Available online at www.sciencedirect.com

ScienceDirect

Journal of Natural Gas Geoscience 1 (2016) 221−230

http://www.keaipublishing.com/jnggs

Original research paper

Application of low pressure gas adsorption to the characterization of pore size distribution of shales: An example from Southeastern Chongqing area, China☆

Tengfei Li [a,b], Hui Tian [a,*], Ji Chen [a,b], Lijun Cheng [c]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
[b] University of Chinese Academy of Sciences, Beijing, 100049, China
[c] Key Laboratory of Shale Gas Exploration, Ministry of Land and Resources, Chongqing Institute of Geology and Mineral Resources, Chongqing, 400042, China

Received 14 May 2016; revised 10 June 2016
Available online 14 July 2016

Abstract

Pore size distribution is vital in the preservation and exploitation of shale gas; the pores in shales are mainly of nanometer scale. This study focuses on the pore structures of the Upper Ordovician-Lower Silurian black shales that were sampled from the Well YC7 in southeastern Chongqing area. Nitrogen and carbon dioxide gas adsorption were conducted at 77.4 K and 273.15K, respectively. Pore structures were characterized by the modified BET, BJH, DFT, and Stoeckli methods. The results show that: (1) micropores, mesopores, and macropores are all well developed in both the Lower Silurian and Upper Ordovician shales; (2) the mean diameter of micropores for our samples is approximately 1.26 nm; and (3) the micropore size distribution curves derived from the Stoeckli method together with the CO_2 adsorption data at 273.15K can be well connected with the calculated DFT model values through nitrogen adsorption data at 77.4 K, indicating that a full pore size distribution curve could be achieved for micropores, mesopores, and a portion of macropores in the shales by combing the N_2 and CO_2 adsorption data.

Keywords: Shale gas; N_2 and CO_2 adsorption; Pore size distribution

1. Introduction

Shale gas is referred to as natural gas retained in shale sequences, it may be biogenetic gas, thermogenic gas, or of both in origin [1−3]. Shale predominantly contains nanoscale pores with complex structures. A thorough understanding of pore structures is essential for the evaluation of gas shale reservoirs [4−8]. According to IUPAC [9], pores in shales can be categorized into three groups based on their size, namely, micropores having a width less than 2 nm, mesopores having a width between 2 and 50 nm, and macropores with a width greater than 50 nm. Furthermore, pores in shale reservoirs can be characterized by their location and nature, such as interparticle and intraparticle pores in the mineral matrix, intraparticle pores in organic-matter grains, and tiny fractures cutting through organic and inorganic grains [10].

There are mainly two approaches to studying shale's pore structure. One is related to direct observation that relies on various microscopy technologies, including optical microscope, transmission electron microscope (TEM), and scanning electron microscope (SEM). While these instruments

☆ This is English translational work of an article originally published in *Natural Gas Geoscience* (in Chinese). The original article can be found at: 10.11764/j.issn.1672−1926.2015.09.1719.

* Corresponding author.
E-mail address: tianhui@gig.ac.cn (H. Tian).

Peer review under responsibility of Editorial Office of *Journal of Natural Gas Geoscience*.

http://dx.doi.org/10.1016/j.jnggs.2016.07.001

present us direct images of various pores, the results brought about are only qualitative [11]. On the other hand, the other method is indirect and it involves various measurement technologies that are utilized to obtain quantitative information for total porosity and full pore size distribution. I.e. helium pycnometry is used for total porosity [12], and high-pressure mercury intrusion and low-pressure N_2/CO_2 gas adsorption for pore size distribution (PSD) [13]. High-pressured mercury intrusion can provide information for both total porosity and PSD for conventional reservoirs such as sandstone and carbonates reservoirs where micrometer-scale pore preponderate [14−16]. Pores in shale reservoirs are largely nanometer in scale; however, the mechanical strength of shale is not as good as sandstone. As much as this method is capable of characterizing shale's PSD, it would potentially create some artificial macropores at exceedingly high pressures [17,18]. In contrast, low-pressure gas adsorption has fewer chances in creating artificial macropores during measurement and is even capable of characterizing the PSD curves for pores ranging from micro to macro in size. Therefore, low-pressure gas adsorption technology has been widely used for the analysis of shale's pore structure [19−21].

Nowadays, it's difficult to use only one method to characterize the full pore size distribution for shales; hence, multiple methods have to be combined to accurately determine so. I.e. Clarkson et al. [22], integrated ultra-small-angle neutron scattering, low-pressure gas adsorption, and high-pressure mercury intrusion methods to study the PSD curves of shales from North American. Tian et al. [23] combined low-pressure gas adsorption and high-pressure mercury intrusion methods to analyze the pore structures of typical lacustrine and marine shales in China. For the reason that different methods are based on distinct theories and analytical procedures, the PSD curves for distinct pore ranges are usually not connected very well, especially in linking micropore and mesopore PSD curves. For example, Hu et al. [24] tried to present a full PSD for artificially matured Woodford shale samples based on low-pressure N_2 and CO_2 adsorption data, but they failed to relate the PSD curves for micropores and mesopores. Furthermore, most of the current models used for pore structure analysis of shale reservoirs, such as BET equation and DR/DA equation, were originally designed for materials with homogeneous chemical properties and structures, thus, their direct application to shale reservoirs with extremely complex pore structures have to be cautious and may result in remarkable errors in some cases [25−27]. In this study, six core samples from Lower Silurian shale in southeastern Chongqing area in China were collected and analyzed for their pore structures using both low-pressure N_2 and CO_2 adsorption techniques through the modified BET equation, Stoeckli equation, BJH, and DFT models. The main objective of this study is to investigate how the selected models influence the results of shale pore structure analysis and to discuss how the PSD curves for both micropores and mesopores can be well connected around 2 nm.

2. Sampling and experiments

Six core samples were collected from the area ranging the Upper Ordovician Wufeng up to Lower Silurian Longmaxi Formations, specifically in the Well YC7 that was drilled in the Youyang area in Chongqing city (Table 1, Fig. 1).

2.1. Organic geochemistry and petrology

Total organic carbon (TOC) was measured by means of the LECO CS-200 analyzer on ground shale samples (about 100 mesh in size) after being treated with hydrochloric acid to remove carbonate minerals. Due to the lack of vitrinite in the sampled shales, the reflectance of pyrobitumen was measured through polished blocks with a 3Y microphotometric system. The random reflectance was measured in oil immersion ($n = 1.518$) at 546 nm using a 50×/0.85 objective lens. The pyrobitumen reflectance can be converted to equivalent vitrinite reflectance with an empirical equation. Due to the high thermal maturity level of the samples, we have chosen the formula proposed by Schoenher et al. [28] to succeed the conversion since it was more suitable for samples with high maturity level.

The X-ray diffraction (XRD) analysis was measured via the Bruker D8 Advance X-ray diffractometers after the crushed shale grains were sieved to be less than 200 mesh. The working condition was 40 kV and 30 mA with a Cu Kα radiation ($\lambda = 1.5406$ for Cu Kα1). Stepwise scanning measurements were performed at the rate of 4° per minute, whereas the result ranges from 3°−85° (2θ). The relative mineral percentage contents were calculated using the semi-quantitative equation proposed by Rietveld [29].

2.2. Low pressure N_2 and CO_2 adsorption

The N_2 and CO_2 adsorption measurements were carried out on Micromeritics ASAP 2020, an automatic surface area and pore size analyzer. Shale samples were crushed into grains about 40−60 mesh (425−250 μm), then it was dried in vacuum oven for 12 h at 383.15 K to remove adsorbed moisture and volatile matter. Then approximately 1 g of sample was loaded into the apparatus and was subjected to degassing under high vacuum (<10 mm Hg) for 10 h at 383.15 K to further remove residual volatiles. As for N_2 adsorption measurement at 77.4 K, the relative pressure (P/P_0) range was set between 0.001 and 0.995 and both adsorption and desorption branches were collected. CO_2 adsorption isotherms were collected within the relative pressure (P/P_0) range of 0.0001−0.03 at 273.15K; the conditions were achieved by a mixture of ice and water.

2.3. Modified BET equation

Among the analytical models for low-pressure gas adsorption, Brunauer−Emmett−Teller (BET) equation was widely used for the calculation of surface areas' porous material [9]. BET equation was originally established for