1 Introduction

Pore system in shales has attracted growing interest, given that gas storage capacity and gas producibility of shale reservoirs critically depend on shale porosity (Loucks et al., 2009; Bernard et al., 2012; Mastalerz et al., 2013). In spite of its importance, the investigation of pores in shale still remains challenging, owing to small pore sizes, wide pore size distributions, and, more importantly, highly heterogeneous pore structure (Loucks et al., 2012).

The fractal dimension characterizes the geometric topography of the surface structure of solid materials (Lowell et al., 2004). This parameter expresses the degree of roughness of a surface or pore wall and can vary from a value of 2 for an ideally flat, smooth surface to 3 for a rough surface with irregular topography and more sorption sites for gases (Lowell et al., 2004). Fractal methods have recently been successfully used in the study of heterogeneous structures in coal (Yao et al., 2008; 2009). However, the fractal characterization of shales still remains scarce (Yang et al., 2014).

This study aims to explore heterogeneous and fractal characteristics of pores in shales from N₂ adsorption isotherms and discuss implications for gas adsorption capacity.

2 Experimental Section

Low pressure gas adsorption porosimetry is employed to investigate the evolution of micro- and mesopores in a suite of 11 New Albany Shale (NAS) samples across a wide range of thermal maturity (vitrinite reflection \( R_o \) 0.35-1.41%). The fractal Frenkel-Halsey-Hill (FHH) model (Pfeifer et al., 1991) and a thermodynamic method (Neimark and Unger, 1993) were used to retrieve fractal dimension from gas adsorption data in this study.

3 Results and Discussion

3.1 Relationships between fractal dimension and thermal maturity and TOC content

Fractal dimension parameters fall in the range of 2.47–2.61 for the shale samples (Table 1) and thus indicate a fractal pore structure. Fractal dimension values derived from FHH and thermodynamic methods are related to mineralogy, pore volume, and surface area, with fractal dimension values derived from thermodynamic methods being systematically higher compared to that obtained via FHH. The experimental disagreement might root in the sensitivity of the FHH equation towards microporous structures (Sahouli et al., 1996).

Fractal dimensions express a nonlinear relation relative to TOC content and \( R_o \) (Fig. 1A, B). The observed initial decrease of fractal dimension values with increasing maturity until \( R_o \sim 0.8\% \) and the subsequent increase at higher thermal maturity (Fig. 1B) are consistent with earlier findings of Yao et al. (2009). Physical compaction of rock at low maturity decreases pore volumes, reduces the heterogeneity of pore surfaces, equalizes the distribution of pore diameters in shale, and therefore reduces fractal dimension values (Yao et al., 2009). During kerogen transformation within the oil window, the generation of new pores adds heterogeneous and rough inner surface areas and leads to elevated anisotropic pore

Table 1 Fractal dimensions derived from Frenkel-Halsey-Hill (FHH) and thermodynamic models

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_o ) (% )</th>
<th>TOC (wt. %)</th>
<th>FHH</th>
<th>Thermodynamic method</th>
</tr>
</thead>
<tbody>
<tr>
<td>472-1</td>
<td>0.35</td>
<td>2.37</td>
<td>2.57</td>
<td>2.74</td>
</tr>
<tr>
<td>634-1</td>
<td>0.50</td>
<td>21.54</td>
<td>2.52</td>
<td>2.69</td>
</tr>
<tr>
<td>MM4</td>
<td>0.55</td>
<td>13.00</td>
<td>2.49</td>
<td>2.60</td>
</tr>
<tr>
<td>552-2</td>
<td>0.61</td>
<td>6.53</td>
<td>2.48</td>
<td>2.60</td>
</tr>
<tr>
<td>NA2</td>
<td>0.65</td>
<td>5.30</td>
<td>2.47</td>
<td>2.59</td>
</tr>
<tr>
<td>IL6</td>
<td>0.70</td>
<td>6.01</td>
<td>2.51</td>
<td>2.70</td>
</tr>
<tr>
<td>IL4</td>
<td>0.83</td>
<td>6.20</td>
<td>2.47</td>
<td>2.57</td>
</tr>
<tr>
<td>IL5</td>
<td>1.15</td>
<td>4.29</td>
<td>2.50</td>
<td>2.62</td>
</tr>
<tr>
<td>IL3</td>
<td>1.27</td>
<td>5.50</td>
<td>2.51</td>
<td>2.54</td>
</tr>
<tr>
<td>IL2</td>
<td>1.30</td>
<td>3.30</td>
<td>2.61</td>
<td>2.77</td>
</tr>
<tr>
<td>IL1</td>
<td>1.41</td>
<td>6.29</td>
<td>2.57</td>
<td>2.58</td>
</tr>
</tbody>
</table>

* Corresponding author. E-mail: yanychen@foxmail.com
Fig. 1. Relationships between Frenkel-Halsey-Hill (FHH) derived fractal dimensional data with $R_o$, TOC content, and mineralogical compositions. Trends lines were drawn to guide the eye.

Fig. 2. Relationships between Frenkel-Halsey-Hill (FHH)-fractal dimensions with meso- and micropore volumes, BET specific surface areas, and mean pore diameters.
diameter distributions and larger fractal dimension values (Yao et al., 2008, 2009). Physical and chemical structural changes during shale maturation, such as the loss of moisture and increased aromaticity of OM, could exert additional effects on the heterogeneity of pores (Yao et al., 2009).

A plot of fractal dimension over TOC content (Fig. 1A) suggests a trough-shaped response of fractal dimension in contrast to Yang et al.’s (2014) finding of a linear correlation; the shale samples in the latter study are of higher maturity (R_{o} 3.0–5.0%, Wang et al., 2013) and narrower ranges of TOC (0.16–9.15 wt. %) and feldspar contents (6.9–28 wt. %; Yang et al., 2014). The discrepancy may be rooted in the fact that the fractal dimension of NAS is not only influenced by TOC, but also by mineralogical composition (Fig. 1C, D, F) and geochemical reactions occurring at low thermal maturity.

3.2 Relationships between fractal dimension and pore characteristics

Surface area and pore size distribution are two central factors controlling the adsorption potential and sorption capacity of shale (Zhou et al., 1999). A large surface area and an abundance of accessible small pores foster extensive interaction between shale surface and gas molecules, and in turn provide a large adsorption potential (Greg and Sing, 1982). Fractal dimensions in NAS express a moderately positive relationship with surface area and a negative correlation with average pore size (Fig. 2C, D). The implied positive correlation between fractal dimension values and gas adsorption capacity underscores the value of fractal dimension as a proxy for the gas adsorption potential of shales.

4 Conclusions

Pore structure and fractal analyses have been applied to a suite of 11 New Albany Shale samples with different thermal maturities to constrain fundamental controls on gas adsorption capacities in fine-grained shales. Pores in shales are highly fractal and heterogeneous in size and shape. The fractal dimension of New Albany Shale positively correlates with surface area and negatively correlates with the average pore diameter. Hence, fractal dimension may serve as a valuable predictor for the gas adsorption capacity of shales.

References


