

Quantifying the Effect of Temperature, Pressure, and Depth on Methane Adsorption in Shale Gas Reservoirs for Longmaxi Shale in Sichuan Basin, China

Nadege Mbula Ngoy¹, Iqbal Muhammad Sayed¹

School of Earth Resources, China University of Geosciences, Wuhan 430074, PR China.

Email address: favourednadeg@gmail.com; iqbalkazmi35@gmail.com

Abstract

Shale gas is an important unconventional energy source and plays an important role in oil and gas exploration. A significant portion of gas in the shale gas reservoir exists in an adsorbed state. Thus, knowledge of gas adsorption behavior is important. The purpose of this study was to analyze the Longmaxi shale gas adsorption in the Sichuan basin in China. Data have been analyzed by using Multiple regressions, the Langmuir model. The methane adsorption isotherms on shale were tested at 25°C, 40°C and 50°C with the pressure. A total of three shale samples with rock properties as total organic carbon (TOC), Illite-Smectite (I / S) clay minerals, and specific area of the Sichuan basin were analyzed to quantify the effect of temperature on methane adsorption in shale gas reservoirs and study the effect of sample properties on the adsorption. The results showed that the isothermal adsorption methane increase with TOC, but temperature and depth have a negative influence on the gas adsorption. We also conclude that clay minerals and area have a positive correlation with Langmuir volume. All data for the methane adsorption isotherms were adjusted with the Langmuir equation.

Keywords: *Temperature; Methane adsorption; Longmaxi shale; Rock properties; Shale gas.*

1. Introduction

Shale gas is formed by the accumulation and bacterial degradation of the material of lagoon and lacustrine sediments. The composition of this organic matter is variable and depends on the conditions of deposit and dilution by quartz and carbonates, it also depends on terrestrial or marine origin [1].

At present, the research and development of shale gas in the world is very intensive, Many countries, especially energy consumers like the United States, Germany, and China, are very interested in shale gas and the United States has made discoveries. [2]

The south-eastern part of the Sichuan Basin is one of the first pilot test areas for shale gas exploration strategies. The Silurian Longmaxi Shale (SLS) is one of the few mature gas shales in China, which has been tested in vertical wells initially and results show that SLS has a large amount of shale gas reserves. [3]

Unlike conventional natural gas, shale gas is difficult to extract because it is trapped in source rocks. They are considered unconventional due to the methods used to extract them and the type of reservoir where they are produced.

Shale gas has become an important source of natural gas [4]. Some forecasters predict that shale gas will truly increase the general energy supply. Recently, some scholars have tried to determine the adsorption capacity of shale samples by conducting laboratory studies. [5], [6], [7]. Some analysts predict that shale gas will greatly expand the global energy supply [8]. China has the largest shale gas reserves in the world. International Energy Agency (IEA) pointed out that shale gas has technically increased the recovery rate of natural gas resources by nearly 50% [9].

The massive exploitation of conventional gases gives us the right to use them. These gases are easy to mine and are used in large quantities. Since the reserves of conventional natural gas are inevitably reduced and may be exhausted in about 60 years according to EIA, a in many countries, mining trapped in shale hydrocarbon or coal Unconventional oil and gas seems to be very attractive options. This phenomenon prompted researchers to become interested in the unconventional natural gas trapped in the source rock. [10]

[11] studied the methane adsorption of the main components of shale to clay rocks, and the results showed that under the experimental conditions, the type of clay minerals had a great influence on the adsorption capacity of methane.

The rapid growth of unconventional natural gas production has set off a global "shale gas revolution" in the energy sector. Shale is a fine-grained sedimentary rock with particles smaller than 62.5 μm , composed of a variable mixture of clay minerals, quartz, feldspar, carbonate, sulfide, amorphous material, and organic matter. [12], [13], [14]

In conventional petroleum systems, shale is generally considered to have no pores, and shale is generally considered to be source rock or caprock [15]. The abundant natural gas resources in shale pores have been widely recognized. In recent years, shale gas has received new attention as an important unconventional natural gas resource. [16], [17], [18], [19]; [20].

Both organic and inorganic substances in shale can adsorb methane and control the pore structure [21]. The total organic carbon (TOC) in the shale gas system is linearly positively correlated with methane adsorption capacity [22]. The maturity of organic matter is also considered to be the controlling factor of methane adsorption capacity. It is observed that the normalized adsorption capacity of TOC increases with the increase of thermal maturity until it reaches a certain level. For critical values, the trend is opposite after high maturity [23].

The methane adsorption capacity of each type of kerogen is in order: Type-III > Type II > Type I [24]. In addition to organic matter, for clay-rich shale, inorganic matter also affects total methane adsorption (Fan et al., 2015). For pure clay minerals, the methane adsorption capacity is reported to decrease in the following order: montmorillonite > mixture of illite and montmorillonite > kaolinite > chlorite > illite [25].

External parameters such as pressure, temperature, and humidity also affect the adsorption capacity of methane in shale. Moisture can greatly reduce methane adsorption capacity by occupying adsorption sites in shale gas reservoirs [26]. The adsorption of methane in shale is an exothermic process, and the adsorption capacity of methane decreases at high temperatures. Many studies on methane adsorption within a certain temperature range show that methane adsorption isotherms are very different at different temperatures ([27], [28])

2. Samples and Experimental Methods

2.1. Sample Preparation

The samples for the experiment were taken from the Longmaxi shale in the Sichuan Basin, China. The sampling depth is 2059 m; the reservoir pressure is about 42 MPa, and the TOC content is 2.19%. Before the experiment, the sample was crushed to 30-100 mesh and dried at 110°C for 18 hours to constant weight. Because shale gas is mainly composed of methane, the corresponding adsorption and adsorption kinetic data were obtained by the volume method using methane as the adsorbate, and the unadsorbed helium gas of shale was used as the test gas for dead volume calibration. The purity of methane and helium used in the experiment are both 99.999%.

Pressure gauge is used to measure the adsorption permission of CH₄. The differential heat flux calorimeter used is Set Aram C80 Tian-Calver. The sample is located in an adsorption cell, which is connected to a pressure gauge inserted in the upper part of the calorimeter. The temperature set by the calorimeter and the pressure measurement method is the same, allowing both parts of the coupling device to be in isothermal conditions. The main added value of this machine is the simultaneous measurement of the differential heat of adsorption, which is a direct measure of the adsorbate/adsorbent interaction.

2.2. High-pressure methane adsorption experiments

First, the shale sample was placed into the sample cell, which was connected to the test system. Then the airtightness of the test unit was checked with helium gas, and the leakage test pressure must be higher than the maximum experimental pressure. After the leak test for 24 h, if the test unit did not leak, the test gas could be released, and the dead volume of each test unit was calibrated with an AJP-100 calibrator. In the experiment, the dead volume was measured multiple times and its average value was calculated to ensure the accuracy. Finally, the oil bath was heated to the experimental temperature, and methane adsorption experiments started after the temperature was stable for 1h.

Adsorption experiments were performed using a pressurization-equilibration-pressurization process, and the adsorbed amount of methane was calculated according to the pre-equilibrium pressure, equilibrium pressure, and dead volume.

In this study, methane adsorption isotherms were obtained at 25°C, 40°C and 50°C. All isotherms were measured up to 52 MPa and fluctuations in temperature during a given isotherm were < 0.2 °C. In high-pressure methane adsorption measurements, only the surface excess can be obtained.

2.3. Data Management and Analysis: The Proposed Modeling Technique for Shale gas adsorption

Adsorption is defined as the concentration or selective retention of one or more components of a gaseous mixture on a solid surface. The adsorbent is solid and the adsorbate is the component. There are diverse types of adsorption isotherms that relate the adsorbed amount per unit mass of the adsorbent to the partial pressure of the adsorbate in the gas phase at equilibrium, depending on the nature of the adsorbent and the adsorbate.

Adsorption studies are very important for adsorption. They indicate by mathematical modeling the performance of the adsorbent under various working conditions such as flow rate, adsorbate concentration, etc.

For the adsorption of shale gas with one component, we conducted two types of analysis for data collected, based on the targeted indicators mentioned above. Data processing and data preparation are important because they influence the accuracy of the reservoir model. A precise reservoir model is important in achieving the success of the study. As for data provided for the achievement of this study, it will be necessary to evaluate if the Longmaxi shale gas adsorption contributes significantly to the Sichuan Basin for China's energy source development.

The adsorption of gases and solutes is usually described through isotherms that are, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (for liquid phase solutes) at constant temperature [29].

2.3.1 Langmuir adsorption model

The basic forms of the Langmuir isotherm have a reasonable arrangement with a large number of experimental systems, including those with different borders between the two phases. The sorption rate at the surface must be relative to the driving force multiplied by the area. The driving force is the concentration of the solution and the surface is the amount of bare surface. If the fraction of area covered is F , the rate per unit of surface is:

$$ra = kaC(1 - F) \tag{1}$$

The sorption of the surface is proportional to the quantities of a surface covered:

$$rd = kdF \tag{1}$$

Where ka and kd are the rate constants, ra is the sorption rate, rd is the desorption rate, C is the concentration in the solution and F is the fraction of the surface covered.

Langmuir adsorption model is a dynamic equilibrium between rates of adsorption and desorption. It also assumes monolayer coverage of gas molecules on a solid surface. We have a specific solid-gas combination that has a maximum for the amount of gas to be occupied by the international surface of adsorbing solid. This parameter will be termed here after as V_L defined as:

$$Vg = \frac{VIP}{P+PI} \tag{2}$$

(It as units of scf/t on Langmuir's model is Here; Vg (scf/ton) is the amount of gas adsorbed at a given gas-phase pressure, P (psi) ;

P_L is the Langmuir's pressure (psi) at which half of the gas capacity V_L remains adsorbed. Both specific solid-gas combinations [30].

This can be rewritten as:

$$\frac{P}{V} = \frac{P}{V_L} + \frac{PL}{V_L} \tag{3}$$

V_L and P_L characterize the Langmuir's isotherm for

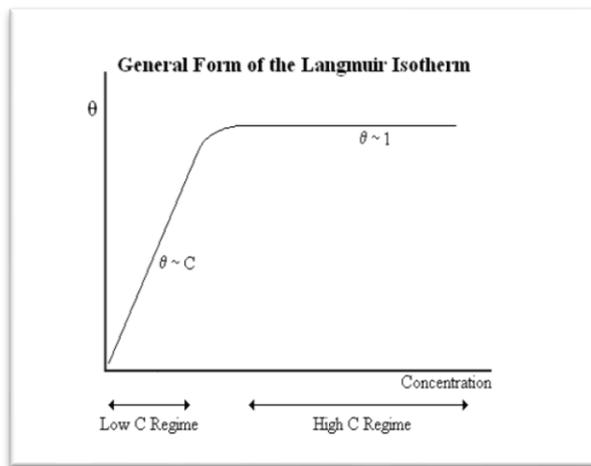


Figure 1: General form of the Langmuir Isotherm, Source: Chem 331L. The Langmuir adsorption isotherm The chemical reaction for monolayer adsorption can be represented as follows:



Where AS signifies a solute molecule bound to a surface site on S . The equilibrium constant

$Kads$ For this reaction is known by:

$$Kads = \frac{[AS]}{[A][S]} \tag{5}$$

Where [A] signifies the concentration of A, while the other two terms [S] and [AS] are concentration equivalents in two dimensions and are expressed in units such as mol/cm². The principle of chemical equilibrium is valid for these terms[31]

The complete form of the Langmuir isotherm considers (Eq.5) in terms of surface coverage, defined as the fraction of the adsorption sites to which a solute molecule is attached. An expression for the fraction of the surface with unattached sites is, therefore.

Given these definitions, we can rewrite the term $[AS]/[S]$ as

$$\frac{[AS]}{[S]} = \frac{\theta}{1-\theta} \tag{6}$$

[A] can be expressed as C, then the Equation (6) can then be rewritten as:

$$Kads = \frac{\theta}{1-\theta} \tag{7}$$

Reorganizing, we get the final form of the Langmuir adsorption isotherm:

$$\theta = \frac{KadsC}{1+KadsC} \tag{8}$$

If we describe Y as the quantity of adsorption in units of moles adsorbate per mass adsorbent, and Ymax and the maximal adsorption, then: $\theta = Y/Ymax$

The figure below shows the linear representation of the Langmuir isotherm.

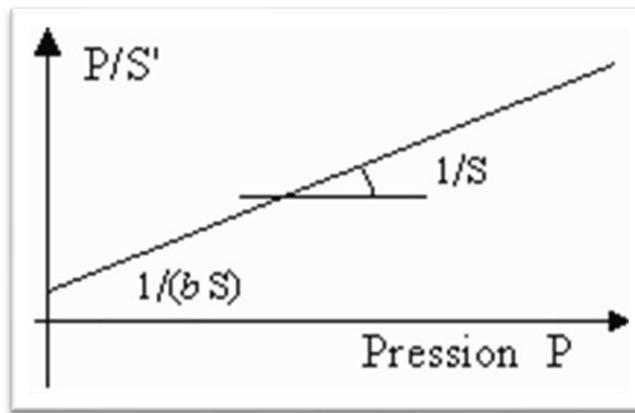


Figure 2: Linear representation of the Langmuir isotherm, Source: La critique en phase heterogene

2.4 Experimental Part

For data analysis, we used samples from Longmaxi Shale in the Sichuan Basin. Three samples were used. Here below are listed in tables 1 and 2 the sample properties.

	Sample	TOC (%)	I/S (%)	Depth (m)	Specific area (m ² /g)	Average pore radius (nm)	
	NO.1	L426	2.19	66	2038	5.21	9.421
	NO.2	L429	1.58	52	2050	4.56	8.546
	NO.3	L432	0.59	46	2059	3.23	5.421

Table: 2. 1 Sample properties

Table 2.1 is representing the sample properties that were used for our study. From this table, we can observe that sample NO.1 has a big amount of organic carbon and a high quantity of clay minerals followed by sample NO.2 and sample NO.3. We can also see from this table that the Sample NO.1 has also higher average pore radius and a big specific area followed by the Sample NO.2 then the Sample NO.3. But for the Depth, the Sample NO.3 is deep, then the sample NO.2 and finally the Sample NO.1.

Sample	Clay minerals (%)					Non-clay minerals (%)						
	C	I	I/S	%S	CRT (%)	QA	KF	AN	CA	DO	P	NCRT (%)
L426	8	26	66	8	75	18	0	3	3	1	0	25
L429	16	32	52	5	42	42	2	5	6	2	1	58
L432	24	30	46	21	18	35	7	6	24	8	2	82

Table 2.2: Percentage of Clay minerals in the sample

Note: C: Chlorite, I: Illite, S: Smectite, I/S: Illite- Smectite, %S: Percentage of Smectite layers in interstratified I/S; CR: the ratio of total clay minerals in the whole minerals; QA: Quartz; KF: K feldspar; AN:

Anorthose; CA: Calcite; DO: Dolomite; P: Pyrite NCR: the ratio of total non-clay minerals in the whole minerals).

3. RESULTS

3.1 Methane adsorption isotherms

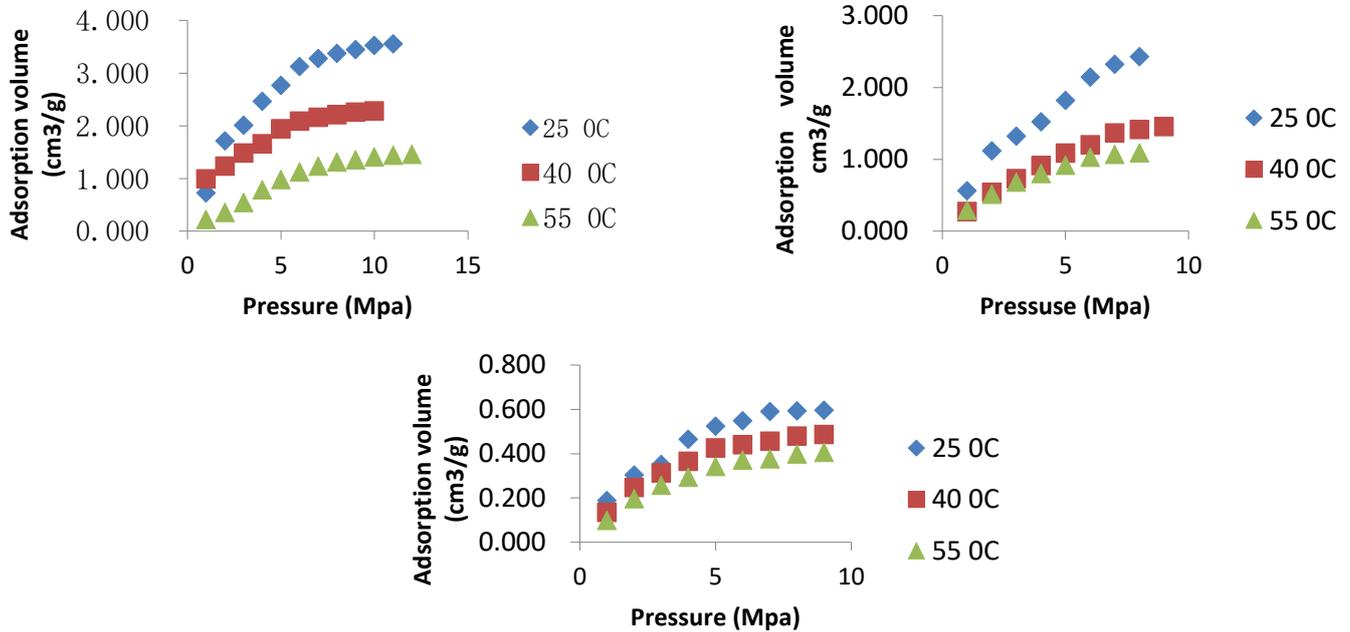


Figure 3.1: showing the Methane adsorption isotherm of the 3 samples at 20 °C, 40 °C, and 55 °C.

3.2 Langmuir volumes versus temperature

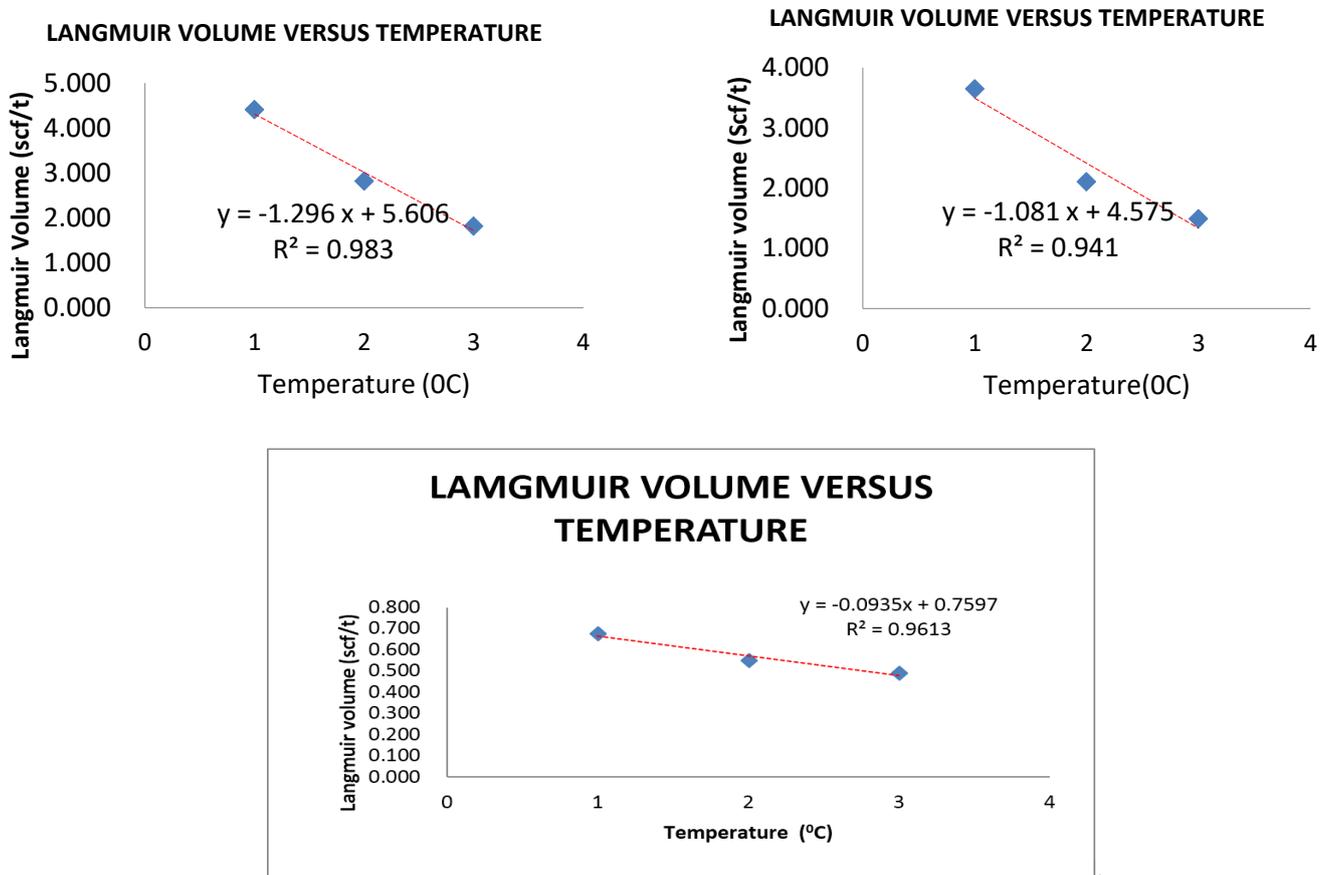


Figure 3.2 showing the isotherms of Langmuir volume versus temperature of the 3 samples.

From the figures above 3.2, we note that when the temperature increases, the Langmuir volume (VL) decreases. This means that the temperature has a negative influence on the volume of Langmuir. It can be justified by the fact that when the temperature increases, the thermal agitation of the gas molecules increases so that they are unable to settle well on the active sites of the rock.

When we observed the evolution of Langmuir volume with the temperature, the Langmuir volume gives us an idea of the quantity of gas adsorbed on the shale. When the temperature increases there is thermal agitation; the molecules become very mobile. So to get to fix a molecule on an adsorbant site becomes more difficult. That's why when we are at 25 °C, the volume adsorbed is large because the thermal agitation is low. But when we increase the temperature with the agitation and the increase of the mobility of the molecules of gas, instead of a molecule being adsorbed by a site it is moving, so there is the difficulty of adsorption because there is agitation and we cannot manage to control gas molecules.

3.3. The correlation between the Langmuir volumes and TOC.

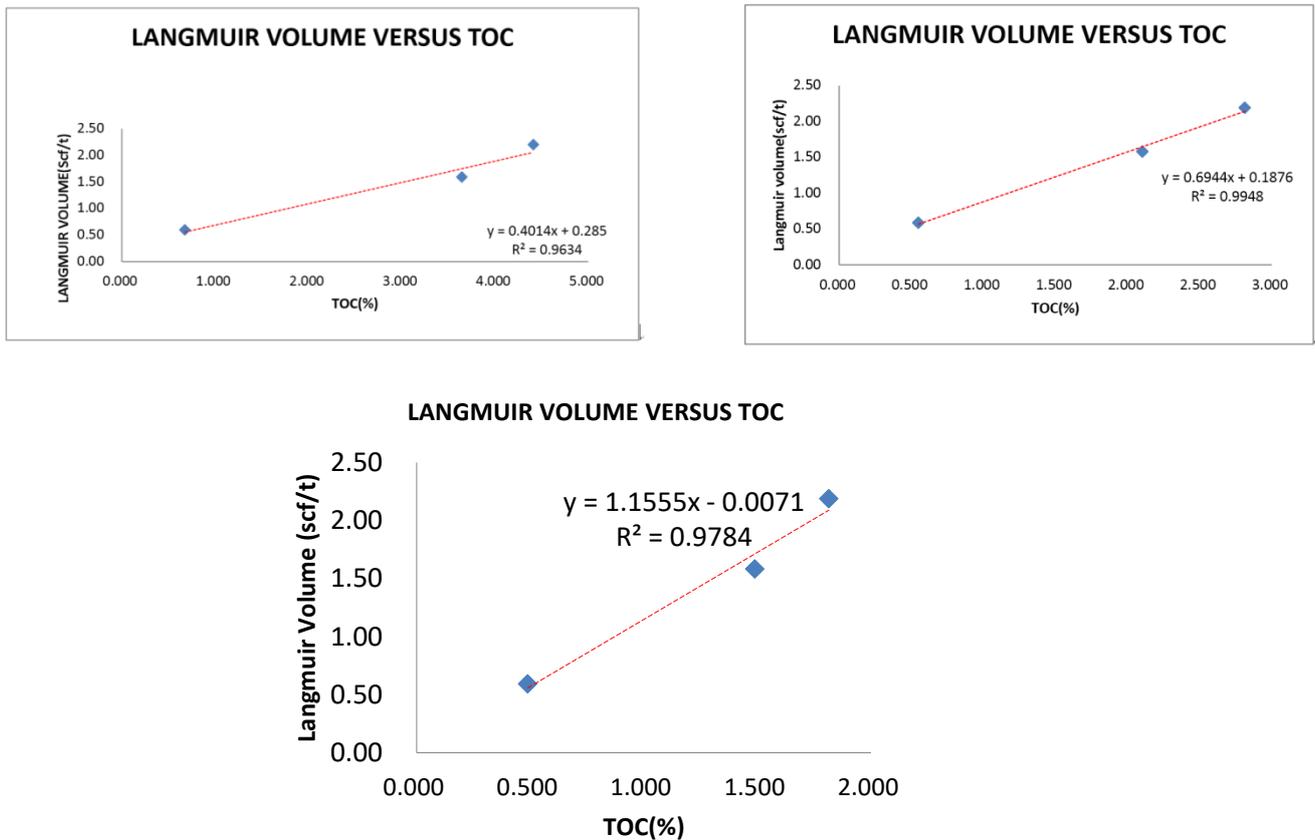
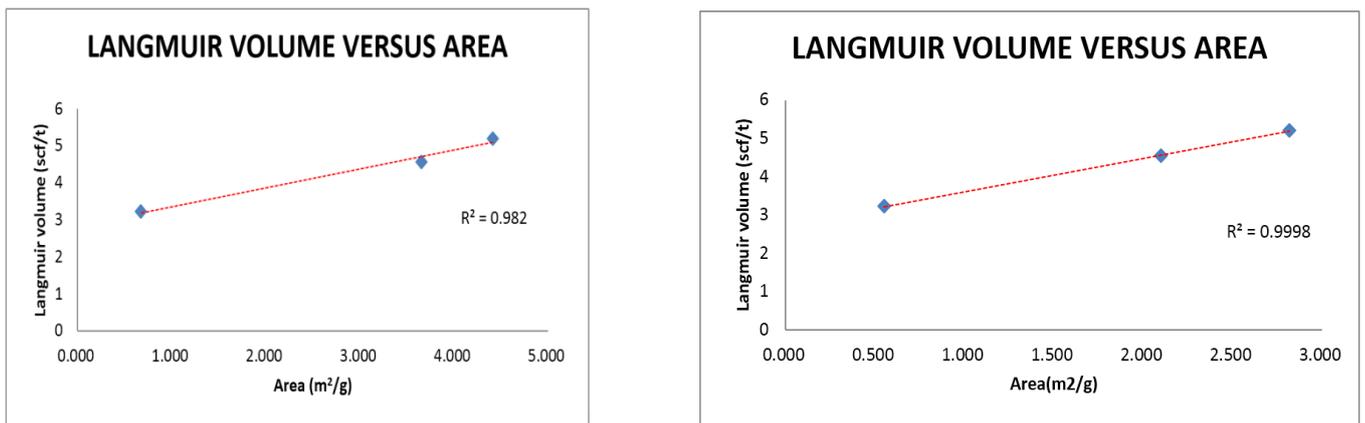


Figure 3.3 showing the correlation between the Langmuir volumes of samples with TOC.

We can see that when increasing the concentration of carbon, the Langmuir volume also increases because we are adsorbing carbon, so it is normal that when there is a big quantity of it in the rock, the volume adsorbed also increases.

3.4. The correlation between Langmuir volumes with the specific area



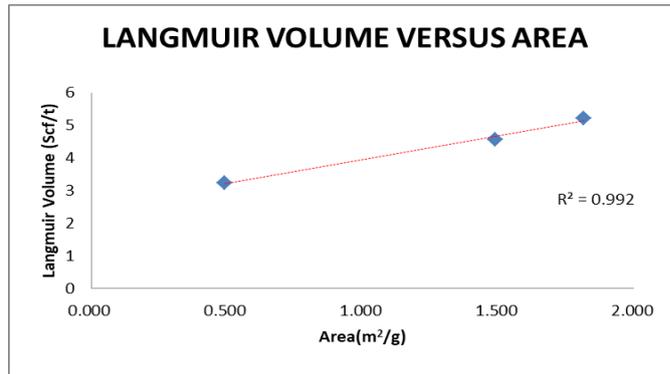


Figure 3.4 showing the correlation between Langmuir volumes of the samples with the specific area.

3.5. The Correlation between Langmuir Volume and Depth

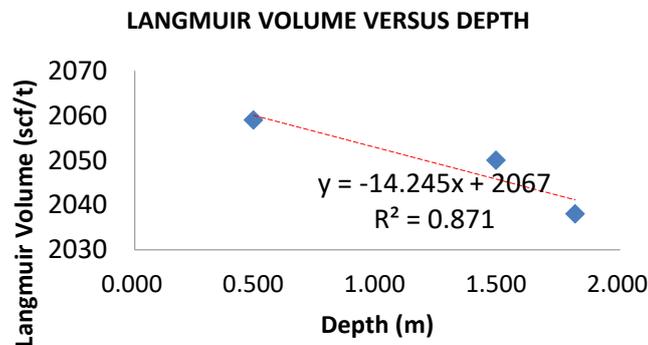
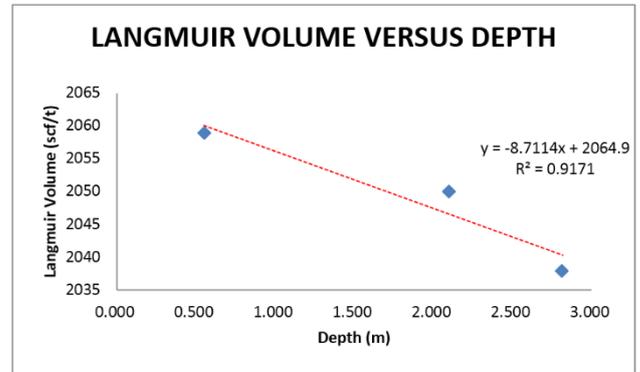
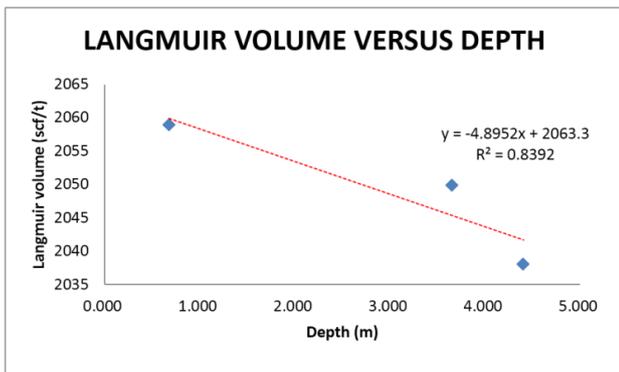


Figure 3.5: Correlation between Langmuir volumes and depth.

As we can see from the figures at 25 °C, 40 °C, and 55 °C, when the depth increases the volume decreases. This is because the molecules will be fixed on the sites at the surface and the sites located deep inside will remain unoccupied and the adsorption volume will reduce.

3.6 The correlation between the Langmuir volumes of samples with clay Mineral

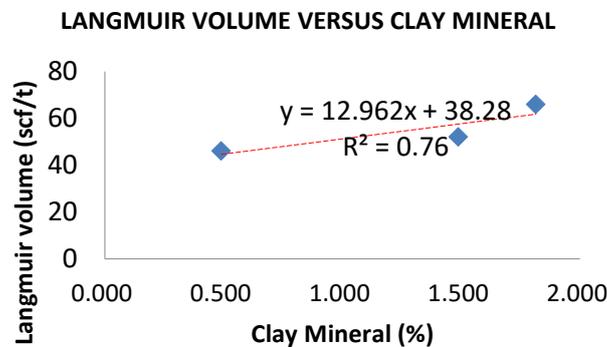
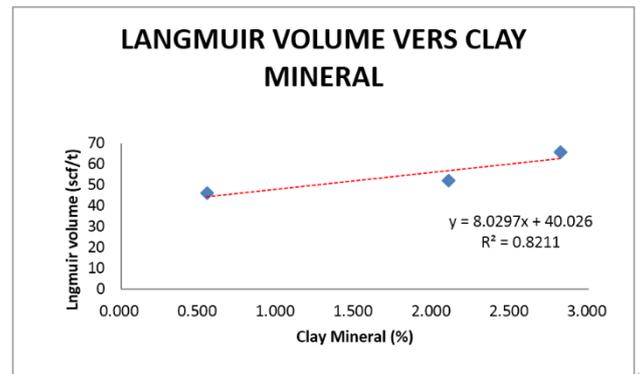
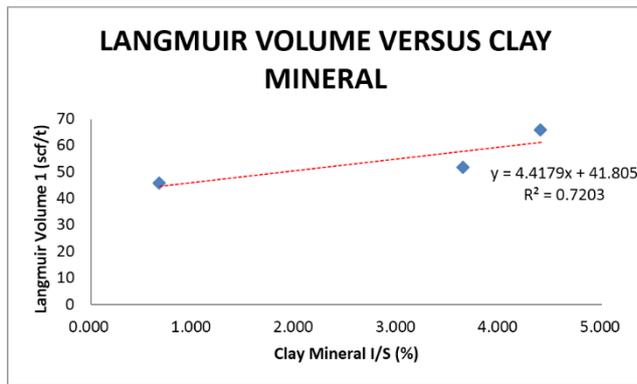


Figure 3.6 showing the correlation between the Langmuir volumes of the samples with clay Mineral.

We can see from the figures that there is a positive correlation between the Langmuir volume and the Clay Mineral. As the clay mineral increases, the Langmuir volume also increases.

Variable	25 °C	40 °C	55°C
TOC	0.9815	0.9974	0.9892
AREA	0.9909	0.9999	0.9960
CLAY MINERAL	0.8417	0.9062	0.8718
DEPTH	-0.9161	-0.9977	-0.9333

Table 3.1: Rock properties analysis

4. Discussion

4.1. Effect of Pressure on Methane adsorption isotherm

Through the different data collected, we demonstrated how the adsorption isotherms of methane for shale samples at different temperatures, such as:

- ✚ As the temperature increases, the adsorption decreases as proved by other studies. At 25°, 40°, and 55°C, the adsorbed gas content of the samples studied decreases in the following order: Sample 1 <Sample 2 <Sample3.
- ✚ Langmuir sample volume of shale shows a different degree of change from 25 ° C to 55°C. For example, samples 1 decrease from 4,407 to 1,815 (Scf/t) (58, 8 % of variation), sample 2 decreases from 3,650 to 1,488 (59, 2 % of variation) and sample 3 decreases from 0,677 to 0,490 (27.2% of variation), respectively.
- ✚ Generally, shale adsorption capacity reduces rapidly with the increase in temperature under a certain pressure [32]
- ✚ The pressure is a major factor affecting shale gas adsorption capacity[33]. The gas adsorption capacity increases with increasing pressure[34].

4.2. Characteristics of methane adsorption

The adsorption characteristics of methane at 25^o, 40^o and 55^o C temperature are controlled both by composition and by pores structure. The Langmuir maximum adsorption capacity also depends on the availability of the surface area of adsorbents as proved in our work [35]. The organic fraction (TOC) is the main determinant of the methane adsorption capacity for shale. As shown in figure 3.3, the Langmuir volume at 25^o, 40^o, and 55^o C has a positive linear correlation with total organic carbon. The methane adsorption capacity is proportional to its surface area in the mature stage and plays an important role in the methane adsorption[36]. The surface area available for adsorption may decrease and the maximum CH₄ adsorption capacity also decreases correspondingly [37].

4.3. Effect of temperature on methane adsorption

The effect of temperature on methane adsorption for shale samples is related to their composition. As shown in figures 3.2, the adsorption of methane decreases with the increase of the temperature. The rate of decrease is used to describe the effect of temperature on methane adsorption, and its change varies with pressure and varies from sample to sample. As a rule of physisorption, the adsorbed gas content increases with the pressure [38]. Therefore, it is reasonable to estimate that the descending speed is related to the adsorbed gas content. The more the adsorbed gas content, the greater the effect of temperature increases on the molecules.

Though, there is no correlation between the rate of decline and the adsorbed gas content for shale samples with different compositions. The correlation between adsorbed gases content and rate of decline follows this order: sample 1 < sample 2 < sample 3. Compared with other samples, Simple 3 is less sensitive to methane adsorption temperature increase.

Table 3.1 shows the calculated correlation coefficient values between rock properties and adsorption capacity. At 25^o C, the relationship between adsorption capacity and specific surface area is the largest, with a correlation coefficient of 0.9909, followed by TOC of 0.9815, depth of 0.8392, and clay minerals of 0.8417. At 40^o C and 55^o C, the highest relationship is with the area, then the TOC, the depth, and last with the clay mineral as shown in table 3. From table 3, we can classify the factors influencing the adsorption capacity. It can be seen that the first main component principally represents the physical factors is the specific surface area, the second major factor represents the geochemical factors (TOC). The adequacy of total organic carbon in rocks is the material basis of oil and natural gas, and it is also a key factor in determining hydrocarbon generation potential. As indicated by [39],[40].

The Langmuir maximum gas adsorption capacity is greatly affected by the TOC. This suggests that TOC considerably stimulates shale gas adsorption capacity, as indicated by previous studies [41],[42].

And the third principal component represents the mineral compositions such as the content of clay minerals. Minerals, especially clay, are also important factors that influence the gas adsorption capacity. Therefore, the gas adsorption capacity of clay is less significant than that of TOC [43].

Therefore, we can classify the factors influencing the methane adsorption Capacity into three types: physical factors, organic geochemical factors, and mineral compositions.

5. Conclusion

The main findings are summarized about the research objectives, questions, and hypotheses. The methane adsorption isotherms on shale samples were measured at three different temperatures (25^o C, 40^o C and 55^o C) to study the effect of temperature, pressure, and rock properties on the adsorption of methane by shale gas reservoirs.

The study has revealed the following points:

- ✚ TOC is the primary determinant of methane adsorption capacity for shale temperature.
- ✚ The effect of temperature on methane adsorption is different for shale samples of different compositions.
- ✚ Methane adsorbed is more sensitive to high temperature, but methane adsorbed on clay minerals is less sensitive to temperature. And the clay minerals have a positive influence on the gas adsorption.
- ✚ The high temperature in shale gas reservoirs can significantly reduce methane adsorption capacity. This could explain why the methane adsorption capacity in shale gas deposits is not related to TOC.

REFERENCES

- [1] C. Zou *et al.*, "Organic-matter-rich shales of China," *Earth-Science Rev.*, vol. 189, pp. 51–78, 2019.
- [2] N. Vedachalam, S. Srinivasalu, G. Rajendran, G. A. Ramadass, and M. A. Atmanand, "Review of unconventional hydrocarbon resources in major energy consuming countries and efforts in realizing natural gas hydrates as a future source of energy," *J. Nat. Gas Sci. Eng.*, vol. 26, pp. 163–175, 2015.
- [3] R. D. Cole, "PRIMARY AND SECONDARY SEDIMENTARY STRUCTURES IN OIL SHALE AND OTHER FINE-GRAINED ROCKS, GREEN RIVER FORMATION (EOCENE), UTAH AND COLORADO.," 1975.
- [4] R. S. Jones Jr, "Producing-Gas/Oil-Ratio Behavior of Multifractured Horizontal Wells in Tight Oil Reservoirs," *SPE Reserv. Eval. Eng.*, vol. 20, no. 03, pp. 589–601, 2017.
- [5] H. Aljamaan, R. Holmes, V. Vishal, R. Haghpanah, J. Wilcox, and A. R. Kovsky, "CO₂ storage and flow capacity measurements on idealized shales from dynamic breakthrough experiments," *Energy & Fuels*, vol. 31, no. 2, pp. 1193–1207, 2017.

- [6] A. Moritz *et al.*, "Methane baseline concentrations and sources in shallow aquifers from the shale gas-prone region of the St. Lawrence Lowlands (Quebec, Canada)," *Environ. Sci. Technol.*, vol. 49, no. 7, pp. 4765–4771, 2015.
- [7] R. Yang, S. He, D. F. Hu, H. Zhang, and J. Zhang, "Characteristics and the main controlling factors of micro-pore structure of the shale in Wufeng Formation-Longmaxi Formation in Jiaoshiba Area," *Geol. Sci. Technol. Inf. (in Chinese)*, vol. 34, no. 5, pp. 105–113, 2015.
- [8] Y. Belmabkhout, R. Serna-Guerrero, and A. Sayari, "Adsorption of CO₂ from dry gases on MCM-41 silica at ambient temperature and high pressure. 1: Pure CO₂ adsorption," *Chem. Eng. Sci.*, vol. 64, no. 17, pp. 3721–3728, 2009.
- [9] G. Boyun, C. William, and G. Ali Ghalambor, "Petroleum production engineering: a computer-assisted approach." Elsevier Science & Technology Books, 2007.
- [10] N. A.-V. Balzani, "The Future of Energy Supply: Challenges and Opportunities Angew," *Chem. Int. Ed.*, vol. 46, 2007.
- [11] L. M. Ji, J. L. Qiu, T. W. Zhang, and Y. Q. Xia, "Experiments on methane adsorption of common clay minerals in shale," *Earth Sci. China Univ. Geosci.*, vol. 37, no. 5, pp. 1044–1050, 2012.
- [12] J. Yang, J. Hatcherian, P. C. Hackley, and A. E. Pomerantz, "Nanoscale geochemical and geomechanical characterization of organic matter in shale," *Nat. Commun.*, vol. 8, no. 1, pp. 1–9, 2017.
- [13] C. Liang, Z. Jiang, Y. Cao, J. Wu, Y. Wang, and F. Hao, "Sedimentary characteristics and origin of lacustrine organic-rich shales in the salinized Eocene Dongying Depression," *GSA Bull.*, vol. 130, no. 1–2, pp. 154–174, 2018.
- [14] C. Liang, Y. Cao, K. Liu, Z. Jiang, J. Wu, and F. Hao, "Diagenetic variation at the lamina scale in lacustrine organic-rich shales: Implications for hydrocarbon migration and accumulation," *Geochim. Cosmochim. Acta*, vol. 229, pp. 112–128, 2018.
- [15] H. Tian, L. Pan, X. Xiao, R. W. T. Wilkins, Z. Meng, and B. Huang, "A preliminary study on the pore characterization of Lower Silurian black shales in the Chuandong Thrust Fold Belt, southwestern China using low pressure N₂ adsorption and FE-SEM methods," *Mar. Pet. Geol.*, vol. 48, pp. 8–19, 2013.
- [16] L. Chen *et al.*, "Effect of lithofacies on gas storage capacity of marine and continental shales in the Sichuan Basin, China," *J. Nat. Gas Sci. Eng.*, vol. 36, pp. 773–785, 2016.
- [17] L. Chen, Z. Jiang, K. Liu, J. Tan, F. Gao, and P. Wang, "Pore structure characterization for organic-rich Lower Silurian shale in the Upper Yangtze Platform, South China: A possible mechanism for pore development," *J. Nat. Gas Sci. Eng.*, vol. 46, pp. 1–15, 2017.
- [18] J. Dai *et al.*, "Geochemical characteristics of marine and terrestrial shale gas in China," *Mar. Pet. Geol.*, vol. 76, pp. 444–463, 2016.
- [19] H. Bi, Z. Jiang, J. Li, F. Xiong, P. Li, and L. Chen, "Ono–Kondo model for supercritical shale gas storage: A case study of Silurian Longmaxi shale in southeast Chongqing, China," *Energy & Fuels*, vol. 31, no. 3, pp. 2755–2764, 2017.
- [20] L. Chen *et al.*, "Mechanisms of shale gas adsorption: Evidence from thermodynamics and kinetics study of methane adsorption on shale," *Chem. Eng. J.*, vol. 361, pp. 559–570, 2019.
- [21] F. Yang, Z. Ning, R. Zhang, H. Zhao, and B. M. Krooss, "Investigations on the methane sorption capacity of marine shales from Sichuan Basin, China," *Int. J. Coal Geol.*, vol. 146, pp. 104–117, 2015.
- [22] W. Dang *et al.*, "Geological controls on methane adsorption capacity of Lower Permian transitional black shales in the Southern North China Basin, Central China: Experimental results and geological implications," *J. Pet. Sci. Eng.*, vol. 152, pp. 456–470, 2017.
- [23] M. Gasparik, P. Bertier, Y. Gensterblum, A. Ghanizadeh, B. M. Krooss, and R. Littke, "Geological controls on the methane storage capacity in organic-rich shales," *Int. J. Coal Geol.*, vol. 123, pp. 34–51, 2014.
- [24] Y. Han, Y. Zhu, Y. Liu, Y. Wang, H. Zhang, and W. Yu, "Nanostructure Effect on Methane Adsorption Capacity of Shale with Type III Kerogen," *Energies*, vol. 13, no. 7, p. 1690, 2020.
- [25] L. Ji, T. Zhang, K. L. Milliken, J. Qu, and X. Zhang, "Experimental investigation of main controls to methane adsorption in clay-rich rocks," *Appl. Geochemistry*, vol. 27, no. 12, pp. 2533–2545, 2012.
- [26] G. R. L. Chalmers and R. M. Bustin, "Lower Cretaceous gas shales in northeastern British Columbia, Part I: geological controls on methane sorption capacity," *Bull. Can. Pet. Geol.*, vol. 56, no. 1, pp. 1–21, 2008.
- [27] S. Guo, "Experimental study on isothermal adsorption of methane gas on three shale samples from Upper Paleozoic strata of the Ordos Basin," *J. Pet. Sci. Eng.*, vol. 110, pp. 132–138, 2013.
- [28] W. Ji *et al.*, "Estimation of marine shale methane adsorption capacity based on experimental investigations of Lower Silurian Longmaxi formation in the Upper Yangtze Platform, south China," *Mar. Pet. Geol.*, vol. 68, pp. 94–106, 2015.
- [29] X.-M. Xiao *et al.*, "Main controlling factors and enrichment area evaluation of shale gas of the Lower Paleozoic marine strata in south China," *Pet. Sci.*, vol. 12, no. 4, pp. 573–586, 2015.

- [30] M. Mastalerz, A. Schimmelmann, A. Drobniak, and Y. Chen, "Porosity of Devonian and Mississippian New Albany Shale across a maturation gradient: Insights from organic petrology, gas adsorption, and mercury intrusion," *Am. Assoc. Pet. Geol. Bull.*, vol. 97, no. 10, pp. 1621–1643, 2013.
- [31] Z. L. Luo, X. K. Zhao, S. G. Liu, and H. B. Song, "Uplift of Longmen mountain orogenic belt and the formation and evolution of Sichuan Basin," *Chengdu Univ. Sci. Technol. Press. Chengdu (in Chinese with English Abstr.)*, 1994.
- [32] M. Wang, "Diagenesis of black shale in Longmaxi Formation, southern Sichuan Basin and its periphery," *Acta Petrolei Sinica*, vol. 36, no. 9, p. 1035, 2015.
- [33] D. J. K. Ross and R. M. Bustin, "The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs," *Mar. Pet. Geol.*, vol. 26, no. 6, pp. 916–927, 2009.
- [34] P. Li, Z. Jiang, M. Zheng, H. Bi, and L. Chen, "Estimation of shale gas adsorption capacity of the Longmaxi Formation in the Upper Yangtze Platform, China," *J. Nat. Gas Sci. Eng.*, vol. 34, pp. 1034–1043, 2016.
- [35] C. Zou *et al.*, "Geological characteristics and resource potential of shale gas in China," *Pet. Explor. Dev.*, vol. 37, no. 6, pp. 641–653, 2010.
- [36] H. Tian *et al.*, "The dual influence of shale composition and pore size on adsorption gas storage mechanism of organic-rich shale," *Nat. Gas Geosci.*, vol. 27, no. 3, pp. 494–502, 2016.
- [37] L. Wang and H. Cao, "Probable mechanism of organic pores evolution in shale: Case study in Dalong Formation, Lower Yangtze area, China," *J. Nat. Gas Geosci.*, vol. 1, no. 4, pp. 295–298, 2016.
- [38] L. Zhou, Y. Zhou, and Y. Sun, "Studies on the mechanism and capacity of hydrogen uptake by physisorption-based materials," *Int. J. Hydrogen Energy*, vol. 31, no. 2, pp. 259–264, 2006.
- [39] F. Yang, Z. Ning, Q. Wang, R. Zhang, and B. M. Krooss, "Pore structure characteristics of lower Silurian shales in the southern Sichuan Basin, China: Insights to pore development and gas storage mechanism," *Int. J. Coal Geol.*, vol. 156, pp. 12–24, 2016.
- [40] C. H. Sondergeld, K. E. Newsham, J. T. Comisky, M. C. Rice, and C. S. Rai, "Petrophysical considerations in evaluating and producing shale gas resources," 2010.
- [41] X. M. Zhang *et al.*, "Reservoir characteristics and controlling factors of shale gas in Jiaoshiba area, Sichuan Basin," *Acta Pet. Sin.*, vol. 36, no. 8, pp. 926–939, 2015.
- [42] Y. Lingjie, F. Ming, C. Hongyu, L. Weixin, Z. Wentao, and X. Ershe, "Isothermal adsorption experiment of organic-rich shale under high temperature and pressure using gravimetric method," *Acta Pet. Sin.*, vol. 36, no. 5, pp. 557–563, 2015.
- [43] R. Yang, S. He, Q. Hu, D. Hu, and J. Yi, "Geochemical characteristics and origin of natural gas from Wufeng-Longmaxi shales of the Fuling gas field, Sichuan Basin (China)," *Int. J. Coal Geol.*, vol. 171, pp. 1–11, 2017.