Fuel 210 (2017) 446–454

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

# A new method for analysis of dual pore size distributions in shale using nitrogen adsorption measurements

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## ARTICLE INFO

*Keywords:*
Shale
Nitrogen adsorption isotherm
Cylindrical pores
Slit pores
Pore size distribution

## ABSTRACT

A new method is proposed to distinguish between cylindrical pores and slit pores of porous materials and obtain their individual pore size distributions (PSDs). The proposed method is based on nitrogen adsorption isotherms at 77.3 K. First, we develop the conventional methods by utilizing both adsorption and desorption branches of the isotherms and deriving the volume distribution of the two types of pores. The method formulation and implementing procedure is given in detail. Then the isotherms of SBA-15 sample are used to verify the proposed method in the case of single-pore-type. Finally, the proposed method is applied to analyze the pore structure characterization of shale sample. The results depict that both the adsorbed quantity and pore volume are separated into two distinct parts contributed by cylindrical pores and slit pores respectively. That's to say, the proposed method can distinguish clearly between the two types of pores. This study can provide us a better understanding of the complicated pore structure of shale. Furthermore, it may have implications for shale gas production.

## 1. Introduction

Pore characterization is one of the most important steps for evaluation of shale reservoirs. As a type of heterogeneous porous material, shale is abundant of pores vary widely in morphology (e.g., slit-shaped, cylinder-shaped) and size (from micropores to macropores), which provide storing space and adsorption place for natural gas. To understand the surface and pore characteristics of porous materials, there are some traditional methods like low pressure gas adsorption, mercury porosimetry [1,2], electron microscopy (scanning and transmission) [3–6], and some innovative methods like NMR-methods [7,8], thermoporometry [9], and small angle X-ray and neutron scattering (SAXS and SANS) [10,11]. Among these methods, low pressure gas adsorption experiment is quite popular [12–14] for its operating convenience and wide measuring range of pore sizes (from 2 Å up to 5000 Å depending on the experiment equipment). In addition, it is commonly known that the pores in shale reservoir are predominantly at nano-scale, which are perfectly covered by the assessment from low pressure gas adsorption experiment.

Low pressure gas adsorption experiment is formerly used to study the pore characteristics of synthetic porous materials in chemical way, including molecular sieves, catalyst carriers and some adsorption materials like active carbons. So the conventional calculation models of PSD are established based on the assumption that pores in these porous materials are uniform in shape. Rocks in shale reservoirs, however, have different shapes of pores, including cylindrical, slit and elliptical or some shapes even more complicated [3]. It is noted that the micropores in shale are composed of the pore shapes above. So regardless of the various shape, for simplicity, we assume that the micropores of shale are composed of two typical types of pores, say cylindrical and slit-shaped pores out of the following reasons: (1) cylinder and slit are the basic shapes of open pores that can allow fluid to flow; (2) either elliptical pores or complicated-shape pores can somehow be regarded as the combination of cylindrical pores and slit pores.

To study the pore characteristics of shale reservoirs, there have been a lot of methods to calculate the specific surface area and PSD based on adsorption isotherms. Specific surface area from the Langmuir equation is more applicable to chemi-sorption or a monolayer physic-sorption. And the BET method, derived decades ago, is still the most popular approach to calculate specific surface area, which can be applied to multilayer adsorption. The BJH method was developed to obtain a PSD from adsorption data based on the modified Kelvin equation [15].

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http://dx.doi.org/10.1016/j.fuel.2017.08.067
Received 17 January 2017; Received in revised form 14 August 2017; Accepted 17 August 2017

Various methods and theories have been developed for interpreting sorption isotherms measured on microporous materials. Some approaches called 'classical methods' are based on macroscopic, thermodynamic assumption, including the KJS method [16] and the DBdB method [17]. In contrast to classical methods, some methods, developed in recent years, offer a microscopic model of adsorption and connect the macroscopic properties to molecular behavior. These methods include Non-Local Density Functional Theory (NLDFT) and Quenched Solid Density Functional Theory (QSDFT) [18–21]. Monte Carlo simulation (MC) [22,23] and Molecular Dynamics (MD) [24,25] are also used for the calculation of PSD. Among all different approaches mentioned above, the BJH method can be considered as the most popular method for mesopore-size analysis while studying the pore characteristics of shale [26]. In the meantime, revised BJH approach were proposed continuously to improve pore size analysis [16,27]. And there are also some study that compared other methods like NLDFT and MC with BJH method published to better understand different pore structures of porous materials [28,29].

As mentioned above, the conventional calculation methods of PSD are based on the assumption of uniform pores, which is inappropriate when we deal with some heterogeneous materials like shale, so they have to be modified to apply to shale.

In fact, the adsorption branch and desorption branch of open cylindrical pores or open slit pores are not overlapped. They separate from each other forming a hysteresis loop. Meanwhile, there exist clear differences between the hysteresis loops of these two kinds of pores presented in Fig. 1. According to the two parts above, we present a modified method to obtain the PSDs of cylindrical pores and slit pores respectively and distinguish between them. It should be mentioned that both cylindrical pores and slit pores are taken full advantage of in the presented method formulation, and both adsorption and desorption branches of nitrogen isotherm are utilized to calculate the PSDs.

Obtaining the PSDs of both cylindrical pores and slit pores can be of great help to better understand the pore characteristics of shale reservoirs. The reasons are as follows: (1) A more accurate mesopore volume distribution can be obtained distinguishing two types of pores, which will help us to better evaluate the gas storing space at nano-scale; (2) Considering the difference between the specific surface area of cylindrical pores and that of slit pores, dual pore-shape model may provide a better understanding of gas adsorption space and capability in shale; (3) Gas content and the ratio of free gas and adsorbed gas can be re-estimated based on (1) and (2); (4) Flow in cylindrical pores and slit pores differs from each other. So microscopic mechanisms of flow in shale need to be re-examined. Obviously a better characterization of pore geometry can be helpful in predicting the flow characteristics and permeability of nanoporous shale samples [30,31].

## 2. Theoretical formulation

Based on the knowledge above, multilayer adsorption and capillary condensation must be considered simultaneously while we are calculating the PSDs of shale samples. For the convenience of analysis, we assume that:

1) Both the cylindrical pores and slit-shaped pores exist in shale.
2) Micropores are all open. That means the two ends of the cylindrical pores and all sides of the slit pores are open.
3) All sizes of cylindrical pores and slit pores ranged continuously from small to large exist in shale.

Obviously, the real pore system is more complicated and can not be simply classified into just two categories. Some other pore shapes are not taken into account in shale samples which have more complicated mechanism, like cone pores, wedge pores, and especially inkbottle pores. In fact, the assumptions made above are to simplify the pore structure on the basis of the perception that cylindrical pores and slit pores are the major types in the pore system. In this sense, the assumptions can be considered reasonable although there are some defects in the hypothesis.

### 2.1. Mathematical derivation

According to the phenomena of condensation and adsorption, when condensation occurs, the gas-liquid interface in open cylindrical pore is a cylinder surface and in open slit pore condensation does not happen until the relative pressure raises up to 1. But when evaporation starts, the gas-liquid interface in open cylindrical pore becomes a hemisphere surface and in slit pore it is a semi-cylinder surface. On the basis of Kelvin equation, the critical radius of sphere surface $r$ and cylinder surface $r'$ can be calculated from relative pressure of adsorption isotherms, which can determine the radius of cylindrical pores and the width of slit pores,

$$\ln x = -\frac{2\gamma v_m}{RTr} = -\frac{2\gamma v_m}{RT\,(r_{c,true}-t)} \tag{1}$$

$$\ln x = -\frac{\gamma v_m}{RTr'} = -\frac{\gamma v_m}{RT\,(r_{s,true}-t)} \tag{2}$$

where $x = p/p_m$ is relative pressure, and $p_m$ is saturation pressure of adsorptive, $T = 77.3K$ which is the liquid-nitrogen temperature, the

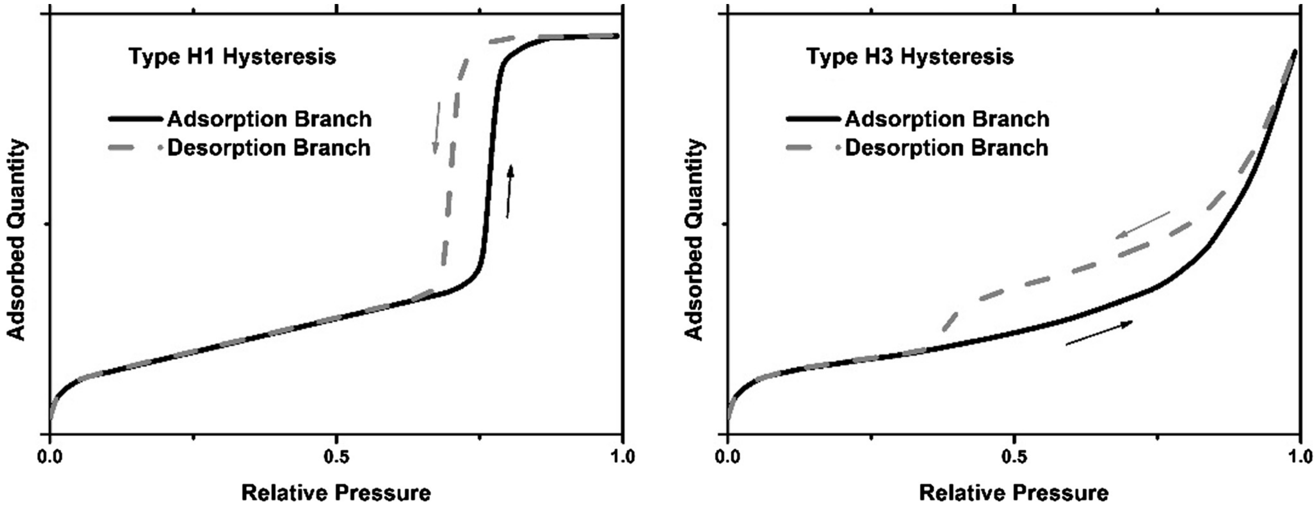

**Fig. 1.** Type H1 and type H3 hysteresis of adsorption isotherms.