12-16, 2011.
- [13] Mastalerz M., He L., Melnichenko Y. B. Rupp J. A. Porosity of coal and shale: insights from gas adsorption and SANS/USANS techniques. *Energy Fuel* 2012; 26: 5109-20.
- [14] Clarkson C. R., Solano N., Bustin R. M., Chalmers G. R. L., He L., Melnichenko A. P., Radliński A. P., Blach T. P. Pore structure characterization of North American shale gas reservoirs using USANS/SANS, gas adsorption, and mercury intrusion. *Fuel* 2013; 103: 606-16.
- [15] Chalmers G. R., Bustin R. M., Power I. M. Characterization of gas shale pore systems by porosimetry, pycnometry, surface area, and field emission scanning electron microscopy/transmission electron microscopy image analyses: examples from the Barnett, Woodford, Hynesville, Marcellus, and Doig units. *AAPG Bull.* 2012; 96: 1099-1119.
- [16] Li J. J., Yin J. X., Zhang Y. N., Lu S. F., Wang W. M., Li J. B., Chen F. W., Meng Y. L. A comparison of experimental methods for describing shale pore features-a case study in the bohai bay basin of eastern China. *Int. J. Coal Geol.* 2015; 152: 39-49.
- [17] Wang M., Xue H. T., Tian S. S., Wilkins R. W. T., Wang Z. W. Fractal characteristics of Upper Cretaceous lacustrine shale from the Songliao basin, NE China. *Mar. Petrol. Geol.* 2015; 67: 144—53.

- [18] Mastalerz M., Schimmelmann A., Drobniak A., Chen Y. Porosity of Devonian and Mississippian New Albany shale across a maturation gradient: insights from organic petrology, gas adsorption, and mercury intrusion. *AAPG Bull.* 2013; 97: 1621-43.
- [19] Schmitt M., Fernandes C. P., da Cunha Neto J. A. B., Wolf F. G., dos Santos V. S. S. Characterization of pore systems in seal rocks using nitrogen gas adsorption combined with mercury injection capillary pressure techniques. *Mar. Petrol. Geol.* 2013; 39: 139-49.
- [20] Mohammad M. L., Rezaee R., Saeedi A., Al Hinai A. Evaluation of pore size spectrum of gas shale reservoirs using low pressure nitrogen adsorption, gas expansion and mercury porosimetry: a case study from the Perth and Canning basins, western Australia. *J. Petrol. Sci. Eng.* 2013; 112: 7-16.
- [21] Kuila U. Prasad M., Derkowski A., McCarty D. K. Compositional controls on mudrock pore-size distribution: an example from Niobrara Formation. *SPE Annual Technical Conference and Exhibition*, San Antonio, Texas; October 8-10, 2012.
- [22] Cao T. T., Song Z. G., Wang S. B., Cao X. X., Li Y., Xia J. Characterizing the pore structure in the Silurian and Permian shales of the Sichuan basin, China. *Mar. Petrol. Geol.* 2015; 61: 140-50.
- [23] Chen Y. Y., Wei L., Mastalerz M., Schimmelmann A. The effect of analytical particle size on gas adsorption porosimetry of shale. *Int. J. Coal Geol.* 2015; 138: 103-12.
- [24] Clarkson C. R., Bustin R. M. The effect of pore structure and gas pressure upon the transport properties of coal: a laboratory and modeling study. 1. Isotherms and pore volume distributions. *Fuel* 1999; 78: 1333-44.

- [25] Zou C. N., Dong D. Z., Wang S. J., Li J. Z., Li X. J., Wang Y. M. Li D. H., Cheng K. M. Geological characteristics and resource potential of shale gas in China. *Petrol. Explor. Dev.* 2010; 37: 641-53.
- [26] Jacob H. Classification, structure, genesis and practical importance of natural solid oil bitumen (“migrabitumen”). *Int. J. Coal Geol.* 1989; 11: 65-79.
- [27] Tian H., Pan L., Xiao X. M., Wilkins R. W. T., Meng Z. P., Huang B. J. A preliminary study on the pore characterization of Lower Silurian black shales in the Chuandong Thrust Fold Belt, Southwestern China using low pressure N₂ adsorption and FE-SEM methods. *Mar. Petrol. Geol.* 2013; 48: 8-19.
- [28] Sondergeld C. H., Newsham K. E., Comisky J. T., Rice M. C., Rai C. S. Petrophysical considerations in evaluating and producing shale gas resources. SPE Unconventional Gas Conference, Pittsburgh, PA, 23-25 February, 2010.
- [29] Chalmers G. R. L., Bustin R. M. On the effects of petrographic composition on coalbed methane sorption. *Int. J. Coal Geol.* 2007; 69: 288-304.
- [30] Do D. D., Do H. D. Pore characterization of carbonaceous materials by DFT and GCMC simulations: a review. *Adsorpt. Sci. Technol.* 2003; 21(5): 389—423.
- [31] Zhang Z., Yang Z. Theoretical and practical discussion of measurement accuracy for physisorption with micro- and mesoporous materials. *Chin. J. Catal.* 2013; 34: 1797—1810.
- [32] Neimark A.V., Lin Y., Ravikovitch P.I., Thommes M. Quenched solid density functional theory and pore size analysis of micro-mesoporous carbons. *Carbon* 2009; 47: 1617—28.
- [33] Brunauer S., Deming L. S., Deming W. E., Teller E. On a theory of the van der Waals adsorption of gases. *J. Am. Chem. Soc.* 1940; 62(7): 1723-1732.

- [34] Gregg S. J., Sing K. S. W. Adsorption, surface area, and porosity. 1982, New York: Academic Press, 303p.
- [35] Sing K. S. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure and Appl. Chem. 1985; 57: 603-19.
- [36] Chalmers G. R. L., Bustin R. M. Porosity and pore size distribution of deeply-buried fine-grained rocks: influence of diagenetic and metamorphic process on shale reservoir quality and exploration. J. Unconv. Oil Gas 2015; 12: 134-42.
- [37] Unsworth J. F., Fowler C. S., Jones L. F. Moisture in coal: 2. Maceral effects on pore structure. Fuel 1989; 68: 18-26.
- [38] Black D. Factors affecting the drainage of gas from coal and methods to improve drainage effectiveness. PhD Thesis, University of Wollongong, Wollongong, Australia; 2012.
- [39] Gamson P., Beamish B. Coal type, microstructure and gas flow behavior of Bowen Basin coals. Symposium on Coalbed Methane Research and Development in Australia, Coalseam Gas Research Institute-James Cook University, Townsville, 19-21 November, 1992.
- [40] Tinni A., Songdergeld C., Rai C. Particle size effect on porosity and specific surface area measurements of shales. International Symposium of the Society of Core Analysts, Avignon, France; September 8-11, 2014.
- [41] Boudriche L., Chamayou A., Calvet R., Hamdi B., Balrd H. Influence of different dry milling processes on the properties of an attapulgite clay, contribution of inverse gas chromatography. Powder Technol. 2014; 254: 352-63.

Table 1. TOC content and mineral composition of the studied sample.

Depth (m)	TOC (wt.%)	eqR _o ^a (%)	Mineral composition (wt.%)						Clay mineral composition (wt.%)			
			Clay	Quartz	Feldspar	Calcite	Dolomite	Pyrite	I/S	Illite	Kaolinite	Chlorite
3112.06	5.36	1.59	38.5	35.3	9.1	1.1	8.6	7.4	49	33	3	15

^a EqR_o is calculated according to the equation established by Jacob [26]. I/S: mixed-layer illite/smectite.

Table 2. Pore volume and surface area for the studied samples.

Particle size (mm)	Pore volume (cm ³ /g)		Surface area (m ² /g)	
	CO ₂	N ₂	CO ₂	N ₂
4	0.0034	0.0076	9.99	10.43
0.83	0.0047	0.0100	14.34	17.12
0.38	0.0047	0.0112	14.41	19.04
0.25	0.0046	0.0124	14.46	21.01
0.15	0.0042	0.0169	13.31	21.81
0.113	0.0055	0.0258	16.85	22.52
0.106	0.0050	0.0210	16.07	22.36
0.075	0.0045	0.0241	14.45	21.12
0.058	0.0044	0.0248	14.60	20.84

CO₂: data obtained from CO₂ adsorption experiments; N₂: data obtained from N₂ adsorption experiments.

The data in Table 2 includes the whole pore size ranges that CO₂ and N₂ detect.

Figure 1. Low-pressure CO₂ adsorption isotherms for the studied samples.

Figure 2. Influence of sample particle size on low-pressure CO₂ adsorption experiments.

Figure 3. Pore volume and surface area data obtained from low-pressure CO₂ adsorption data for the studied samples.

Figure 4. Pore size distributions obtained from low-pressure CO_2 adsorption data for the studied samples.

Figure 5. Low-pressure N_2 adsorption isotherms for the studied samples.

Figure 6. Influence of sample particle size on low-pressure gas (CO_2 and N_2) adsorption experiments.

Figure 7. Pore volume and surface area data obtained from low-pressure N₂ adsorption data for the studied samples.

Figure 8. Relationships between surface area and pore volume obtained from low-pressure N₂ adsorption data for the studied samples.

Figure 9. Pore size distributions obtained from low-pressure N_2 adsorption data for the studied samples.