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Multifractal analysis of gas adsorption isotherms for pore structure characterization of the Bakken Shale

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ABSTRACT

Understanding pore heterogeneity can enable us to obtain a deeper insight into the flow and transport processes in any porous medium. In this study, multifractal analysis was employed to analyze gas adsorption isotherms (CO_2 and N_2) for pore structure characterization in both a source (Upper-Lower Bakken) and a reservoir rock (Middle Bakken). For this purpose, detected micropores from CO_2 adsorption isotherms and *meso*-macropores from N_2 adsorption isotherms were analyzed separately. The results showed that the generalized dimensions derived from CO_2 and the N_2 adsorption isotherms decrease as q increases, demonstrating a multifractal behavior followed by *f(α)* curves of all pores exhibiting a very strong asymmetry shape. Samples from the Middle Bakken demonstrated the smallest average *H* value and largest average α_{10-}-α_{10+} for micropores while samples from the Upper Bakken depicted the highest average α_{10-}-α_{10+} for the *meso*-macropores. This indicated that the Middle Bakken and the Upper Bakken have the largest micropore and *meso*-macropore heterogeneity, respectively. The impact of rock composition on pore structures showed that organic matter could increase the micropore connectivity and reduce micropore heterogeneity. Also, organic matter will reduce *meso*-macropore connectivity and increase *meso*-macropore heterogeneity. We were not able to establish a robust relationship between maturity and pore heterogeneity of the source rock samples from the Bakken.

1. Introduction

Oil and gas unconventional shale and conventional hydrocarbon plays contribute a significant amount of petroleum production. Various pore sizes, from nano- to macro- are reported in these reservoirs all around the globe; for example, Second White Speckled Shale [1], Dalong Shale [2], Perth Shale [3], Bakken Shale [4], Barnett Shale [5], and Marcellus Shale [6]. Therefore, understanding the pore structures can result in a deeper insight about the flow and storage capabilities of any porous medium [7,8].

During the past decade, a wide range of methods have been applied to characterize these pores including: mercury intrusion porosimetry (MIP) [9], gas adsorption method [10], small angle neutron scattering (SANS) and ultra-small angle neutron scattering (USANS) [11], nuclear magnetic resonance (NMR) [12], direct observation methods such as: field emission scanning electron microscope (FE-SEM) [13–15], atomic force microscopy (AFM) [16,17], microfocus X-ray computed tomography (u-CT) [18,19] and transmission electron microscope (TEM) [20]. In this regard, each method has advantages and disadvantages. For example, FE-SEM can directly detect size and distribution of larger pores but cannot provide any information about micropores because of limitations in tool resolution [4]. MIP determines the largest entrance of mercury into a pore (i.e., pore-throat size) instead of measuring the true pore size [21]. Moreover, a high injection pressure rate will potentially damage the pore structures of the shale with high clay content [22]. The methods that mentioned above can provide us with acceptable information about the porosity and pore size distribution (PSD) of rocks. However, in addition to PSD and porosity as a quantity, the complexity of the pore network is another major parameter that needs to be characterized due to its importance in affecting flow properties and gas storage capacity in different rock samples [23]. Notwithstanding the importance, understanding the complexity of pore structure and pore network in shale formations is still a task that needs further attention.

It is well understood that pore size in shales is not uniformly distributed thus cannot be represented by traditional Euclidean geometry

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[23–25]. Thus, in order to describe the complexity that exists in pore structures, fractal theory, initially proposed by Mandelbrot [26], has been widely used instead. A fundamental characteristic of a fractal object is that the measured properties are a function of the scale of measurement [27]. So far, several methods have been proposed and used extensively by researchers on methods to define a fractal behavior, such as: box-counting [28,29], fractional Brownian methods [30] and area measurement methods [31,32]. The box-counting method was defined by Russel et al. [28] and became one of the most popular methods for gas adsorption isotherms data analysis. This method is defined by applying different boxes of various lengths to cover the whole signal spectrum to be analyzed [28,29]. In addition to box-counting, fractional Brownian is also another method that has been used for fractal analysis and is based on a non-stationary model to describe random phenomenon. This model is a generalized form of Brownian motion where the expected value of intensity differences between two points should be zero. However, the square of the differences should be proportional to the distance between these two points and fit the power law [30]. Another commonly used method for fractal analysis is the area measurement, which uses structuring elements such as triangle, erosion, or dilation of various scales and then computes the area of the signal intensity surface at that corresponding scale. Three algorithms: isarithm method, blanket method, and the triangular prism method are the most popular ones in the area measurement methods to calculate the fractal dimensions [31–33].

However, fractal models can only capture a simple fractal behavior that can be described only by one parameter-fractal dimension (D_0). This parameter describes the irregularity within limited size intervals [23,34,35]. However, in heterogeneous rocks, the pore size distribution (PSD) curve usually fluctuates randomly, jumps off at different pore size intervals [23,34], and the pore size intervals may exhibit various types of self-similarity [36]. All these complexities make it difficult to characterize PSD curves with one single fractal dimension.

Considering the above discussion, multifractals can resolve the issue that is a feature of complex pore structures in heterogeneous rocks. Multifractals can be counted as the extension of fractals or the superposition of monofractal structures [27]. Multifractal analysis, which decomposes self-similar measures into intertwined fractal sets, is characterized by singularity strength of fractal sets and can provide more accurate information about pore structures. The multifractal theory has recently been applied to study pore structures of different rock types such as chalk, carbonate, and shale gas formations [37–39].

Bakken is one of the largest unconventional shale oil plays in the world. The Bakken Formation consists of three members: organic-rich Upper and Lower Bakken and the Middle member, which is composed of mixed carbonates and fine-grained clastics [40]. In previous studies, we analyzed the multifractal behavior of pore structures of the Bakken Formation using SEM images [13]. However, it was described that SEM imaging technique was only able to detect pores that are larger than 9 nm. In order to access and evaluate smaller pores, gas adsorption was later acquired. This made it possible to characterize pores beyond SEM resolution. Accordingly, gas adsorption (CO_2 and N_2) was utilized to analyze pore structure of the Bakken in another study [4]. In our current research approach, we focused on applying multifractal method to analyze the complexity of pore structures in a wide range of pore sizes, ranging from micro- to macro- that exist in the Bakken both in the reservoir (Middle member) and source section (Upper and Lower member) of the formation.

2. Methods and experiments

2.1. Samples

In order to study the heterogeneity of pore structures and compare pore network complexity that may occur in rocks due to the changes in mineralogy and main constituent components, it was decided to study a few samples from each member of the Bakken Formation and compare the results. With respect to the goals of this research attempt, 4 samples were selected from the Upper Bakken (Samples 1–4), 4 samples were selected from the Middle Bakken (Samples 5–8) and 3 samples were selected from the Lower Bakken (Sample 9, 10 and 11). The numbers were decided based on sample availability. Thus, a total number of 11 samples were crushed to less than 250 μm to be tested by the gas adsorption (CO_2 and N_2) method.

2.2. Mineralogy and geochemistry analysis

A D8 Advance X-ray diffractometer was used to study the mineralogical content of the samples. The scanning measurements were performed at the rate of 2°/min in the range of 3–90°. Then, the mineral percentages were estimated by calculating the curve of major peaks [41]. In the next step, Rock-Eval 6® was used to quantify the total organic carbon (TOC) of the samples. This part is specifically important for the samples selected from the source section of the Bakken (Upper and Lower members). To evaluate the TOC of the samples, the trademarked Shale Play method by IFP (Institut Françcais du Pétrol) was applied, and the geochemical properties were derived following the steps suggested by Behar et al. [42]. The temperature program for the Shale Play method was set as the following: the initial temperature was 100 °C which was increased to 200 °C at 25 °C /min and was then kept constant for 3 min (for Sh0 calculation). In the next step, temperature was increased to 350 °C at 25 °C/min and held steady for 3 min (for Sh1 calculation). Finally, the temperature was raised to 650 °C at 25 °C/min. The oxidation cycle reached up to 850 °C. This procedure resulted in measuring all Rock-Eval parameters along with TOC of the samples.

2.3. Gas adsorption

All samples were degassed for at least 8 h at 110 °C to remove moisture and volatiles that might be present in the samples. Low-pressure nitrogen was measured on a Micromeritics® Tristar II apparatus at 77 K while carbon dioxide adsorption was measured on a Micromeritics® Tristar II plus apparatus at 273 K. Gas adsorption volume was evaluated 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 [4]. We utilized the density functional theory (DFT) molecular model to quantify pore size distributions from low temperature N_2 adsorption isotherms [43] along with non-local density functional theory to obtain and interpret PSD curves by the CO_2 adsorption method [44,45]. Based on the fundamental principles of statistical mechanics in explaining the molecular behavior of confined fluids in pore spaces, DFT can be used to describe the adsorption and phase behavior of fluids that are confined in the pore structures. Thus, the density functional theory can better define the thermodynamics behavior and density profiles of such fluids in a molecular level compared to other methods such as Brunauer–Emmett–Teller (BET). Based on the reasons explained earlier, DFT, in comparison with other common techniques, can capture the essential features of both micropore and mesopore filling fluids and their hysteresis response. This can result in a more reliable assessment of pore size distribution curves over a more complete range of values (from micropores to mesopores) [46,47].

2.4. Multifractal analysis

The box-counting method, a frequently used method in other studies [28,29,13], was applied to our data to study the multifractal behavior believed to exist in our data. In order to execute multifractal analysis in a porous media, a set of different boxes with equal length ε should be used and be laid over the interval in the recorded signal to be analyzed. The boxes are labeled by index i where $N(\varepsilon)$ indicates the total number of boxes with size of ε that is needed to cover the interval understudy