

A Novel Method for Analyzing Pore Size Distribution of Complex Geometry Shaped Porous Shale

Yang Ming^{1,2,a}, Lin Mian^{1,2,b*}

¹Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China

²School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China

^ayangming@imech.ac.cn, ^blinmian@imech.com

Keywords: Pore size distribution; BJH; Adsorption; Capillary condensation; False peak; Cylinder pore; Slit pore

Abstract. This article proposes the differential BJH equation based on the principles of multilayer adsorption and capillary condensation, which was simplified by theoretical investigation and experiments. This work indicates that the differential function of isotherm and the differential function of pore size to relative pressure determine the pore size distribution of porous media. The differential BJH model can be used to explain the source of the false peak in pore size distribution and to calculate the pore size distribution of different shapes of pores in a porous media with a porous structure. It has an excellent application prospect in the characterization of complex pore structure represented by shale.

Introduction

The study of the adsorption behavior of porous media has drawn much attention historically. Researchers put forward a series of adsorption theories to describe the adsorption phenomenon and developed various methods to characterize the pore structure parameters of porous media, among which BJH (Barrett-Joyner-Halenda) method is widely recognized and utilized^[1]. This problem is so significant that it applies in various industries fields, such as petroleum, chemical industry, medicine, food, catalysis, and presently natural gas. New requirements of new materials, new industries, and environment bring about new challenges, especially in unconventional oil and gas research. With the deepening of the research on the nanoscale adsorption process, the requirements of more refinement, automation, and clarity in principle have been put forward in the process of understanding microstructure from macro phenomena^[2, 3], which require a deep and intuitive understanding of adsorption mechanism. In the characterization of PSD (pore size distribution, the same below) of mesoporous porous media represented by shale, BJH method often bring the confusion of "false peak"^[3, 4, 5], which has no clear explanation for this phenomenon; at the same time, because the pore structure of unconventional oil and gas reservoir is not formed by a single cylindrical hole, but the coexistence of porous shapes, the assumption of single PSD is not suitable for accurate research. However, it is the key to accurately characterize the PSD of complex porous media to understand the process of capillary condensation and multilayer adsorption further. Cohen introduced the Kelvin equation to explain the adsorption isotherm hysteresis in cylindrical pores, which was caused by the difference between the shape of the meniscus in the adsorption process and that in the desorption process^[6]. Wheeler put forward the theory based on the combination of multilayer adsorption and capillary condensation at a catalyst symposium in 1948, namely Eq.1.

$$V_s - V = \int_{r_{pn}}^{\infty} (r - t)^2 L(r) dr \quad (1)$$

V_s is the volume of gas adsorbed at saturated vapor pressure, V is the volume of gas adsorbed under pressure P . $L(r)dr$ is the total length for pores with radius at r reach $r + dr$. r_{pn} is the critical radius, the radius of the largest pore, which is still filled by liquid adsorbate in the pore under any special pressure. t is the thickness of the multilayer adsorption normally established under pressure P . Shall corrected the adsorption thickness with the experimental data [7], based on which de Boer established the t-Plot method [8]. Halsey further proposed the Halsey equation [9] to describe the thickness of multilayer adsorption. Barrett and others assumed that the pores are cylindrical, and the adsorption phase is composed of multilayer physical adsorption and capillary coacervation and put forward the famous BJH method [11]. Additional corrections of the BJH model are focused on two aspects: one is the emendation of adsorption film thickness, the other is the improvement of the Kelvin equation. Melrose proposed that the Kelvin equation used to describe the condensation phenomenon needs to introduce correction factors related to the adsorption system [1, 10]. The radius of the adsorption test was corrected by XRD experiments and observations on nonporous silicon, and then the Kelvin equation was modified [10]. All these correction schemes for the Kelvin equation are empirical, and the scope of application is only limited to the experimental system [11]. With the discovery of various new materials, the rise of new industries, and the unique requirements of the environment, such work will be more and more restricted. At the same time, we can see that the BJH method is not complete; it is only a discretized and simplified method to solve the PSD. The assumptions made by the BJH method for individual cases not only bring about the inaccuracy, but also inconvenience. Based on the idea of coupling multilayer adsorption and capillary coacervation, a differential BJH method is proposed in this work, and a clear and straightforward model for shale PSD is found through experimental verification. This model is a general method to solve the PSD of rock by using the low-temperature nitrogen adsorption data. It can directly explain the "false peak" phenomenon in the PSD of porous media and can be used to study the PSD of complex porous media. It has significant theoretical and application value.

The Differential BJH Model for PSD Analysis

In the derivation below, for the convenience of expression, p indicates relative pressure P/P_0 .

If the adsorption process is assumed to be coupled by physical adsorption and capillary condensation, only two corresponding relations are needed to establish the PSD solution method:

1. The relationship between pore size and relative pressure under the critical condition of adsorption;
2. The relationship between adsorption volume and pore volume under the adsorption process on different pore shapes.

Consistent with the BJH method, set the thickness of the adsorption layer $t = f(p)$, capillary condensation radius r_k determined by the Kelvin equation, then the relationship between pressure and pore size is established by $r = r_k + t$,

$$r(p) = f(p) + \frac{2\gamma V_m}{RT \ln(p)} \quad (2)$$

For the second question, introduce length distribution function $L(r)$, by defining $L(r)dr$ the total length for pores whose radius from r to $r + dr$ in range. When the relative pressure drops from

$p + dp$ to p , the volume of the released capillary condensed phase is $dV_c = \pi r_k^2 N(r) dr$, which can be represented by relative pressure p ,

$$dV_c = \left(\frac{2\gamma V_m}{RT \ln(p)} \right)^2 \pi L(r(p)) \frac{dr(p)}{dp} dp \quad (3)$$

with the infinitesimal pressure variable Δp , the change of the adsorption layer thickness is $\Delta t = f^{\wedge}(p) \Delta p$. The volume of multilayer adsorbed gas released from pores with radius r is $dV_m(r) = \pi((r-t)^2 - (r-t-\Delta t)^2) L(r) dr$. With integration over r , the volume of multilayer adsorption from the pore system is obtained as shown in Eq.4, then the total volume of gas released by the process of pressure reduction is $dV_t = dV_c + dV_m$. *isotherm*(p) represents adsorption isotherm measured experimentally, the volume of gas released in this process is the differential increment of isotherm, $dV_t = d(\text{isotherm}(p(r)))$. So $d(\text{isotherm}(p(r))) dp/dr$ can be calculated from the adsorption isotherm, that is, the right term of Eq.5 is known, while the left terms are divided into three terms, which are respectively called capillary term, positive multilayer adsorption term, and negative multilayer adsorption term. Eq.5 is the principle to solve the pore length distribution function using physical adsorption and capillary condensation. This formula assumes that the pores are cylindrical. We will further analysis these three items to find out the simplified solution, the relationship between $L(r)$ with the volume, PSD plot in Eq.6,

$$dV_m = 2\pi f^{\wedge}(p) dp \left(\int_{r(p)}^{\infty} rL(r) dr - f(p) \int_{r(p)}^{\infty} L(r) dr \right) \quad (4)$$

$$\frac{dV_t}{dp} = r_k^2 \pi L(r) \frac{dr}{dp} + 2\pi \frac{f^{\wedge}(p(r))}{r^{\wedge}(p(r))} \int_r^{\infty} rL(r) dr - 2\pi \frac{f^{\wedge}(p(r))f(p(r))}{r^{\wedge}(p(r))} \int_r^{\infty} L(r) dr \quad (5)$$

$$\frac{dV}{dr} = \pi r^2 L(r) \quad (6)$$

Quantitative analysis of different terms

Dollimore recommended that ^[12], $f(p)$ can be expressed in nanometers as follows:

$$f(p) = -0.37 \left(\frac{5}{\ln(p)} \right)^{1/3} \quad (7)$$

According to Barrett's work ^[1], we can simplify the Kelvin equation to the following formula, r_k is in nanometers,

$$\ln(p) = -\frac{0.9533}{r_k} \quad (8)$$

Subsequently, we will discuss the right terms of Eq.6 about its three coefficients on the parameters of the distribution function $L(r)$.

Capillary condensation term

Because the adsorption of this process is mainly capillary condensation, it is evident that the coefficient r_k is close to the value r naturally, similarly πr_k^2 and πr^2 . As shown in Fig.1, the first coefficient πr_k^2 and πr^2 vary with the relationship r is very relevant.

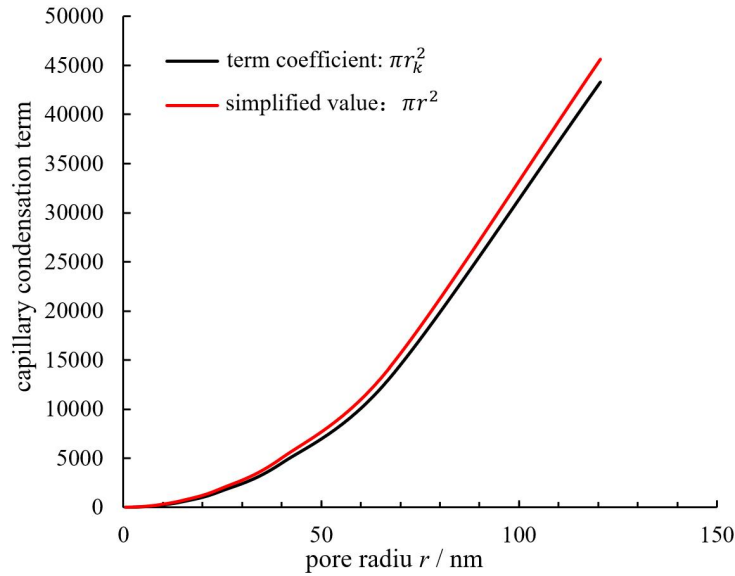


Figure 1. Coefficient of capillary condensation term and its approximate simplification

A conclusion can directly reach from Fig. 2 that the capillary condensation radius and pore radius are considered to be equal, while the coefficient of capillary condensation term itself is positively related to the quadratic power of the pore radius and has a large quantity in value. It is considered available for replacing πr_k^2 with πr^2 to some extent.

Positive multilayer adsorption term

Considering the coefficient of positive multilayer adsorption term, Fig.2 shows the relationship between this term and the pore radius. It is obvious that inconsistent with the situation that the coefficient of capillary condensation term increases with the pore radius, the overall magnitude of the factor is significantly small and decreases with the pore radius. When the pore radius is larger than 0.7nm, the ratio of positive multilayer adsorption term coefficient to capillary condensation term coefficient is less than 1. Moreover, when the pore radius is larger than 5nm, this ratio decays to less than 0.01. The coefficient of positive multilayer adsorption term is negligible compared with that of the capillary condensation term.

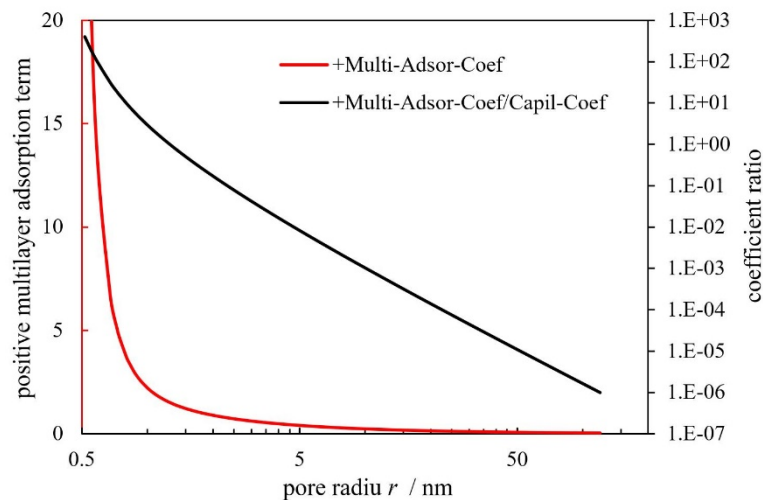


Figure 2. Change of coefficient of positive multilayer adsorption term with pore radius

+Multi-Adsor-Coeff: positive multilayer adsorption coefficient

Capil-Coeff: Capillary Coefficient

Negative multilayer adsorption term

To make it convenient to discuss and present, we further investigated the absolute value of the term coefficient with the pore size. Fig.3 shows the relationship between this term and the pore radius. Similar to the positive term, the coefficient of this term is considerably small overall with magnitude and decreases with the pore radius. It is consistent with the positive multilayer adsorption that when the pore radius is larger than 0.7nm, the ratio of the coefficient to the coefficient of capillary condensation is less than 1, and when the pore radius is larger than 4nm, the ratio will be less than 0.01. In most cases, the negative multilayer adsorption coefficient is also negligible.

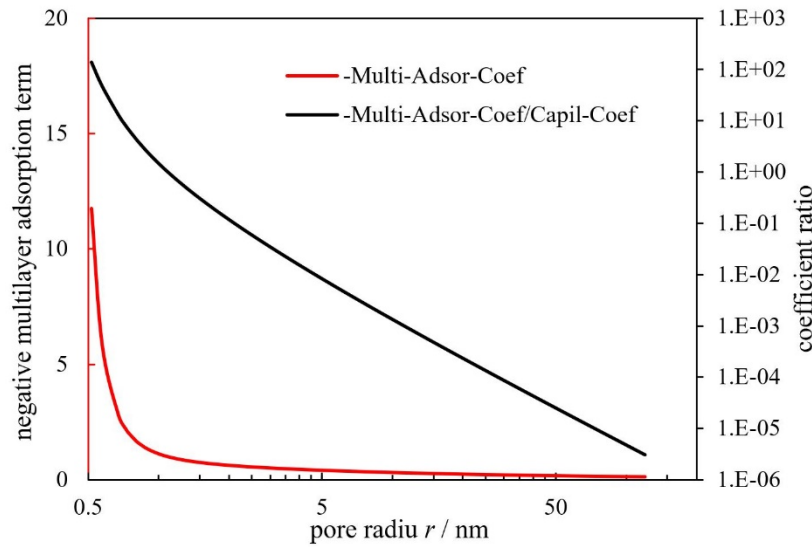


Figure 3. Change of coefficient of negative multilayer adsorption term with pore radius
-Multi-Adsor-Coeff: negative multilayer adsorption coefficient

Simplification and experiments analysis

Based on the analysis of the coefficient of capillary condensation term, positive multilayer adsorption term, and negative multilayer adsorption term, it can be concluded that the coefficient of positive and negative multilayer adsorption terms are too small compared with the coefficient of capillary condensation term. The positive and negative multilayer adsorption terms will partly balance themselves out, so the influence of multilayer adsorption terms on the condensation term can be removed. That is, the length distribution of porous materials $L(r)$ can be calculated by the Eq.9,

$$\frac{d(isotherm(p))}{dp} / \frac{dr}{dp} = \pi r^2 L(r) \quad (9)$$

The PSD of the sample can be calculated from $L(r)$, and Eq.10 can be obtained from Eq.6 and Eq.9,

$$\frac{dV}{dr} = \frac{d(isotherm(p))}{dp} / \frac{dr}{dp} \quad (10)$$

Eq.10 is of great significance for indicating that the PSD is only related to the slope function of isotherm and the relation of r and p .

The shale nitrogen adsorption test was carried out at 77.4K. Firstly, ground the rock samples into debris by ball mill, and then sieved the powder samples of 100-150 mesh out by vibration. After degassing for 8 hours in a vacuum environment of 120 °C, the adsorption isotherm was measured by the domestic specific surface instrument BeiShiDe 3H-2000PS2 (pressure transducer error $\leq 0.15\%$, the highest precision in the current industry). Due to the limitation of accuracy, it is necessary to deal with the isotherms measured and remove the points with relative pressure less than 0.005 or greater

than 0.998. One of the isotherms and its slope curve is shown in Fig.4. According to the method in this proposed, the corresponding hole length distribution can be easily calculated. Furthermore, to evaluate the effect of the neglected multilayer adsorption term on the distribution results, substitute pore length distribution $L(r)$ into the integrated calculation of the previously neglected multilayer adsorption term, and the results are taken as the correction term, use Eq.5 to calculate the pore length distribution corrected by multilayer adsorption term $C(r)$ (See Eq.11), and the results before and after correction are converted to PSD, as shown in Fig.5.

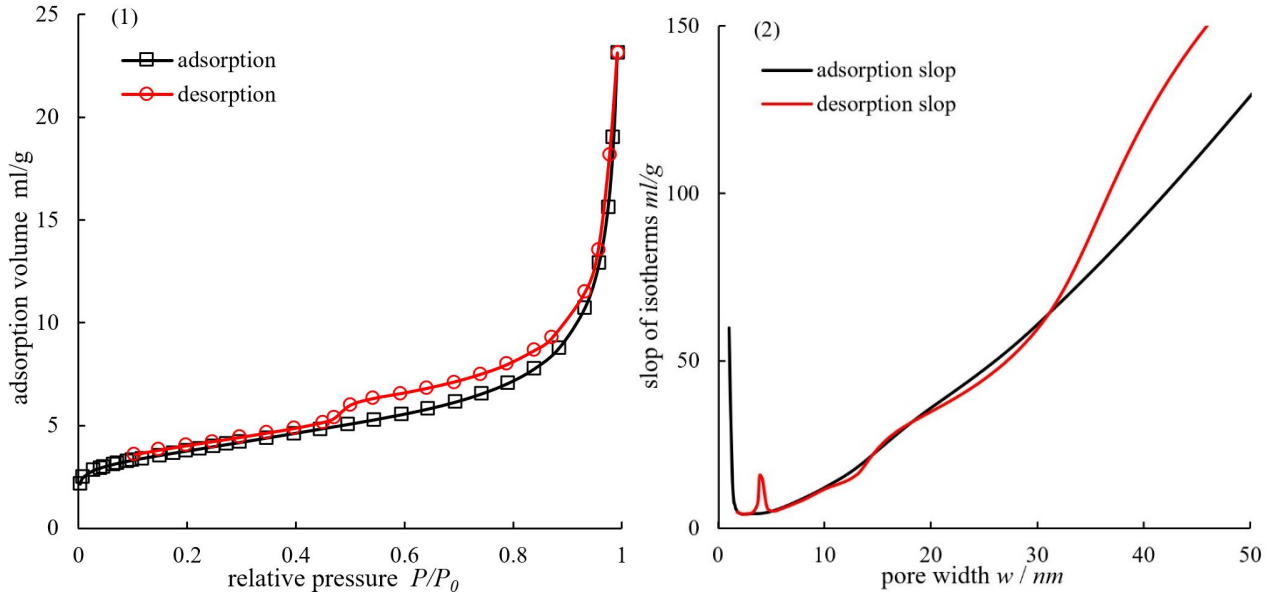


Figure 4. Adsorption isotherm and its slope of shale nitrogen at liquid nitrogen temperature

$$\frac{dV}{dr} = \frac{d(\text{isotherm}(p))}{dp} / \frac{dr}{dp} - C(r) \quad (11)$$

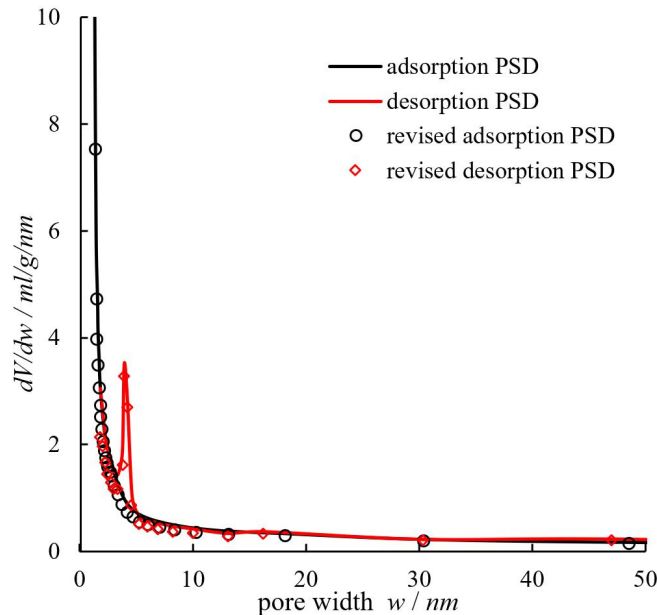


Figure 5. PSD of adsorption and desorption branches before and after multilayer adsorption revision

Fig.6 The results are of great value. The red line and the hollow red square dot represent the PSD of the desorption branch before and after the correction, respectively; the black line and hollow black circle represent the PSD of the adsorption branch before and after the correction respectively. It is clear from Fig.6 that the PSDs are almost the same no matter being corrected or not, which

provides strong evidence that the multilayer adsorption term has little effect on PSD calculation or $C(r) \approx 0$. It is reasonable to consider only the capillary condensation term when calculating the adsorption volume, and we find a simplified model for calculating PSD of shale and other mesoporous porous media.

The simplified BJH differential model also tells us a direct truth, which can refer to Fig.4 and Fig.5 that the jump of isotherm slope leads to the peak of PSD. Specifically speaking, the false peak in the BJH method is caused by the abrupt change of the slope of the desorption branch, ultimately coming from the abrupt closure of the desorption branch of isotherm at relative pressure between 0.42 and 0.50. The closure point is the so-called spinodal^[13]. Groen considered this mechanism as the tensile strength enhancement effect^[14], that is when the diameter is smaller than a specific size, the capillary condensation surface will be stretched and destroyed, thus eliminating the capillary condensation and also the hysteresis loop under low pressure. Because the PSDs calculated from the adsorption branch and desorption branch are of considerable consistency except for the false peak, it is reasonable to calculate the PSD from the adsorption branch of isotherm too.

Deviation analysis and a brief discussion

Some deviation is inevitable for only considering the influence of capillary condensation term on adsorption volume, but if it can be kept within the controllable range, the simplification is practical and reasonable. In this section, the magnitude of deviation caused by simplified treatment will be discussed by testing 20 groups of shale adsorption samples. These isotherms are measured from the rock samples of different burial depths of several shale gas wells of Longmaxi formation and Wufeng formation. Calculate PSD using the simplified differential BJH model, and then evaluate the pore volume of the sample by integrating the PSD, while the isotherm directly gives the accurate pore volume. The results are shown in Fig.6. The overall deviation between the estimated pore volume of the simplified model and the measured pore volume of 20 groups of shale samples is within 20%, and the calculated pore volume of the adsorption branch is closer to the measured value, with the deviation controlled within 10%. When using isotherm adsorption branch data, the variance of PSD obtained by the simplified model is acceptable, which proved that the simplified method is effective and reasonable by ignoring multilayer adsorption terms. It is also noticeable that the deviation of the desorption branch result is slightly larger, and it may be caused by the false peak, which should avoid in practical application.

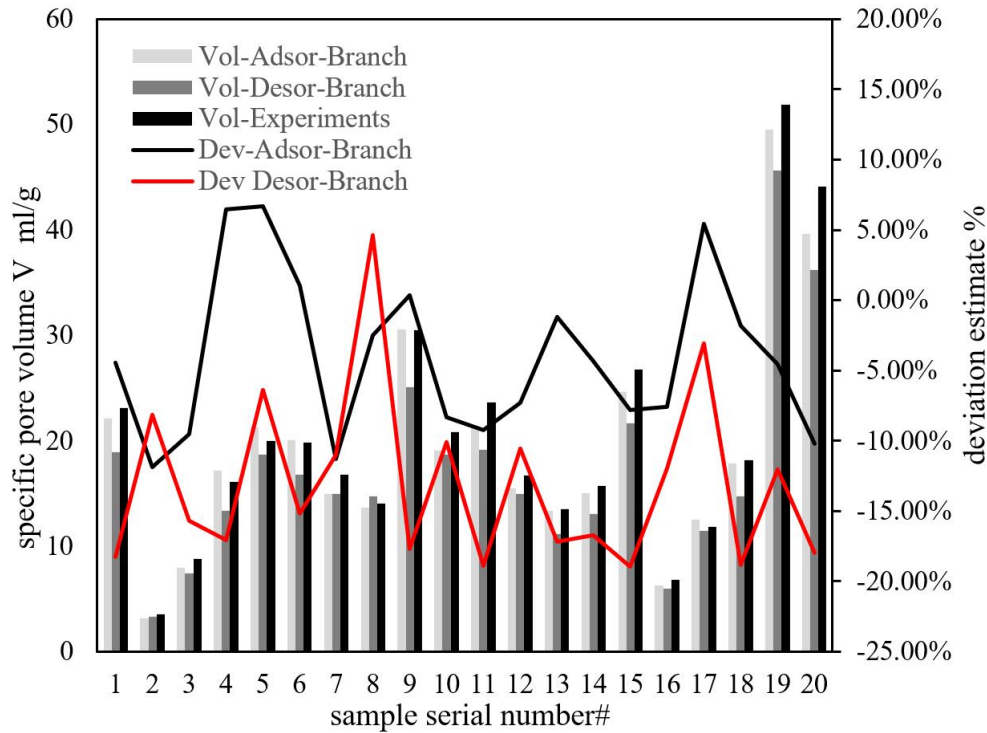


Figure 6. Comparison between estimated pore volume and the measured value of 20 groups of shale samples using the simplified model

Vol: Volume; Dev: Deviation

Through coefficient analysis and experimental analysis of differential BJH model, it is found feasible only to consider the contribution of total adsorption volume brought by capillary condensation, and the contribution of positive and negative multilayer adsorption terms can be ignored, from which a simplified BJH model was conceived. The deviation analysis shows that the overall deviation of the reduced model is acceptable.

In this section, we obtain a simplified differential BJH model, as shown in Eq.10, which only needs three steps:

- (1) According to Kelvin equation and the formula of adsorbed layer thickness, converse relative pressure to pore radius;
- (2) Calculate the derivative of isotherm, and obtain the relationship between isotherm slope and pore radius;
- (3) Calculate the slope distribution of pore radius to pressure. Divide the isotherm slope distribution by the size slope distribution to obtain the pore diameter distribution.

Analyzing PSD of Complex Geometry Shaped Porous Media

The simplified differential BJH model is based on the assumption of the hole shape of a cylindrical hole, which dr/dp represents; thus, it generally can apply to different hole shapes. Specifically, for cylindrical pores, the expression has been given,

$$r_c = -\frac{2\gamma V_m}{RT \ln(p)} - 0.37 \left(\frac{5}{\ln(p)} \right)^{1/3} \quad (12)$$

For slit pores, it can be translated into the following^[15]:

$$r_s = -\frac{\gamma V_m}{RT \ln(p)} - 0.37 \left(\frac{5}{\ln(p)} \right)^{1/3} \quad (13)$$

To quantify the PSD for different pore shapes in the porous media containing cylinder and slit pores, dV_c/dr and dV_s/dr can be solved by the Eq.14,

$$\frac{d(\text{isotherm}(p(r)))}{dp} = \frac{dV_c}{dr} * \frac{dr_c}{dp} + \frac{dV_s}{dr} * \frac{dr_s}{dp} \quad (14)$$

Considering that a porous media has n compositions of different shapes of pores, we only need to find the relationship between the critical radius of each pore shape and the relative pressure, and then get the dr/dp value. The Eq.15 can quickly obtain the PSD of n kinds of pore shapes in the porous media,

$$\frac{d(\text{isotherm}(p(r)))}{dp} = \sum_{i=1}^n \frac{dV_i}{dr} * \frac{dr_i}{dp} \quad (15)$$

Eq.14 and Eq.15 are challenging to solve directly, and however, if process the data to a matrix, we can quickly obtain the optimal solution.

Summary

Based on the phenomenon of multilayer adsorption and capillary coacervation, this work proposed the differential BJH model for determining the PSD of a porous media, and further discuss the influence of capillary condensation term, and multilayer adsorption term on adsorption through coefficient analysis and adsorption experiments. It proved that the impact of the multilayer adsorption term can be ignored in this system, so the simplified differential BJH model proposed. The overall volume deviation caused by this simplification is controlled at about 10%. This model is simple and clear and adequately accurate.

On the other hand, the simplified differential BJH model shows that the PSD is directly related to two factors, namely, the slope function of adsorption isotherm and the derivative function of pore size with pressure. The former is determined by adsorption isotherm, the latter is determined by the relationship between pore size and pressure, and the latter makes it possible to evaluate the PSD of different pore shapes in a complex porous media. It is believed that the differential BJH model will have a more comprehensive application and the simplified differential BJH model will be a powerful tool for analyzing the PSD of porous media.

Acknowledgment

This research work was carried out under the financial support of the National Natural Science Foundation of China (Grant No. 41690132 and 41574129), the Strategic Priority Research Program of the Chinese Academy of Sciences (grant No. XDA14010304) and the Major National Science and Technology Special Program of China (Grant No. 2017ZX05037-001), and under the meticulous guidance of my supervisor, Dr. Lin Mian (Email: linmian@imech.com; Tel.: 010-62561284).

References

- [1] Barrett E P, Joyner L G, Halenda P P. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms [J]. *Journal of the American Chemical Society*, 1951, 73(1): 373-80.
- [2] Liu W, Cui S, Wang Z, Ding B. Research progress of adsorption materials for gas hydrate production by displacement method. *Modern Chemical Industry*, 2019, 39(11): 53-57
- [3] Yang F, Ning Z F, Zhang S D, et al. Characterization of pore structures in shales through nitrogen adsorption experiment. *Natural Gas Industry*, 2013, 33(04): 135-140
- [4] Kuila U, Prasad M. Specific surface area and pore-size distribution in clays and shales [J]. *Geophysical Prospecting*, 2013, 61(2): 341-362.
- [5] Silvestre-Albero A M, Juarez-Galan J M, Silvestre-Albero J, et al. Low-Pressure Hysteresis in Adsorption: An Artifact? [J]. *Journal of Physical Chemistry C*, 2012, 116(31): 16652-16655.
- [6] Cohan L H. Sorption Hysteresis and the Vapor Pressure of Concave Surfaces [J]. *Journal of the American Chemical Society*, 1938, 60(2): 433-435.
- [7] Shull C G. The Determination Of Pore Size Distribution From Gas Adsorption Data [J]. *Journal of the American Chemical Society*, 1948, 70(4): 1405-1410.
- [8] Boer J H D. The dynamical character of adsorption [J]. *Soil Science*, 1953, 76(76): 166.
- [9] D. H G. Physical Adsorption of Gases [J]. *Journal of the American Chemical Society*, 1969, 235(1): 1214-1225.
- [10] Melrose J C. Thermodynamic Aspects Of Capillarity [J]. *Industrial & Engineering Chemistry*, 1968, 60(3): 53-70.
- [11] Kruk M, Jaroniec M, Sayari A. Application of Large Pore MCM-41 Molecular Sieves To Improve Pore Size Analysis Using Nitrogen Adsorption Measurements [J]. *Langmuir*, 1997, 13(23): 6267-6273.
- [12] Dollimore D, Heal G R. Pore-size distribution in typical adsorbent systems [J]. *Journal of Colloid and Interface Science*, 1970, 33(4): 508-519.
- [13] Horikawa T, Do D D, Nicholson D. Capillary condensation of adsorbates in porous materials [J]. *Advances in Colloid and Interface Science*, 2011, 169(1): 40 - 58.
- [14] Groen J C, Peffer L A A, Perez-Ramirez J. Pore size determination in modified micro- and mesoporous materials. Pitfalls and limitations in gas adsorption data analysis [J]. *Microporous and Mesoporous Materials*, 2003, 60(1-3): 1-17.
- [15] Horvath G, Kawazoe K. Method for the calculation effective pore size distribution in molecular sieve of carbon [J]. *Journal of Chemical Engineering of Japan*, 1983, 16(6): 470-475.