

Methane adsorption comparison of different thermal maturity kerogens in shale gas system

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Abstract To determine the effect of thermal maturity on the methane sorption in shale gas system, two different thermal maturity kerogens of type II isolated from Barnett shale of Fort Worth Basin were used to measure the methane adsorption amount under the pressure ranging from 0 to 14 MPa at constant temperatures. One kerogen was called Lee C-5-1 with 0.58% of vitrinite reflectance; the other was called Blakely#1 kerogen with 2.01% of vitrinite reflectance. The results suggested that the methane sorption capacity of kerogen Blakely#1 was higher than the immature kerogen Lee C-5-1, and its Langmuir constant and Langmuir maximum sorption amount, which were reached by fitting the measured data for at least square method, greater than the immature kerogen Lee C-5-1. This may be associated with that nanopores opened up during the degradation of organic matter, and which increased the specific surface area of kerogen. Therefore, the over mature kerogen has greater methane adsorption capacity.

Key words shale gas; methane adsorption; thermal maturity

1 Introduction

Shale gas system is unconventional natural gas resource in that shale is both source and reservoir of gas, and increasingly attracts more and more attention (Montgomery et al., 2005; Loucks and Ruppel, 2007; Ross et al., 2007, 2008, 2009; Rowe et al., 2008; Ruppel and Loucks, 2008). Shale gas has succeeded in the US and Canada, especially Barnett shale gas field has become the famous shale gas center in the world (Jarvie et al., 2007; Ross and Bustin, 2007, 2008). Natural gas stored in shale-gas reservoirs is believed to exist in three forms: (1) free gas in pores and fractures, (2) sorbed gas in organic matter and inorganic minerals, and (3) dissolved gas in oil and water.

Adsorption methane is among the second form of above stored forms, and studying controlled elements of adsorption methane is important for shale gas accumulation. Elements affecting methane sorption are organic matter content (TOC), kerogen type, etc. (Ross and Bustin, 2009; Zhang et al., 2012). However, how thermal maturity affect the methane sorption is not fully understood in shale gas system although

methane sorption amount affected by coal rank were documented by many researchers (Ryan, 1992; Laxminarayana and Crosdale, 2002; Reeves et al., 2005; Chalmers and Bustin, 2007). This paper will focus on the effect of kerogens in different thermal maturity on the methane adsorption in shale gas system.

2 Samples and methods

Kerogens type II were isolated from well cored shale samples in Barnett shales, Fort Worth Basin, US of 0.58% and 2.01% vitrinite reflectance, respectively. Their methane adsorptions were measured at varying temperatures and pressure. The kerogen having 0.58% vitrinite reflectance was recorded as Lee C-5-1 with the 381 m burial depth, and another kerogen having 2.09% vitrinite reflectance was called Blakely#1 with 2191 m of burial depth.

Samples were crushed to 100–270 mesh, removed moisture and degassed in 110°C oven in which helium is kept flowing for 18 hours. The 1–2 g kerogens were weighted by the balance with 0.01 mg error. Then samples were loaded onto stainless steel sample

cell. All adsorption experiments were carried out in the dry system. The methane adsorption isotherm was measured by the instruments worked by volumetric method principle.

Adsorption is a process that surface energy adsorbs minimized gas molecules, which is always expressed by the isotherm, and characterized the correlation between the adsorbed capacity and gas pressure at a constant temperature. The monolayer adsorption theory can be expressed by the Langmuir equation or Langmuir isotherm (Gregg and Sing, 1982; Keller and Starudt, 2005) as follows,

$$\Gamma = \Gamma_{\max} \frac{K \times P}{1 + K \times P} \quad (1)$$

Where, Γ is adsorbed gas capacity; Γ_{\max} refers to the Langmuir maximum adsorption amount; P is pressure of adsorbed gas in MPa, and K is the Langmuir constant in 1/MPa. The least square method was used to fit the measured experimental data to get the Langmuir constant K and Langmuir maximum adsorption capacity Γ_{\max} .

Langmuir coefficient which is the ratio of adsorption rate, K_a , and desorption rate, K_d , as a function of temperature, is released by Xia et al. (2006), and Xia and Tang (2012). It can be obtained by the Langmuir adsorption equation.

$$K = \exp\left(\frac{q}{RT} + \frac{\Delta S^0}{R}\right) \quad (2)$$

where, $q = E_a - E_d$ is the isosteric heat of adsorption; and $\Delta S^0 = R \cdot \ln(Aa/Ad)$ is the standard entropy of adsorption.

3 Results and discussion

The results were measured under the pressure varied from 0 to 14 MPa at a constant temperature of 35, 50, 65, and 75 °C, respectively. Compared with the methane sorption of kerogens, the results showed over mature kerogen was greater than the immature one at each different temperature (Fig. 1A–D, Table 1).

Organic matter content (TOC) has a positive correlation to methane sorption capacity in shale gas system (Ross and Bustin, 2009; Zhang et al., 2012). Immature and over mature kerogens have different organic matter contents although both are isolated from the same series of shale. So it is necessary to normalize TOC to determine the effect of various levels of thermal maturity on methane adsorption. After the normalization of TOC, it showed that the methane sorption amount of over mature kerogen still were

more than the immature one although their difference was shortened (Fig. 2A–D). It suggested that even the effect of TOC element was eliminated, the methane sorption amount of over mature kerogen would be higher than that of the immature one, meaning the thermal maturity level is one key element controlled methane adsorption capacity in shale gas system.

The examined results of both kerogens showed the methane adsorption capacity increased with the increasing pressure while decreased with the increasing temperature. The measured results fits well with the Langmuir function (Figs. 3 and 4). Langmuir maximum sorption amount and Langmuir constant were reached by the least square method based on the examined data (Table 2). Langmuir constant defines the capacity of sorbent to adsorb methane, Langmuir maximum amount means the highest adsorption amount of the sample. The Langmuir constant of Blakely#1 was higher than that of Lee C-5-1 at every examined temperature (Fig. 5), suggesting that high thermal maturity sample has stronger ability to adsorb methane and the methane sorption increased with increasing thermal maturity level. For Langmuir maximum amount, Blakely#1 was 1000 SCF/ton rock, and the immature one was 306 SCF/ton rock. After the normalization of TOC, Langmuir maximum amount of Blakely#1 was 1429 SCF/ton rock, and higher than the immature one, Lee C-5-1, 875 SCF/ton rock. The isosteric heat of adsorption (q) and the standard entropy of adsorption are two important thermodynamic parameters to characterize the methane adsorption, which can be calculated by method of Equation 2. Lee C-5-1 had 13 kJ·mol⁻¹ of isosteric adsorption heat and -51 J·mol⁻¹·K⁻¹ of adsorption entropy, respectively, and Blakely#1 had 20 kJ·mol⁻¹ of isosteric adsorption heat and -69 J·mol⁻¹·K⁻¹ of adsorption entropy, respectively.

Blakely#1 was higher than Lee C-5-1 in the methane isotherm amount, Langmuir constant and Langmuir maximum amount capacity before and after normalization of TOC. Therefore, it can be figured out that thermal maturity level affected the methane sorption within shale gas system.

Methane sorption capacity of coal rank was focused by many researchers (Ryan, 1992; Laxminarayana and Crosdale, 2002; Krooss et al., 2002; Reeves et al., 2005; Chalmers and Bustin, 2007). Some thought that methane sorption amount increased with coal rank; some believed that it decreased; some supposed that it show a “U” shape change (Weniger et al., 2012). Many researcher have observed the nanopores in organic matters of shale such as the Barnett Shale and Woodford Shale in US, Posidonia Shale in Germany and Devonian–Mississippian Shale in Canada by the scanning electron microscopy (Loucks et al., 2009; Curtis et al., 2010; Bernard et al., 2012; Chalmers et al., 2012;

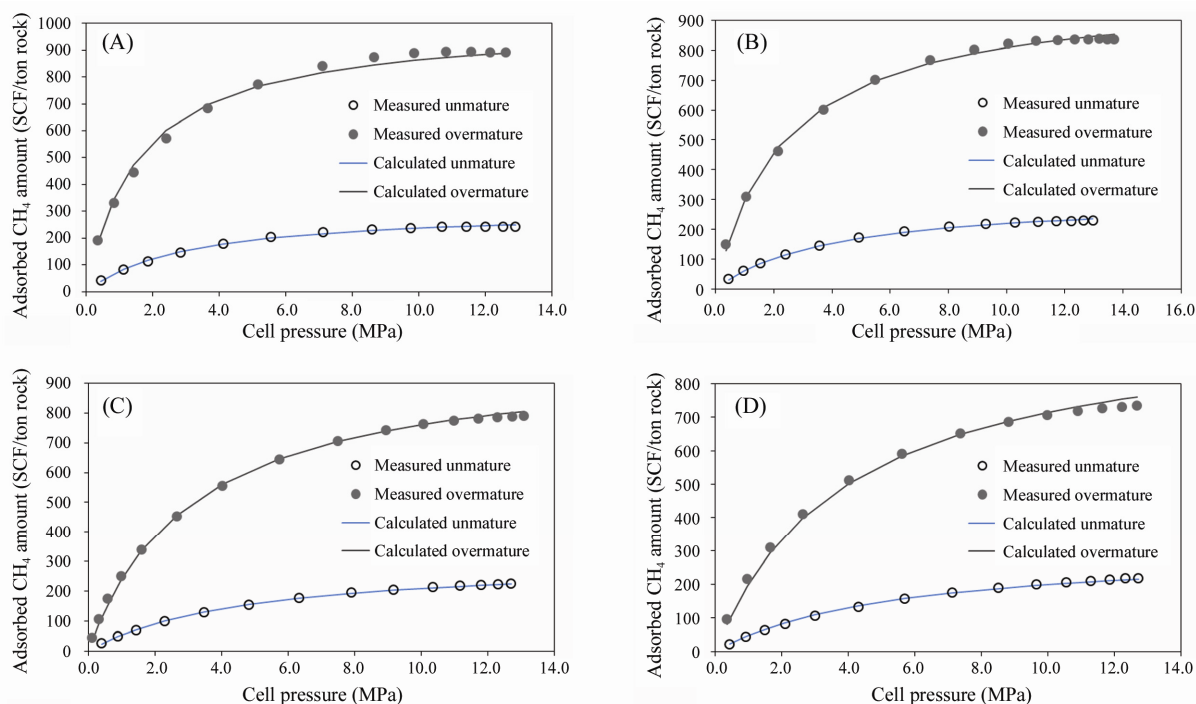


Fig. 1. CH₄ adsorption isotherm for different thermal maturity kerogens before the normalization to TOC at the temperature (A) 35°C, (B) 50°C, (C) 65°C, and (D) 75°C.

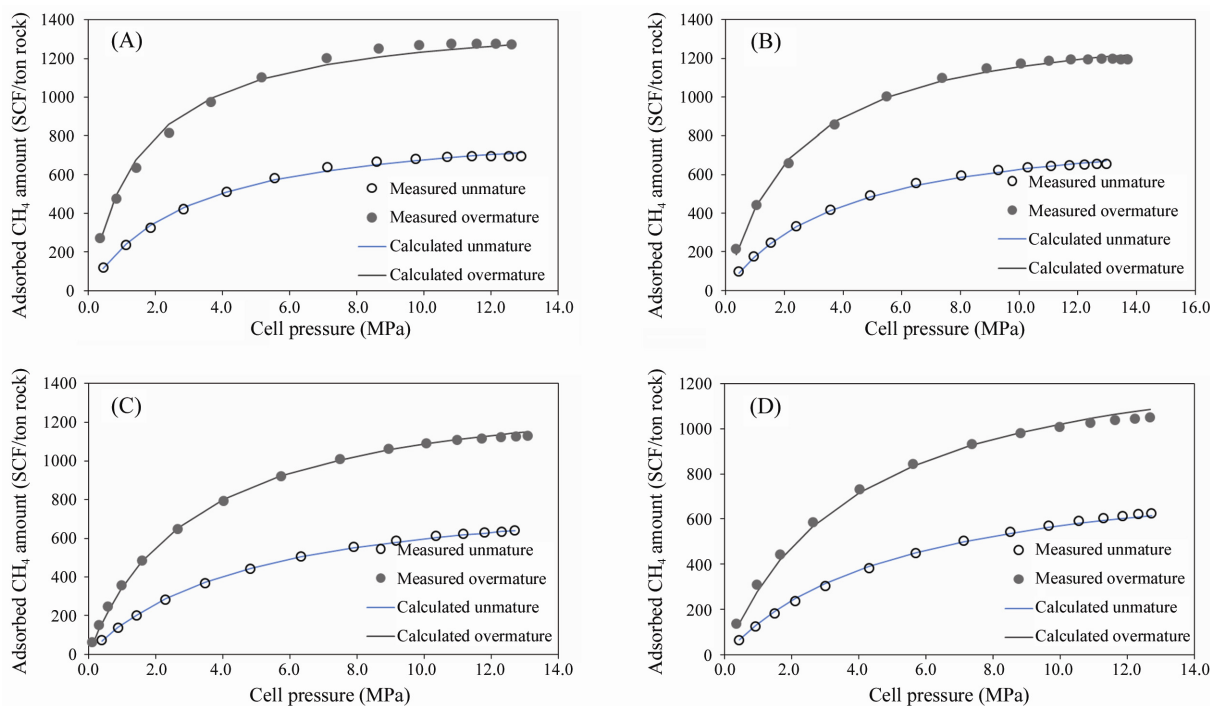


Fig. 2. CH₄ adsorption isotherm for different thermal maturity kerogen after the normalization to TOC at the temperature (A) 35°C, (B) 50°C, (C) 65°C, and (D) 75°C.

Table 1 CH₄ adsorption capacity for different thermal maturity kerogens at different temperatures

35 °C		50 °C		65 °C		75 °C	
P (MPa)	CH ₄ (SCF/ton rock)	P (MPa)	CH ₄ (SCF/ton rock)	P (MPa)	CH ₄ (SCF/ton rock)	P (MPa)	CH ₄ (SCF/ton rock)
Immature kerogen A $R_o=0.58\%$							
0.4	41.7	0.4	34.0	0.4	25.7	0.4	22.3
1.1	82.7	1.0	61.9	0.9	48.6	0.9	43.4
1.9	114.1	1.5	86.3	1.4	71.0	1.5	63.2
2.8	147.1	2.4	115.9	2.3	98.7	2.1	82.2
4.1	178.5	3.6	146.0	3.5	128.9	3.0	106.0
5.5	203.4	4.9	172.3	4.8	155.2	4.3	133.5
7.1	222.6	6.5	194.3	6.3	177.6	5.7	156.9
8.6	233.3	8.0	208.7	7.9	194.9	7.1	175.9
9.8	238.6	9.3	217.8	9.2	205.6	8.5	190.3
10.7	241.8	10.3	223.2	10.4	214.3	9.6	199.8
11.4	243.2	11.1	225.6	11.2	218.2	10.6	206.8
12.0	243.1	11.7	227.4	11.8	220.6	11.3	211.0
12.5	243.2	12.2	228.1	12.3	222.5	11.9	214.7
12.9	242.8	12.6	229.3	12.7	224.6	12.3	217.5
		13.0	229.4			12.7	219.2
Overmature kerogen B $R_o=2.01\%$							
0.34	190.7	0.35	150.0	0.10	44.9	0.35	95.7
0.83	332.4	1.04	310.0	0.30	106.5	0.97	216.8
1.42	445.1	2.14	461.9	0.57	173.9	1.64	310.2
2.40	571.5	3.71	600.7	0.97	250.3	2.62	410.5
3.66	682.7	5.49	701.6	1.59	339.0	4.03	511.5
5.17	772.2	7.37	768.9	2.66	452.8	5.61	591.3
7.10	841.9	8.88	803.0	4.02	556.0	7.37	652.7
8.65	874.8	10.06	822.5	5.73	644.6	8.81	687.2
9.87	888.3	11.01	831.7	7.49	707.2	9.98	706.7
10.81	892.7	11.75	835.1	8.93	743.1	10.90	719.8
11.57	893.4	12.34	836.7	10.07	763.8	11.64	728.0
12.15	892.6	12.80	837.5	10.99	775.8	12.22	731.7
12.61	890.8	13.17	838.0	11.71	782.7	12.68	734.9
		13.47	837.1	12.28	786.7		
		13.70	837.1	12.73	789.6		
				13.09	791.1		

Table 2 Langmuir parameters and thermodynamic parameters of the different thermal maturity kerogens

	Langmuir constant (1/MPa)				Langmuir maximum amount (SCF/ton rock)	Langmuir maximum amount (SCF/ton TOC)	Isosteric heat of adsorption (kJ·mol ⁻¹)	Standard entropy of adsorption (J·mol ⁻¹ ·K ⁻¹)
	35.4 °C	50.4 °C	65.4 °C	75.4 °C				
Lee-5-1	0.34	0.25	0.21	0.19	306	1000	13	-51
Blakely#1	0.63	0.42	0.32	0.25	875	1429	20	-69

Bernard et al., 2012). These nanopores were associated with organic matter degradation during thermal maturity (Hover et al., 1996; Loucks et al., 2009), so the porosity of kerogen tends to increase with the burial depth or thermal maturity level (Sondergeld et al., 2010; Modica and Lapierre, 2012), whereas the matrix porosity tends to decrease with the burial depth as a result of compaction and cementation. The pore space result measured by N₂ isotherm indicated that thermally mature shales have larger micropore volumes and N₂ BET surface areas per wt% TOC, hence the methane sorption amount is greater in thermally mature strata than immature strata (Ross and Bustin, 2009). Therefore, based on the above results and researches, it can be well interpreted that the over mature kerogen has larger methane sorption capacity, Langmuir constant and Langmuir Maximum amount than those of the immature kerogen resulted from that kerogen opened up nanopores during thermally maturity and these pores increased the specific surface area.

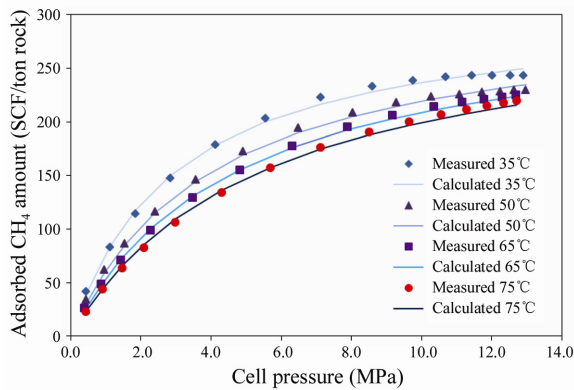


Fig. 3. CH₄ adsorption isotherm for the immature kerogen A at the different temperatures ($R_0=0.58\%$).

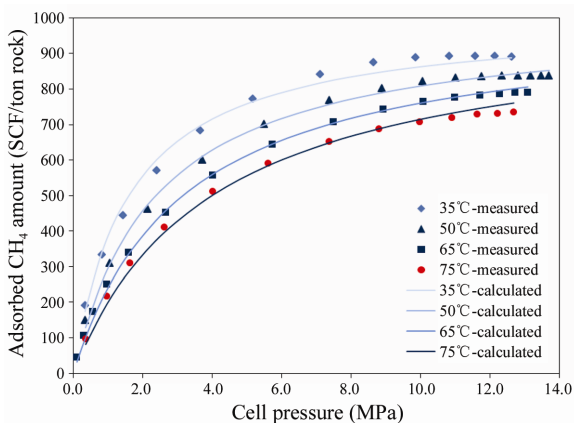


Fig. 4. CH₄ adsorption isotherm for over-mature kerogen B at the different temperatures ($R_0=2.01\%$).

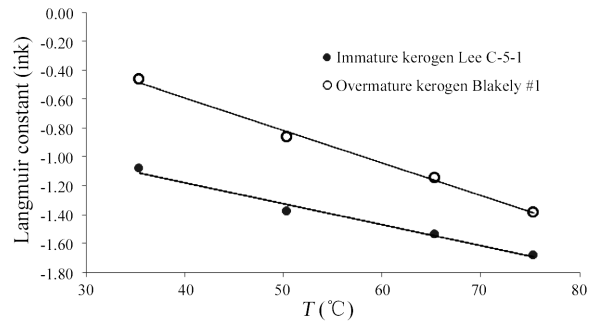


Fig. 5. Langmuir constants for kerogens at the different temperatures.

However, it is difficult to obtain a series of samples of different thermally mature levels in the same shale, so it could not be fully demonstrated that the quantified correlations between the methane adsorption capacity and thermal maturity levels and how sorption amount change with the increasing thermally mature levels in shale gas system.

4 Conclusions

Analyzed different thermal maturity kerogens type II isolated from the Barnett Shale, Fort Worth Basin, it indicated that over mature kerogen has higher sorption capacity and other related chemical parameters than those of the immature one, and it was associated with nanopores opened up by kerogen during thermal degradation.

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