Research Article

An Investigation of Fractal Characteristics of Marine Shales in the Southern China from Nitrogen Adsorption Data

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We mainly focus on the Permian, Lower Cambrian, Lower Silurian, and Upper Ordovician Formation; the fractal dimensions of marine shales in southern China were calculated using the FHH fractal model based on the low-pressure nitrogen adsorption analysis. The results show that the marine shales in southern China have the dual fractal characteristics. The fractal dimension D_1 at low relative pressure represents the pore surface fractal characteristics, whereas the fractal dimension D_2 at higher relative pressure describes the pore structure fractal characteristics. The fractal dimensions D_1 range from 2.0918 to 2.718 with a mean value of 2.4762, and the fractal dimensions D_2 range from 2.5842 to 2.9399 with a mean value of 2.8015. There are positive relationships between fractal dimension D_1 and specific surface area and total pore volume, whereas the fractal dimensions D_2 have negative correlation with average pore size. The larger the value of the fractal dimension D_1 is, the rougher the pore surface is, which could provide more adsorption sites, leading to higher adsorption capacity for gas. The larger the value of the fractal dimension D_2 is, the more complicated the pore structure is, resulting in the lower flow capacity for gas.

1. Introduction

With the increase of the global energy demands and the importing of advanced techniques, the unconventional gas reservoirs (including tight sands, coal bed methane, and shale gas) have gradually been the focus of exploration and development in many countries such as Canada, China, and Europe [1, 2], especially in China [3]. Shale gas, as one kind of unconventional gas reservoirs, is not only an important energy supplement but also a clean and green energy. In 2011, the “World Shale Gas Resources: An Initial Assessment of 14 Regions Outside the United States,” conducted by the U.S. DOE’s Energy Information Administration, evaluates the risk technically recoverable of shale gas resource to be $36.1 \times 10^8 \text{ m}^3$ in China and $19.6 \times 10^8 \text{ m}^3$ in Sichuan Basin, located in Southwest China [4]. And according to “the nation survey and devaluation of shale gas resource and favorable area selection,” issued by the Ministry of Land and Resources of the People’s Republic of China, the risk technically recoverable of shale gas reservoir is estimated to be approximately $25.08 \times 10^{12} \text{ m}^3$ in China and $14.58 \times 10^{12} \text{ m}^3$

in southern China. Some studies also suggested that there is a great development potential of shale gas resources in southern China [3, 5].

To reduce exploration risk and determine economic feasibility, considerable efforts are being undertaken to understand the knowledge of storage mechanism of shale gas and transport mechanisms of shale gas [6, 7], and pore structure of shale has a significant influence on storage mechanism and transport mechanisms. Therefore, the complex pore structure of shale is an important research field. To understand the complex pore structure of marine shales in southern China, researchers have utilized several measurement techniques to characterize the characteristics of pore structure of marine shales in southern China. Many methods such as scanning electron microscopy, field emission scanning electron microscopy, transmission electron microscopy, focused ion beam scanning electron microscopy, low-pressure gas adsorption analyses, mercury injection capillary pressure, and small-angle neutron scattering have been used to investigate characteristics of pore structure [6–16]. Among these, low-pressure nitrogen (N_2) adsorption

TABLE 1: Shale samples properties.

Region	Number	Age/formation	Types	Source
Changning-Xingwen area, Sichuan Province	L1			
	L2			
	L3		Core	[1, 8]
	L4			
	L5			
	L6			
	L7			
Changning area, Sichuan Province	L8	Lower Silurian		
	L9	Longmaxi		
	L10	Formation	Core	In this study
	L11			
	L12			
	L13			
	L14			
Shizhu area, Chongqing	L15		Outcrop	In this study
	L16			
	L17			
	L18			
Wuhu area, Anhui Province	G1	Lower Permian Gufeng Formation	Core	[11]
	G2			
	G3			
	G4			
Sichuan Basin	N1	Lower Cambrian Niutitang Formation	Core	[7, 13, 14]
	N2			
	N3			
	N4			
	N5			
Well Yuke 1, southern Chongqing	N6	Lower Cambrian Niutitang Formation	Core	[10, 15]
	N7			
	N8			
	N9			
	N10			
	N11			
	N12			
Well Youke 1, southern Chongqing	N13			
	N14			
	N15			
	N16			
	N17			
Qilongcun section, Xishui contry, Guizhou Province	WL1	Upper Ordovician	Outcrop	[24]
	WL2	Wufeng		
	WL3	Formation-		
	WL4	Lower Silurian		
	WL5	Longmaxi		
	WL6	Formation		
	WL7			

TABLE 1: Continued.

Region	Number	Age/formation	Types	Source
	WL8			
	WL9			
	WL10			
	WL11			
	WL12			
	WL13			
	WL14			

analysis had been proven to be an effective method to characterize pore structures of shale [10–16]. In addition, the N_2 adsorption data had also been used to investigate the fractal characteristics of sands or coals [17–20]. There are only few reports on the fractal characteristics of shales from the Lower Cambrian Niutitang Formation in Sichuan Basin of China [7] and from the Chang-7 of the Upper Triassic Yanchang Formation in the Ordos Basin of China [16].

Compared with the extensive investigations on the fractal characteristics of sandstones and coals [17–22], similar studies on the fractal characteristics of shale in China have only received attention in recent years [7, 16]. There are several sets of marine shales with rich organic matter in southern China, including the Lower Cambrian, Upper Ordovician, Lower Silurian, and Lower Permian shale [5, 23], and those shale gas reservoirs in southern China are regarded as the main area for shale gas development [3, 23]. The objectives of the paper are to apply the fractal theory to investigate the irregularity of pore structure and study the fractal characteristics of marine shales in southern China based on the nitrogen adsorption analysis. And a parameter, fractal dimension, can be adopted to describe the fractal characteristics, which was calculated by the fractal Frenkel-Halsey-Hill (FHH) model from the N_2 adsorption data. Meanwhile, the relationships between pore structure parameters and fractal dimension have been investigated, and the relationships between fractal dimension and adsorption capacity and flow capacity of shale are also discussed. It was anticipated that our research provides the critical data presenting the fractal characteristics of the marine shales in southern China and understanding the influence of the fractal dimension on the adsorption capacity and flow capacity of the marine shales in southern China.

2. Samples and Methods

In order to investigate the fractal characteristics of marine shales with rich organic matter in southern China, four geological ages and formations are selected for the research objects, including the Lower Cambrian Niutitang Formation, Upper Ordovician Wufeng Formation, Lower Silurian Longmaxi Formation, and Lower Permian Gufeng Formation. The sample number, age, formation, and types are shown in Table 1. Part of shale samples is obtained from the Lower Silurian Longmaxi Formation in Changning area of Sichuan Province and Shizhu area of Chongqing, located in southern

China. And the obtained samples were characterized by low-pressure N_2 adsorption analysis and permeability analysis. In addition, more detailed information on low-pressure N_2 adsorption analysis, permeability analysis, and high-pressure methane adsorption analysis of the other part of shale samples can be gained in [1, 7, 8, 10, 11, 13–15, 24].

Low-pressure N_2 adsorption analysis was measured on a Quadrasorb SI Surface Area Analyzer and Pore Size Analyzer at the temperature of liquid nitrogen following Chinese National Standard (GB/T) 19587-2004 and (GB/T) 21650.2-2008. Shale samples were crushed to grains of 60–80 mesh size and then outgassed at 378 K for 24 h. For all samples, nitrogen adsorption isotherms at 77 K were measured for the relative pressure ranging from 0.01 to 0.99. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method [25], and the total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of 0.98.

The permeability of core plug samples was measured following the Chinese Oil and Gas Industry Standard (SY/T) 5336-1996. Permeability measurements were conducted using a pulse-decay permeability measurement (Low Gas Permeability Measurement 700) with nitrogen as the medium.

Fractal analysis can be used to describe the geometric and structural properties of the solid surface [26, 27], and the quantitative evaluation of the fractal geometry was to use a parameter, the fractal dimension D , which was used as an index of pore surface roughness or pore structure complexity of the solid [27]. That is to say, the solid with more fractal dimension D has more complicated pore structure or irregular pore surface. Based on the N_2 adsorption data, the fractal dimension can be determined by applying the Frenkel-Halsey-Hill (FHH) equation [27], and the FHH model can be described as follows [22, 27, 28]:

$$\ln(V) = (D - 3) \ln \left(\ln \left(\frac{p_0}{p} \right) \right) + \text{constant}, \quad (1)$$

where V is the volume of N_2 adsorbed at each equilibrium pressure p ; p_0 is the saturation pressure; and D is the fractal dimension. Thus, according to the fractal FHH model, a plot of $\ln(V)$ versus $\ln(\ln(p_0/p))$ shows a linear relationship, and the slope may be used to calculate the fractal dimension D .

3. Results and Discussions

3.1. Pore Structure Parameters and Permeability. The results from the low-pressure N_2 adsorption analysis are shown in Table 2. From Table 2, we observe that pore structure parameters of marine shales in southern China exhibit a wide range. The specific surface area calculated from the N_2 adsorption data using the BET model ranges from 1.6545 to 32.5015 m^2/g with a mean value of 15.4417 m^2/g . The nitrogen adsorption volume at p/p_0 , about 0.98, can be used to estimate total pore volume and mean pore size. The total pore volume varies from 0.00195 to 0.04374 cm^3/g with an average of 0.00209 cm^3/g , and average pore size generally is in the range of 3.567–9.723 nm with an average of 5.7215 nm, which belongs to mesopore according to the International Union

TABLE 2: Pore structure parameters of shale samples from N_2 adsorption isotherms.

Number	Total pore volume (cm^3/g)	Specific surface area (m^2/g)	Monolayer volume (cm^3/g) ^a	Average pore size (nm) ^b
L1	0.03074	18.821	0.006685	6.532
L2	0.03313	16.509	0.005864	8.028
L3	0.02744	19.592	0.006959	5.602
L4	0.02246	15.593	0.005539	5.762
L5	0.02297	9.885	0.003511	9.296
L6	0.02823	16.881	0.005996	6.690
L7	0.01263	7.147	0.002539	7.069
L8	0.01176	6.354	0.002257	7.404
L9	0.01417	7.991	0.002839	7.095
L10	0.01602	12.458	0.004425	5.144
L11	0.01962	12.030	0.004273	6.524
L12	0.02504	14.817	0.005263	6.760
L13	0.01776	13.290	0.004721	5.345
L14	0.01769	17.358	0.006166	4.076
L15	0.01785	16.719	0.005939	4.271
L16	0.01754	16.130	0.005730	4.349
L17	0.01674	16.441	0.005840	4.074
L18	0.01700	16.993	0.006036	4.002
G1	0.02268	9.330	0.003314	9.723
G2	0.03582	19.707	0.007000	7.270
G3	0.04374	24.236	0.008609	7.219
G4	0.04097	22.473	0.007982	7.292
N1	0.03810	32.501	0.011545	4.689
N2	0.03466	25.529	0.009068	5.431
N3	0.01443	7.310	0.002597	7.897
N4	0.01908	8.361	0.002970	9.128
N5	0.02636	12.241	0.004348	8.616
N6	0.01596	11.522	0.004093	5.539
N7	0.01463	12.708	0.004514	4.605
N8	0.02181	23.903	0.008491	3.649
N9	0.02408	27.001	0.009591	3.567
N10	0.00195	1.645	0.000584	4.749
N11	0.00272	2.760	0.000981	3.947
N12	0.00528	4.770	0.001694	4.424
N13	0.00327	1.969	0.000699	6.638
N14	0.00520	3.615	0.001284	5.757
N15	0.00414	2.464	0.000875	6.718
N16	0.01894	20.172	0.007165	3.755
N17	0.00548	2.755	0.000979	7.951
WL1	0.03652	30.101	0.010692	4.853
WL2	0.02327	20.838	0.007402	4.467
WL3	0.01267	10.750	0.003818	4.716
WL4	0.02802	22.616	0.008033	4.956
WL5	0.02652	24.178	0.008588	4.387

TABLE 2: Continued.

Number	Total pore volume (cm ³ /g)	Specific surface area (m ² /g)	Monolayer volume (cm ³ /g) ^a	Average pore size (nm) ^b
WL6	0.02577	23.487	0.008343	4.389
WL7	0.02420	20.779	0.007381	4.658
WL8	0.01992	16.694	0.005930	4.773
WL9	0.02391	22.12	0.007857	4.324
WL10	0.02433	22.321	0.007929	4.360
WL11	0.02993	17.34	0.006159	6.904
WL12	0.02194	19.528	0.006936	4.494
WL13	0.02092	18.65	0.006625	4.488
WL14	0.02174	17.027	0.006048	5.106

^aThe monolayer volume is calculated by BET method [25]. ^bAverage pore size = $4 \times \text{Total pore volume} / \text{specific surface area}$.

of Pure and Applied Chemistry (IUPAC) classification [29]. The marine shales in southern China are similar to the North American shales in terms of specific surface area and total pore volume [6, 30, 31].

The permeability and Langmuir volume of marine shale samples are illustrated in Table 3. From Table 3, the pulse-decay permeability values of marine shale samples are commonly less than $1 \mu\text{D}$. Permeability values of these shale samples were lower than the Besa River, Muskwa, and Fort Simpson shale from Northeastern British Columbia [32]. And permeability values of these shale samples were bigger than the Barnett shale from Fort Worth Basin [33], which may be related to types of samples for measuring. Type of marine shale samples in southern China for measuring permeability was core plug, whereas type of Barnett shale samples was crushed sample. In addition, we observe that the difference of Langmuir volume of shale samples from the different references was great, which may be related to the experiment conditions of shale samples.

3.2. N_2 Adsorption-Desorption Isotherms. The isotherms for the low-pressure N_2 adsorption analysis of some shale samples are listed in Figure 1. The isotherm of each shale sample has difference in shape, while the isotherm of all shale samples belongs to type IV isotherms according to the BDDT classification [34]. The adsorption branch and the desorption branch of N_2 adsorption-desorption isotherm at higher relative pressure (more than 0.45) exist separation because of capillary condensation, resulting in a hysteresis loop [35], which mean that shale samples contain mesopore [36]. Meanwhile, from the figure, we can note that the absence of total closure of the hysteresis loop of shale samples L2 and L7 was interpreted as being due to the effect of swelling [35].

The shape of the hysteresis loop can be used to understand the pore shape of shale [36]. According to the hysteresis loop shape of N_2 adsorption-desorption isotherms, the shale samples can be divided into two groups: group A (sample L2, sample L7, and sample N2) and group B (sample N5, sample WL4, and sample WL11) (Figure 1 and Table 4). The adsorption-desorption isotherms of some shale samples

TABLE 3: Permeability and methane adsorption results for some shale samples.

Number	Permeability (μD)	Langmuir volume (cm ³ /g)	Source
L1	—	—	[1]
L2	—	0.52	
L3	—	0.58	
L4	—	0.52	
L5	—	0.43	
L6	—	0.51	
L7	0.6999	—	In this study
L8	0.6039	—	
L9	0.7431	—	
L10	0.4142	—	
L11	0.3502	—	
L12	0.3782	—	
L13	0.4264	—	
N1	0.40	13.44	
N2	0.32	12.10	
N3	0.67	9.63	
N4	0.70	9.41	
N5	0.55	4.03	
N6	—	3.34	[7]
N7	—	2.43	
N8	—	4.36	
N9	—	5.04	
N10	—	2.01	
N11	—	1.83	
N12	—	2.62	
N13	—	1.13	
N14	—	1.24	
N15	—	1.18	
N16	—	4.69	
N17	—	2.20	

belong to group A, which are reversible at low relative pressure, but, at higher relative pressure (more than 0.45), the desorption branches of the isotherms exist inflection point. And type of the hysteresis loops may be considered as type H2 according to the IUPAC classification [36]. Type H2 hysteresis loop is usually observed in open pores, which contain mainly inkbottle-shaped pores and a small amount of parallel-plate pores or cylindrical pores [7, 22, 36]. In contrast, at higher relative pressure (more than 0.45), the desorption branches of the isotherms of some shale samples belonging to group B do not exist inflection point. According to the IUPAC classification [36], type of the hysteresis loops may be classified as type H3, which is usually associated with slit-shaped pores [7, 22, 36].

3.3. Fractal Dimension from N_2 Adsorption Data. According to the fractal FHH model, the plots of $\ln(V)$ versus $\ln(\ln(p_0/p))$ from N_2 adsorption data are illustrated in Figure 2. From Figure 2, we observe that there are two distinct straight line segments at the whole relative pressure range,

FIGURE 1: Low-pressure N_2 adsorption-desorption isotherms of some shale samples.

and the liners can obtain different slopes with piecewise fitting. A demarcation point between straight line segment at low relative pressure range and straight line segment at high relative pressure range can be gained, and the pores would be divided into small pores and large pores, respectively. Meanwhile, both of them show good fitting, suggesting that the fractal characteristics at the two intervals are different, and the fractal dimensions D_1 and D_2 are calculated from

the two linear segments (Table 4). From Table 4, we observe that all correlation coefficients are more than 0.94, suggesting that there are the fractal characteristics for marine shales in southern China. Values of fractal dimension D_1 range from 2.0918 to 2.718 with a mean value of 2.4762, and values of fractal dimension D_2 range from 2.5842 to 2.9399 with a mean value of 2.8015, indicating that there are irregular pore surface and sophisticated pore structure in shales.

FIGURE 2: Plots of $\ln(V)$ versus $\ln(\ln(p_0/p))$ reconstructed from the N_2 adsorption data of some shale samples.

The value of fractal dimension D_1 is generally less than fractal dimension D_2 , indicating that the complexity of pore structure of large pore is more than that of small pore. This conclusion is consistent with previous work on coals and sandstones [21, 22]. In addition, Figure 3 reports that no clear correlation between fractal dimension D_1 and fractal dimension D_2 is observed, suggesting that they represent two different fractal dimensions of marine shales in southern China. This conclusion shows that the marine shales have double fractal characteristics, which is in disagreement with the previous study on the continental shales [16]. This may be related to the continental shales that included a small amount of micropores.

From Table 4, we also observe that the fractal dimension D_1 ranges from 2.0918 to 2.693 with an average of 2.4339 and

the fractal dimension D_2 ranges from 2.713 to 2.9399 with an average of 2.8144 in group A and the fractal dimension D_1 ranges from 2.2438 to 2.718 with an average of 2.5654 and the fractal dimension D_2 ranges from 2.5842 to 2.8692 with an average of 2.7762 in group B. Comparisons of fractal dimension D_1 and fractal dimension D_2 of shale in groups A and B are shown in Figure 4. Comparing samples in groups A and B (Figure 4), the minimum, average, and maximum of fractal dimension D_1 in group A are smaller than those in group B; the minimum, average, and maximum of fractal dimension D_2 in group A are greater than those in group B. The hysteresis loop shape of shale samples in group A can be considered as type H2, which occurs mainly in inkbottle-shaped pores, whereas the hysteresis loop shape of shale samples in group B can be considered as type H3, which

TABLE 4: Fractal dimensions derived from fractal FHH model.

Number	D_1	Coefficient (R^2)	D_2	Coefficient (R^2)	Group ^a
L1	2.6896	0.9981	2.812	0.9788	A
L2	2.4605	0.987	2.7412	0.9881	A
L3	2.6734	0.9982	2.8218	0.9899	B
L4	2.58	0.9836	2.8033	0.9978	B
L5	2.2438	0.9944	2.6854	0.9917	B
L6	2.6261	0.9918	2.7729	0.9956	B
L7	2.2125	0.9913	2.7318	0.986	A
L8	2.0918	0.9959	2.7248	0.979	A
L9	2.1558	0.9857	2.7467	0.9724	A
L10	2.2654	0.9785	2.8091	0.971	A
L11	2.2039	0.9416	2.8364	0.9718	A
L12	2.2978	0.9134	2.8395	0.9785	A
L13	2.1908	0.9254	2.8044	0.9795	A
L14	2.5074	0.9905	2.8355	0.9649	A
L15	2.5324	0.991	2.8303	0.9753	A
L16	2.4979	0.958	2.8541	0.9471	A
L17	2.4588	0.9915	2.8356	0.9544	A
L18	2.4784	0.9838	2.8429	0.9789	A
G1	2.3986	0.9815	2.6615	0.9906	B
G2	2.621	0.9841	2.6746	0.9901	B
G3	2.718	0.9796	2.8109	0.979	B
G4	2.708	0.987	2.7977	0.9902	B
N1	2.6687	0.9652	2.9399	0.9807	A
N2	2.619	0.9769	2.8764	0.9689	A
N3	2.4077	0.9865	2.8075	0.9563	A
N4	2.4372	0.9565	2.7718	0.9471	A
N5	2.2647	0.9887	2.7702	0.986	B
N6	2.6032	0.9878	2.808	0.9932	A
N7	2.5529	0.9893	2.8402	0.9745	A
N8	2.6577	0.9879	2.8615	0.9671	A
N9	2.6515	0.9885	2.8654	0.9575	A
N10	2.2483	0.9771	2.7687	0.9719	A
N11	2.3956	0.9757	2.8015	0.993	A
N12	2.4447	0.9939	2.7269	0.9972	A
N13	2.2019	0.9783	2.713	0.9878	A
N14	2.2416	0.9992	2.7849	0.9949	A
N15	2.2559	0.9904	2.8384	0.9935	A
N16	2.5229	0.9747	2.8901	0.9649	A
N17	2.2298	0.9935	2.5842	0.9823	B
WL1	2.693	0.9954	2.8513	0.9622	A
WL2	2.6797	0.9968	2.8336	0.9926	A
WL3	2.2749	0.9863	2.8044	0.9786	A
WL4	2.6555	0.9981	2.8252	0.9901	A
WL5	2.6358	0.9859	2.8259	0.9453	A
WL6	2.6267	0.996	2.8533	0.9632	B
WL7	2.6055	0.9962	2.7681	0.9902	B

TABLE 4: Continued.

Number	D_1	Coefficient (R^2)	D_2	Coefficient (R^2)	Group ^a
WL8	2.4996	0.9962	2.8259	0.9902	A
WL9	2.5891	0.9864	2.8062	0.9821	B
WL10	2.6265	0.9972	2.8418	0.975	B
WL11	2.614	0.9976	2.7807	0.9823	B
WL12	2.5759	0.9652	2.8395	0.958	B
WL13	2.5519	0.9981	2.8698	0.9565	B
WL14	2.5966	0.9858	2.8316	0.9683	B

^aTypes of adsorption-desorption isotherms are divided into group A and group B.

FIGURE 3: Relationship between fractal dimension D_1 and fractal dimension D_2 .

is usually associated with slit-shaped pores. And the pore structure of shale samples in group A is more complicated than that in group B. Therefore, the fractal dimension D_2 at higher relative pressure may be used to characterize the complexity of pore structure in shales, which is in agreement with previous study on coals [22], suggesting that the fractal dimension D_2 at higher relative pressure represents the complexity of pore structure in coals.

3.4. Relationships between Fractal Dimension and Pore Structure Parameters. The relationships between fractal dimension and pore structure parameters (specific surface area, total pore volume, and average pore size) are listed in Figure 5. From Figure 5, we observe that there is good positive correlation between the fractal dimension D_1 and specific surface area ($R^2 = 0.6584$ in Figure 5(a)) and moderate positive correlation between the fractal dimension D_1 and total pore volume ($R^2 = 0.472$ in Figure 5(b)). However, the fractal dimension D_2 has a poor positive relationship with specific surface area ($R^2 = 0.3622$ in Figure 5(a)) and no obvious relationship with total pore volume ($R^2 = 0.0756$ in Figure 5(b)). The good or moderate positive relationships indicate that shale with a higher total pore volume or specific

FIGURE 4: Comparison of fractal dimension D_1 and fractal dimension D_2 of shale in groups A and B.

surface area may have a greater fractal dimension D_1 . This finding is in agreement with previous research on coals [22]. Meanwhile, we also observe that there is a good positive relationship between fractal dimension D_1 and monolayer volume ($R^2 = 0.6584$ in Figure 5(c)), whereas a poor positive relationship between fractal dimension D_2 and monolayer volume ($R^2 = 0.3622$ in Figure 5(c)), indicating that shale with a higher monolayer volume would have more roughness pore surface and higher fractal dimension D_1 . In addition, the relationship between fractal dimension and average pore size is shown in Figure 5(d). From this figure, the fractal dimension D_1 has a moderate negative correlation with the average pore size ($R^2 = 0.4321$ in Figure 5(d)), while the fractal dimension D_2 has a poor negative correlation with the average pore size ($R^2 = 0.1465$ in Figure 5(d)), suggesting that the fractal dimension D_2 decreases with increasing average pore size. Shale with smaller average pore size would have more micropores [7] and higher fractal dimension D_2 , reflecting more complicated pore structure in shale.

Comparing the relationships in Figures 3–5, the fractal dimension D_1 at low relative pressure may reflect the surface fractal dimension, which may be used to characterize the roughness of pore surface of shale. However, the fractal dimension D_2 at higher relative pressure may represent the pore structure fractal dimension, which may be used to describe the complexity of pore structure of shale. From Table 4, we observe that the fractal dimension D_1 has large variable ranges, indicating that the surface of some pores in shale is regularity, whereas the surface of some pores is toughness. With the fractal dimension D_1 increasing, the pore surface in shale transforms gradually from smoothness to toughness, which suggests that the roughness of pore surface in shale exists difference, and the interaction potential energy between gas and soil surface shows uneven distribution, resulting in gas adsorption sites for gas in shale being inhomogeneous. Meanwhile, the fractal dimension D_2 has

little variable ranges, indicating that the discrepancies among fractal characteristic of pore structure of each shale sample are relatively low. A higher fractal dimension D_2 indicates that a shale sample has a more irregular pore structure.

3.5. Relationships between Fractal Dimension and Adsorption Capacity and Flow Capacity. The fractal dimension D_1 and fractal dimension D_2 represent the two different types of fractal characteristics of shale, which are pore surface fractal characteristics and pore structure fractal characteristics, respectively. Shale with a higher fractal dimension D_1 has a more rough pore surface, whereas shale with a higher fractal dimension D_2 has a more complicated pore structure. Relationships between fractal dimension and Langmuir volume of shale samples are shown in Figure 6. From this figure, there are significant positive correlations between fractal dimension D_1 and Langmuir volume from different literatures, which means that the adsorption capacity of shale increases with increasing fractal dimension D_1 , whereas fractal dimension D_2 has different relationships with Langmuir volume from different literatures. Therefore, the fractal dimension D_1 has greater influence on adsorption capacity of shale than the fractal dimension D_2 . This finding is in agreement with results from previous work on coals [22]. Shale with a higher fractal dimension D_1 has a more irregular pore surface that can provide more adsorption sites and the interface force between gas and the shale surface is greater, which would be beneficial to increase the adsorption amount of gas, leading to higher adsorption capacity of shale.

However, Yao et al. [19] and Cai et al. [20] suggested that the pore structure in coal had great effects on gas transport and coal with higher fractal dimension had less flow capacity. Chen et al. [21] studied the relationship between pore structure fractal dimension and permeability of sandstone and found that there was negative correlation

FIGURE 5: Relationships between fractal dimension and specific surface area (a), total pore volume (b), monolayer volume (c), and average pore size (d).

between pore structure fractal dimension and permeability, which mean that sandstone with a higher pore structure fractal dimension has more complex pore structure, resulting in lower permeability. Figure 7 reports relationship between fractal dimension and permeability of shale samples. There is a good-moderate negative relationship between fractal dimension D_1 and permeability ($R^2 = 0.5635$ in Figure 7), and the fractal dimension D_2 has a poor negative correlation with permeability ($R^2 = 0.1109$ in Figure 7). This finding suggests that the fractal dimension D_2 has greater influence on flow capacity of shale than the fractal dimension D_1 . Therefore, shale with a higher fractal dimension D_2 has more complicated pore structure, resulting in lower permeability

and flow capacity for gas, which makes gas adsorption, diffusion, and percolation much more difficult in shale.

Therefore, the two fractal dimensions have different impact on the development of shale gas reservoirs. Higher fractal dimension D_1 represents more roughness of pore surface of shale that offers more adsorption sites, leading to higher adsorption capacity of shale. However, higher fractal dimension D_2 represents more complicated pore structure, resulting in the decrease of permeability of shale, which makes gas adsorption, diffusion, and percolation become much more difficult. Comparing the influences of two fractal dimensions on the adsorption capacity and flow capacity, we consider higher surface fractal dimension D_1 and lower pore structure fractal dimension D_2 in shale as having

FIGURE 6: Relationships between fractal dimension and Langmuir volume (data in (a) from [1]; data in (b) from [7]; data in (c) from [10]).

higher adsorption capacity for gas and flow capacity for gas, which has an important significance in the development of shale gas reservoirs. In conclusion, shale with a greater fractal dimension D_1 has stronger adsorption capacity and should use stimulation treatment forming fracture networks to increase the flow capability for gas (decrease the fractal dimension D_2), which lead to accelerating velocity of gas desorption and increasing the gas production.

4. Conclusions

In this paper, the FHH fractal model has been applied to investigate the fractal characteristics of marine shales in southern China from nitrogen adsorption data. The relationships between pore structure parameters and fractal

dimension have been investigated. Furthermore, the relationships between fractal dimension and adsorption capacity and flow capacity of shale are also discussed. The following conclusions can be made:

- (1) The marine shales in southern China have two different types of fractal characteristics; the fractal dimension D_1 at low relative pressure represents the pore surface fractal characteristics and the fractal dimension D_2 at higher relative pressure describes the pore structure fractal characteristics.
- (2) The fractal dimensions D_1 range from 2.0918 to 2.718 with a mean value of 2.4762, and the fractal dimensions D_2 range from 2.5842 to 2.9399 with a mean value of 2.8015, indicating that there are irregular pore

FIGURE 7: Relationship between fractal dimension and permeability.

surface and sophisticated pore structure in marine shales.

- (3) The fractal dimension D_1 has good or moderate positive relationships with specific surface area or total pore volume, whereas the fractal dimension D_2 shows moderate negative correlation with average pore size.
- (4) The higher fractal dimension D_1 represents more roughness of pore surface of shale that offers more adsorption sites, leading to higher adsorption capacity for gas in shale. However, the higher fractal dimension D_2 represents higher heterogeneity of pore structure and more complicated pore structure, resulting in the lower flow capacity for gas in shale.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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