Full Length Article

Nanoscale pore structure characterization of the Bakken shale in the USA

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ABSTRACT

Understanding the pore structures of unconventional reservoirs such as shale can assist in estimating their elastic transport and storage properties, thus enhancing the hydrocarbon recovery from such massive resources. Bakken Shale Formation is one of the largest shale oil reserves worldwide located in the Williston Basin, North America. In this paper, we collected a few samples from the Bakken and characterized their properties by using complementary methods including X-ray diffraction (XRD), N_2 and CO_2 adsorption, and Rock-Eval pyrolysis. The results showed that all range of pore sizes: micro (< 2 nm), meso (2–50 nm) and macro-pores (> 50 nm) exist in the Bakken shale samples. Meso-pores and macro-pores are the main contributors to the porosity for these samples. Compared with the Middle Bakken, samples from Upper and Lower Bakken own more micro pore volumes. Fractal dimension analysis was performed on the pore size distribution data, and the results indicated more complex pore structures for samples taken from the Upper and Lower Bakken shales than the Middle Bakken. Furthermore, the deconvolution of the pore distribution function from the combination of N_2 and CO_2 adsorption results proved that five typical pore size families exist in the Bakken shale samples: one micro-pore, one macro-pore and three meso-pore size families. The studies on the correlations between the compositions and the pore structures showed that mostly feldspar and pyrite affect the total pore volume of samples from Middle Bakken Formation whereas clay dominates the total pore volume of samples from Upper/Lower Bakken Formation. TOC and clay content are the major contributors to the micro-pore size family in the Upper/Lower Bakken. Also, it was observed that the increase of hard minerals could increase the percentage of macro-pore family in the Middle Bakken Formation.

1. Introduction

The recent advancements in horizontal drilling and hydraulic fracturing have significantly increased the recovery from unconventional shale reservoirs such as Bakken shale. The Bakken "shale", located in the Williston Basin in Montana, North Dakota (USA), and southern Saskatchewan (Canada), is now the second largest hydrocarbon reservoir in the USA. Compared with massive studies of shale gas reservoirs, such as the Barnett [1], Marcellus [2], Albany [3], Long maxi [4], Perth [5], Toarcian [6], Boom clay [7], Posidonia Shale [8], Opalinus clay [9], the study of shale oil reservoirs is still limited and in the primary stages. Consequently, the physical properties, especially the porosity and pore size distributions of shale oil formations (i.e. Bakken shale) are still poorly understood. Porosity and pore size distributions are the most important parameters in shale reservoirs which influence the mechanical, storage and transport properties of the porous media [10–12]. In comparison to the conventional reservoirs such as sandstone or limestone, the pore structures in shale reservoirs are more complex due to the abundance of the nano-pores.

According to the International Union of Pure and Applied Chemistry (IUPAC) (1994) [13], pores can be divided into three categories: micropores (< 2 nm), meso-pores (2–50 nm) and macro-pores (> 50 nm). Many researchers have applied this criterion to analyse the pore structures of shale gas formations with various analytical methods. Field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are the image analysis methods to semi-quantify the pores [8,14–19]. Low-pressure gas adsorption, mercury injection capillary pressure (MICP), small angle neutron scattering (SANS), nuclear magnetic resonance spectroscopy (NMR) are other common techniques to quantify the pore size distributions [20–26]. With respect to MICP, the potential shortage is that under high pressure of around 60,000 psia, the injection of mercury will distort, compress and damage the pore structures especially if the sample contains a large amount of compressible clay minerals [27]. The theoretical calculation shows that MICP cannot measure the pores with sizes below 3.6 nm, while the practical limit will be

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higher [28]. A significant number of pores in the shale which are less than 3.6 nm is too small to be characterized by the MICP. Regarding nuclear magnetic resonance (NMR), the relaxation time (T_2) increases as the pore size increases, which can be used to characterize the pore size distributions. However, the sample preparation for NMR is complicated and the extraction and injection of the liquid can potentially damage the weak pore structures of the rock. This process can limit the accuracy of NMR, and the variations that would occur in surface relaxation render the results inaccurate [20].

Gas adsorption is of major importance of measuring the pore structures over a wide range of porous materials. Since Dewar [29] reported the adsorption nitrogen and other gases at liquid air temperature when studying the composition of the atmosphere gases, nitrogen has become a potentially available adsorption material. The monumental work on the monolayer adsorption by Langmuir [30] attracted a great interest from researchers for the interpretation of adsorption data. In the 1930s, Benton and White [31] published on the existence of the multilayer adsorption of nitrogen at the temperature of 77 K. Brunauer and Emmett applied gas adsorption to analyse the surface area of samples [32]. In 1938, the publication of the Brunauer-Emmett-Teller (BET) theory, which is the extension of the Langmuir monolayer adsorption model to a multilayer adsorption model, provided researchers the theoretical method to determine the surface area of porous medi [33]. In the late 1940s, by using the Kelvin equation, Barrett, Joyner, and Halenda (BJH) proposed a method [34] to derive the pore size distributions from the appropriate nitrogen isotherm. The BJH method is still one of the most popular methods used to date. In the early 2000s, based on the established principles of statistical mechanics and assuming a model solid structure and pore topology, the DFT method was proposed and has been an important tool in characterizing the pore size distribution of porous samples [35].

For the geological materials, such as rocks, gas adsorption has been applied frequently nowadays to study the shale formations [36–39]. One limitation of nitrogen, which originates from the gas molecule and pore throat sizes, makes it inaccurate in characterizing the micro-pore size range (less than 2 nm). CO_2 adsorption was then used to analyse the micro-pores since it works well in the media containing pores less than 2 nm [39]. The combination of nitrogen and CO_2 can give us information about the whole pore size distributions less than 200 nm.

The purpose of this work is to provide extensive information on the pore size and structure using gas adsorption methods (N_2 and CO_2). In addition, the impacts of the mineral compositions on the pore structures of Bakken shale is investigated.

2. Experiments procedure

2.1. Sample preparation

The Bakken Formation consists of three members (Fig. 1): Upper Bakken and Lower Bakken that are dark marine shales with high organic content, and serve as both the source and trap for the generated hydrocarbons, whereas the Middle Bakken, composed of mixed carbonates and fine-grained clastics, is the main production unit [40–41]. In this study, 12 samples were collected from Upper Bakken (Sample #1, #2, #3, #4, #5), Middle Bakken (Sample #6, #7, #8, #9, #10) and Lower Bakken (#11, #12) to conduct experimental pore structure analysis.

The nano-darcy permeability of the Bakken formation makes the diffusion, penetration, and equilibration of the gas molecules impossible or impractical for the intact samples. In order to solve this problem, the samples were crushed in order to decrease the path length for the gas to access the entire pore structures and acquire the equilibrium within a reasonable time. Based on the study by Kuila and Prasad [28], the creation of the new surfaces during the crushing process will not affect the pore structure data within the range of investigation. In this paper, samples were crushed to < 250 um to be used for gas adsorption analysis [5].

2.2. Mineral composition analysis

X-ray diffraction (XRD) was used to analyse the mineralogical compositions of the samples. Sample powders with sizes less than 650 mesh were put in the Bruker D8 Advance X-ray diffractometer. The scanning measurements were performed at the rate of 2°/min in the range of 3–90°. The relative mineral percentages were estimated by calculating the curve of the major peaks of each mineral with correction for Lorentz Polarization [43].

2.3. Geochemical analysis

Rock-Eval pyrolysis is applied to quantify the total organic carbon (TOC) and thermal maturity. Following the detailed procedures proposed by Behar et al. (2001) [44], 60–70 mg of each sample was used for the analysis. In this study, we applied the shale reservoir method to carry out the Rock-Eval analysis. Shale reservoir method is best-suited for assessing the hydrocarbon potential in these unconventional shale reservoirs compared with other two methods (default method and reservoir method). This is because the shale reservoir method captures the thermos-vaporizable (light) hydrocarbons in the C1–C15 range [45]. The initial temperature was 100 °C, which was increased to 200 °C at 25 °C/min steps and held constant for 3 min (for Sh0 calculation), then the temperature is increased to 350 °C at 25 °C/min steps, and held steady for 3 min (for Sh1 calculation), and finally raised to 650 °C at 25 °C/min steps. For vitrinite reflectance (R_o) analysis, the whole-rock samples were crushed to 20 mesh (850 um) particles, mixed with the epoxy resin and hardener (ratio of 2:1) and left to harden under vacuum conditions for 24 h [46]. The samples were polished to ensure that the surface is scratch and relief free by using Buehler EcoMet/AutoMet 250 automated polishing equipment. A Carl Zeiss Axio Imager A2m microscope, equipped with a white light source and a UV light to analyse the reflectance in oil (R_o) and fluorescence, was used for reflectance measurements and visual kerogen analysis.

2.4. Gas adsorption

Prior to adsorption measurement, the samples were degassed for at least 8 h at 110 °C to remove moisture and volatile in the sample pores. Low-pressure nitrogen was measured on a Micromeritics® Tristar II apparatus at 77 K. Carbon dioxide adsorption was measured on a Micromeritics® Tristar II plus apparatus at 273 K. Gas adsorption volume was measured over the relative equilibrium adsorption pressure (P/P_0) range of 0.01–0.99, where P is the gas vapor pressure in the system and P_0 is the saturation pressure of nitrogen.

The gas adsorption experimental data was used to quantify the amount of the gas adsorbed at different relative pressures (P/P_0) where P_0 is the saturation pressure of the absorbent and the P is gas vapor pressure in the system.

For the surface area determination, we used the multipoint to calculate the BET. We plotted a straight line $1/v[(P_0/P) - 1]$ as the y axis and P/P_0 (range as the 0.05–0.3) as the x axis, which is also called the BET plot according to the requirement of ISO 9277 [47]. The value of the slope and the y intercept of the line were used to calculate the monolayer adsorbed gas quantity and the BET constant. The surface area can then be calculated from the BET (Brunauer, Emmett and Teller) theory [33].

For nitrogen adsorption, the total volume can be derived from the total amount of vapor adsorbed at the relative pressure (P/P_0) which is close to 1, assuming that the pores are filled with the liquid adsorbate. The average pore radius of the sample can be calculated as:

$$r_p = \frac{2V}{S},$$

(1)