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Multifractal characteristics of Longmaxi Shale pore structures by N_2 adsorption: A model comparison

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ABSTRACT

N_2 adsorption is one of the most widely used techniques to assess pore structures of shale samples due to its ability for characterizing pores in nanoscale. Various models have been developed to quantify pore structures based on adsorption isotherms. In this regard, using a suitable model can give us more accurate pore structure information. The Barret, Joyner and Halenda (BJH) model along with density functional theory (DFT), two most frequently used ones for pore structures of shales, employed on Longmaxi shale samples and compared. BJH model can be divided into two sub-models: adsorption (BJHAD) and desorption (BJHDE). First, the multifractal analysis was used to quantify the heterogeneity of pore size distributions derived from these models. Second, partial least regression analysis (PLS) was employed to quantify the correlations between pore structures and rock compositions. The results showed that pore structures (volume and surface area) and pore heterogeneity derived from BJHAD, BJHDE and DFT model would differ. In addition, PLS results indicated that minerals (except dolomite and clay) and organic matter would correlate positively while clay minerals negatively with pore surface area and volume independent of the method that was used. Finally, the comparison of results from these three methods demonstrated that DFT model is superior to BJHAD and BJHDE for pore structure characterization in shale gas formations.

1. Introduction

Unconventional shale plays have become one of the major sources of hydrocarbon production. Comparing their system of pores with conventional reservoirs, these shale plays are more complex and heterogenous (Zhong, 2012; Li et al., 2016; Liu and Ostadhassan, 2017; Zhao et al., 2017). The abundance of very small pore sizes in shale reservoirs have provided plenty of space for hydrocarbons to accumulate. Understanding their pore structures such as: size distribution, volume and surface area can help us to better define phenomenon that are related to the adsorption, desorption, diffusion and flow of gas in shales (Hu et al., 2014; Loucks et al., 2009; Boadu, 2000; Sanyal et al., 2006; Wang et al., 2012; Kong et al., 2018; Zhang et al., 2016). All these can impact the amount of gas that can be recovered from shale reservoirs. Thus, accurate knowledge of pore structures is essential for further development of unconventional shale plays.

Gas adsorption is one of the most widely used methods to assess pore structures of shales (Huang and Zhao, 2017; Liu et al., 2017; Wang et al., 2016; Shao et al., 2017). Among all the gases available as adsorptive, nitrogen has become a leading agent for its strong ability in mesopore characterization (Sing, 2001). In this method, at 77 k (−321 °F), nitrogen adsorption volume versus pressure will be measured, and then pore structure information can be estimated from the isotherms based on different models. Adesida (2011) employed the nitrogen gas adsorption to analyze the pore size distributions of Barnett shale and found that the average pore size of Barnett shale samples is less than 10 nm. Clarkson et al. (2012) used nitrogen adsorption to derive the pore information from the core plugs instead of crushed samples and found that the illite and TOC can influence the pore-throat size more than other existing components. Comparing the results of pore size distributions of shales from several methods such as small angle and ultra-small angle neutron scattering (U/SANS), low-pressure gas adsorption and mercury intrusion, Clarkson et al. (2013) derived more information about the pore structures such as pore geometry, pore size distribution and accessible versus inaccessible porosity. Adsorption of water can change shale structures significantly due to the presence of clay minerals which was studied bu Chenevert (1970). Zolfaghari et al. (2017a, b) applied water sorption to investigate the role of clays, in particular, in water sorption of shale samples. In combination with nitrogen gas adsorption, he characterized the inorganic and organic

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pore size distributions of gas samples.

Several models are widely being used to interpret gas adsorption isotherms currently. The method that is proposed by Barret, Joyner and Halenda (BJH model) is one of the most popular ones that is being used in nitrogen adsorption experiments to calculate pore size distributions (mesopores and smaller macropores) (Barrett et al., 1951). BJH model is based on Kelvin equation which describes the changes in vapor pressure due to a curved liquid-vapor interface. BJH model can be applied to analyze the adsorption branch (BJHAD) or the desorption branch (BJHDE) of the curve. Both of these two methods have been widely employed to analyze pore size distributions (PSD) of shale rocks and other porous media (Klimakow et al., 2012; Hassan, 2012; Labani et al., 2013; Hou et al., 2014; Xiong et al., 2015; Carati et al., 2003; Esparza et al., 2005; An et al., 2015; Luca et al., 2015; J. Li et al., 2015). Density functional theory (DFT) is another method that has been used frequently for characterization of porous materials (Lastoskie and Gubbins, 2000; Ravikovitch and Neimark, 2001; Ravikovitch et al., 1997; Neimark et al., 1998; Groen et al., 2003). DFT is based on statistical mechanics where pores with various sizes are assumed to have regular shapes (slit or cylindrical) and each pore acts independently. In this method, the solid-fluid (nitrogen-pore surface) and the fluid-fluid (nitrogen-nitrogen) interactions are known to control pore fillings.

Researchers usually utilize one of the above methods to analyze pore structures of shale rocks from gas adsorption data. However, this question has never been fully answered whether which method is superior for pore structure analysis of shales to provide the most precise results. This is important since employing the wrong model to characterize pore structures can cause under or over estimation of the reserve or failed enhanced oil recovery (EOR) and further economic loss. It is well understood that pore size in shales is not uniformly distributed. In order to quantify pore size distributions of shale samples, fractal methods were usually applied.

The main advantage in acquiring fractal method is due to its strong ability to describe irregularity of fragmented shapes of various features in nature that cannot be analyzed by traditional Euclidean geometry (Lopes and Betrouni, 2009). Fractal analysis has already been used extensively in porous media characterization such as to determine pore size distributions (Xia et al., 2018), electrical conductivity (Cai et al., 2017), permeability (Liu et al., 2016) and effective stimulated reservoir volume (Sheng et al., 2017). Regarding pore structure analysis of shale formations, fractal theory is a powerful tool that has been employed successfully in conjunction with imaging techniques (Liu and Ostadhassan, 2017), gas adsorption (Liu et al., 2017), micro-CT (Chen et al., 2017), mercury intrusion (Ding et al., 2017) and small angle neutron scattering (Clarkson et al., 2013) to prove the fractal behaviors of shale reservoirs. Multifractal is the extension of fractal theory which decomposes self-similar measures into intertwined fractal sets and is characterized by singularity strength of fractal sets. Multifractal theory can provide more accurate information about pore structures (Lopes and Betrouni, 2009). Moreover, multifractal analysis can describe random fluctuations around some specific sub pore size intervals and characterize pore size intervals that may exhibit various types of self-similarity (Li et al., 1999).

In this study, seven samples from the Longmaxi Formation, a typical shale gas play in China are analyzed for pore structures by nitrogen gas adsorption. Then the pore structures of the samples are analyzed using three different methods: BJHAD, BJHDE and DFT to find the most appropriate one for such unconventional reservoirs. This study is the first approach which provides a comparative result of various existing methods that are being used extensively by researchers for characterizing the pore sizes of shale reservoirs. We provided more insight and suggestions on the most appropriate ones to be used based on our results.

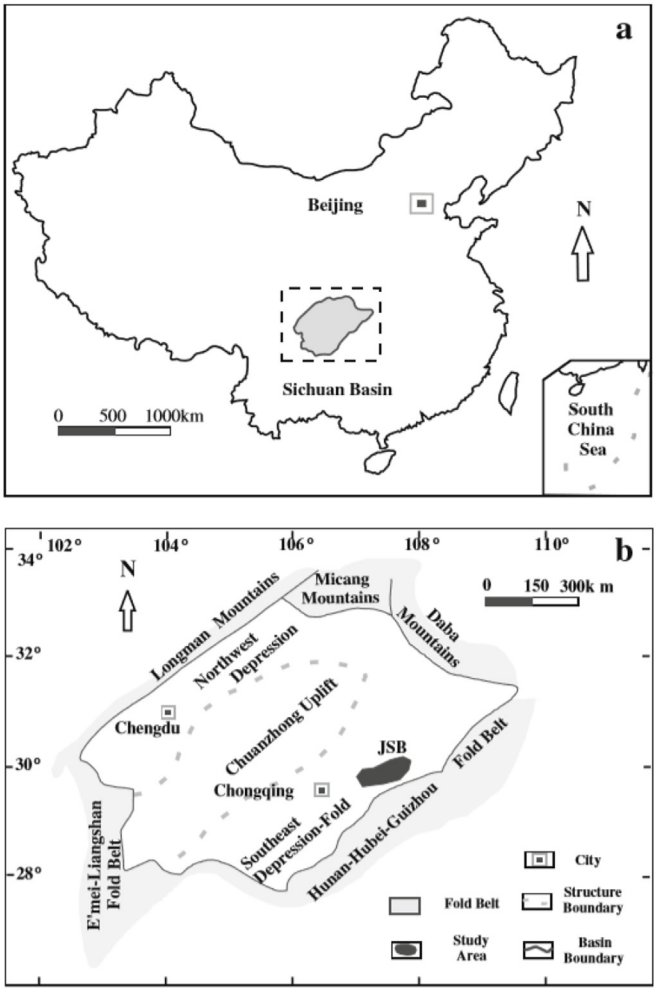

Fig. 1. Information of the locations of Sichuan basin and the JSB gas field (a Sichuan Basin, b JSB gas field) (Wang et al., 2016).

2. Geological settings of Longmaxi Formation

Sichuan Basin located in southwestern of China (Fig. 1a), is oil bearing and gas rich which produces from many different stratigraphic units from the Upper Sinian (Upper Neoproterozoic) up to the Cretaceous (Hao et al., 2008; Liu et al., 2011). Silurian Longmaxi Formation which is composed of eight lithofacies is the most important source rock in Sichuan Basin described as black shale, dark-gray mudstones, and shale gas (Zhao et al., 2016). The total organic carbon (TOC) content of the Longmaxi Formation varies from 0.2 wt% to 6.7 wt% and the organic matter is mainly Type II kerogen. The organic matter is over mature with VR% from 2.4% to 3.6% while the porosity measured on core plugs from 0.58% to 0.67% (Liu et al., 2013). In this study, seven samples were collected from the Longmaxi Formation of Jiaoshiba gas field from 2370 to 2410 m depth which is in the Fuling District of Chongqing Municipality (Fig. 1b).

3. Experiments

3.1. Mineral composition and TOC analysis

First core samples were grinded to 100 mesh, and then X-ray diffraction (XRD) analysis was performed. The types of minerals were quantified based on the main peaks that are derived from each sample. In the next step, samples were crushed into grains less than 100 mesh and subjected to hydrochloric acid treatment for the removal of