Advances in Geo-Energy Research

Vol. 9, No. 3, p. 146-151, 2023

Perspective

Quantitative characterization of fluid occurrence in shale reservoirs

Junqian Li[1]*, Jianchao Cai[2]

[1]National Key Laboratory of Deep Oil and Gas, China University of Petroleum (East China), Qingdao 266580, P. R. China
[2]National Key Laboratory of Petroleum Resources and Engineering, China University of Petroleum, Beijing 102249, P. R. China

Keywords:
Shale oil
shale gas
shale pore water
quantitative characterization
occurrence mechanism

Cited as:
Li, J., Cai, J. Quantitative characterization of fluid occurrence in shale reservoirs. Advances in Geo-Energy Research, 2023, 9(3): 146-151.
https://doi.org/10.46690/ager.2023.09.02

Abstract:
Shale oil and gas, as important unconventional resources, have been widely discussed in the last decade. The occurrence characteristics of fluids (oil, gas, and water) in shale reservoirs are closely related to the exploitation of shale oil and gas, therefore the quantitative characterization of fluid occurrence in shale reservoirs has received extensive attention. In this paper, the latest advances and potential challenges on this subject are summarized. With respect to shale oil, the amounts, ratios and micro-distributions of shale oil in different states can be determined using the state equation of liquid and adsorption ratio equation, which contributes to identifying high-quality shale oil reservoirs. However, it is still necessary to strengthen the research on the multi-attribute coupling relationship and oil-rock interaction of shale oil reservoirs, and the determination of occurrence characteristics of adsorbed and free oil under in situ reservoir conditions. In terms of shale gas evaluation, the process analysis method and isotope fractionation method effectively solve the problem of evaluating in situ gas-bearing characteristics of shale, and can accurately estimate the amounts of total, adsorbed and free gas. The quantum physisorption behavior of gas could be a new research direction to reveal the microscopic occurrence mechanism of shale gas. As for shale pore water, a complete evaluation procedure for determining the amounts and micro-distributions of adsorbed and free water in shale matrix pores has been established, which provides insight into the storage and flow of oil and gas. In future work, a study on the quantitative evaluation of water-rock interaction is significant for obtaining the adsorbed and free water under in situ reservoir conditions.

In recent years, China's dependence on foreign oil and gas continues to rise, and the national energy security has been severely challenged. With increasing difficulty for conventional oil and gas exploitation, unconventional shale oil and gas has gradually become a significant alternative for enhancing oil and gas production in China (Wang et al., 2022; Jin, 2023). The success of the shale oil and gas revolution in the United States has achieved energy independence and changed the world's energy pattern. China is rich in shale oil and gas resources (Zhao et al., 2020), and the commercial development of marine shale gas in south China has been successfully achieved. Breakthroughs in the exploration and development of terrestrial shale oil have also been made in many Chinese basins, showing a broad prospect (Zou et al., 2022). Unlike conventional oil and gas reservoirs (traps), shale oil and gas are distributed continuously in a large area, where oil, gas and water simultaneously occur in the shale reservoir without obvious differentiation (Zou et al., 2014). The particularity of fluid occurrence in shale reservoir is that the fluids in various states (e.g., adsorbed and free) often coexist in the pore system of rocks, and the recoveries of fluids in different states are obviously diverse. Therefore, it is very important to reveal the microscopic occurrence of fluids in shale reservoirs and further determine the "sweet spot" of oil and gas enrichment for efficient exploitation of shale oil and gas. This paper focused on the shale reservoir fluids (shale oil, shale gas and shale pore water), and summarized the latest advances and possible challenges of the theories and methods in this field, in order

Yandy Scientific Press

*Corresponding author.
E-mail address: lijunqian@upc.edu.cn (J. Li); caijc@cup.edu.cn (J. Cai).

Received July 25, 2023; revised August 10, 2023; accepted August 15, 2023; available online August 18, 2023.

to provide an inspiration for the researchers concerned about this field.

1. Shale oil

Shale oil is a complex mixture of hydrocarbons (saturated and aromatic hydrocarbons) and 'NSO'-containing compounds (non-hydrocarbon, asphaltene). China is rich in shale oil resources, especially in medium-low maturity shale oil (Zhao et al., 2020). However, there are many unfavorable factors in shale oil exploitation. For example, different from the medium-high maturity shale oil in North America, the medium-low maturity shale oil in China is characterized by complex composition, heavy oil quality and high viscosity/density, resulting in a poor oil flow; different from conventional sandstone reservoirs, the micro-nano scale pore-throat network of shale is extremely developed, adsorbed and free oil coexist in the shale matrix pores and are influenced by the confinement effect of nanopores, which makes shale oil more difficult to flow (Li et al., 2018a). Therefore, one key issue in shale oil exploration and development is to reveal the microscopic occurrence mechanism of shale oil and determine the amounts and distributions of shale oil in different occurrence states.

The microscopic pore-throat structure and oil-rock interaction comprehensively affect shale oil storage, which makes it difficult to quantitatively characterize the amounts of adsorbed and free oil due to the extremely heterogeneous pore system and rock compositions in shale. Recently, many experimental methods have been developed in the quantitative characterization of shale oil occurrence, including oil saturation index (Jarvie, 2012; Hu et al., 2021; Pang et al., 2023), two dimensional nuclear magnetic resonance (Li et al., 2020a; Mukhametdinova et al., 2021), multi-temperature pyrolysis (Li et al., 2020a; Hu et al., 2021), stepwise solvent extraction (Hu et al., 2021), combination between centrifugation and nuclear magnetic resonance (Zhang et al., 2022), oil adsorption (Li et al., 2016; Dang et al., 2022), etc. These methods provide technical support for determining the adsorbed, free and movable capacities of shale oil. At the micro level, molecular simulation plays an important role in the analysis of shale oil multiphase occurrence mechanism, revealing that oil adsorbs on shale pore surface in a multilayer way, and free oil is distributed in the interior pore. The occurrence characteristics of adsorbed and free oil are comprehensively affected by many factors such as pore size and morphology, temperature and pressure, oil composition, and rock surface properties etc. (Tian et al., 2017; Ahsani et al., 2021; Tazikeh et al., 2022; Fei et al., 2023).

In terms of mathematical description, models for evaluating the adsorption capacity of shale oil are established. From the perspective of oil-rock interaction, a comprehensive evaluation model of oil adsorption capacity is proposed by combining kerogen swelling, organic pore adsorption and clay pore adsorption (Li et al., 2022). This model considers the control effect of maturity (R_o) on kerogen adsorption-swelling, the influence of clay pore adsorption capacity and formation temperature. The model reveals that the adsorbed oil in the middle-low maturity stage ($R_o < 1.0\%$) is mainly controlled by total organic matter content. With the increase in maturity, the adsorption effect of clay pores is gradually obvious. When $R_o > 1.2\%$-1.3%, the adsorbed amount of shale oil is mainly of clay pore adsorption. From a different perspective, theoretical models of the "adsorption ratio equation" and "state equation of liquid" are proposed to describe the microscopic occurrence of shale oil based on shale microscopic pore-throat structure and oil-rock interaction (Li, 2021a). These two equations establish a connection between characteristic parameters of fluid occurrence (adsorbed and free amounts, densities of adsorbed and free phases, adsorption thickness) and pore structure parameters of porous media (size, shape, volume, specific surface area of pores), which can be used to estimate the amount, ratio, micro-distribution, density and thickness of adsorbed oil (Li et al., 2018a; Zhang et al., 2022). To further establish the coupling relationship among sedimentary environment, lithology/lithofacies, physical properties of shale, occurrence and mobility of shale oil and reservoir fluid properties (Fig. 1) is a research direction that needs to be strengthened. In the coupling relationship, oil-rock interaction is a key factor. For a rock, oil will be free in all pores if there is no oil-rock interaction. Otherwise, the occurrence characteristics of oil in different types of pores (related to rock composition) are remarkably different if oil-rock interaction appears, which complicates the occurrence of shale oil under the superimposed influence of microscopic pore-throat structure. Additionally, the study of oil-rock interaction is also helpful to obtain in situ the amounts of shale oil in different states. Therefore, the oil-rock interaction at different pore surfaces is also the subject of urgent research.

2. Shale gas

Methane (CH_4) is a main component of shale gas, and is stored in natural fractures and matrix pore-cracks in a free form, and partially adsorbs on the surface of organic matter and clay particles with a ratio of 20%-85%. There is a small amount of dissolved gas overall. The quantitative characterization of in situ shale gas amount, including the determination of total, adsorbed and free gas amounts and ratio of adsorbed or free gas, is very important for efficient shale gas exploitation and has been paid special attention. According to different evaluation processes, the methods of evaluating in situ gas-bearing amount of shale mainly include direct method and indirect method. The direct method is based on the field desorption data to estimate the total gas amount, which is divided into three parts: lost gas, desorbed gas and residual gas. Among them, desorbed and residual gas can be accurately measured by instruments. The lost gas is the gas that escapes during coring, lifting and before loading into the desorption tank. This part of gas cannot be measured directly, so the gas loss estimation is the key to determining the accuracy of the direct method. At present, widely used methods for assessing the lost gas mainly include the linear fitting method proposed by the United States Bureau of Mines, polynomial curve fitting method, Smith-Williams method, Amoco curve fitting method and improved curve fitting method. The common problem of these methods is that they are more suitable for coalbed methane reservoirs with

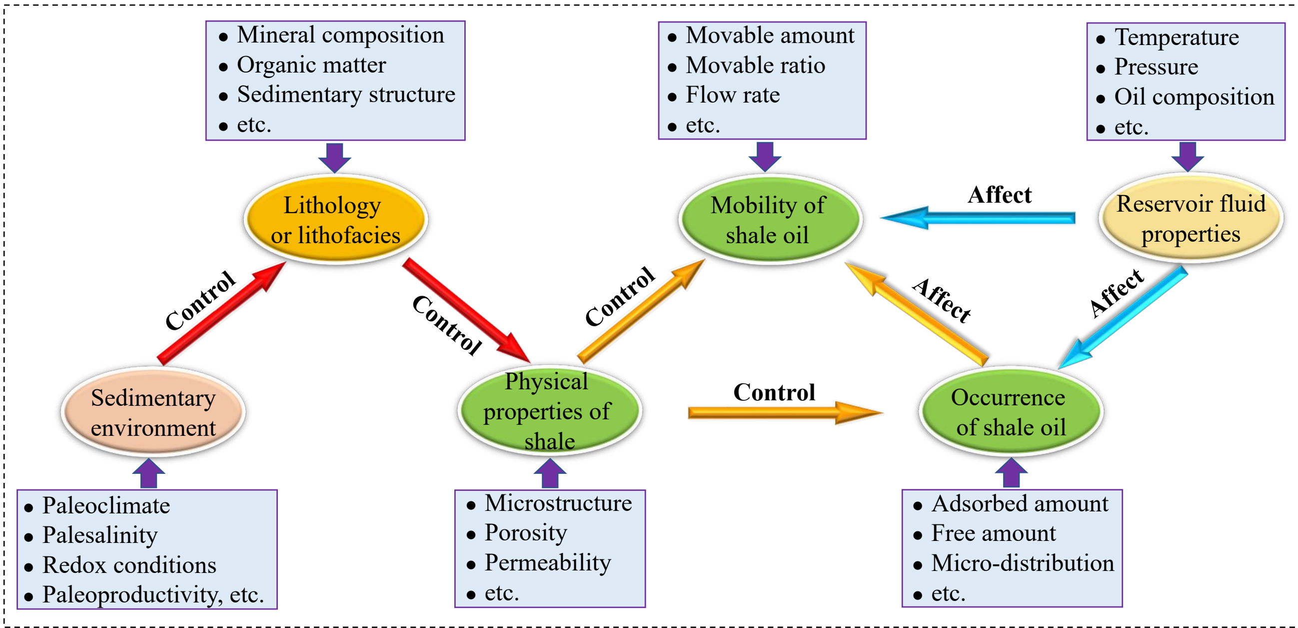

Fig. 1. Coupling relationship among various geological attributes.

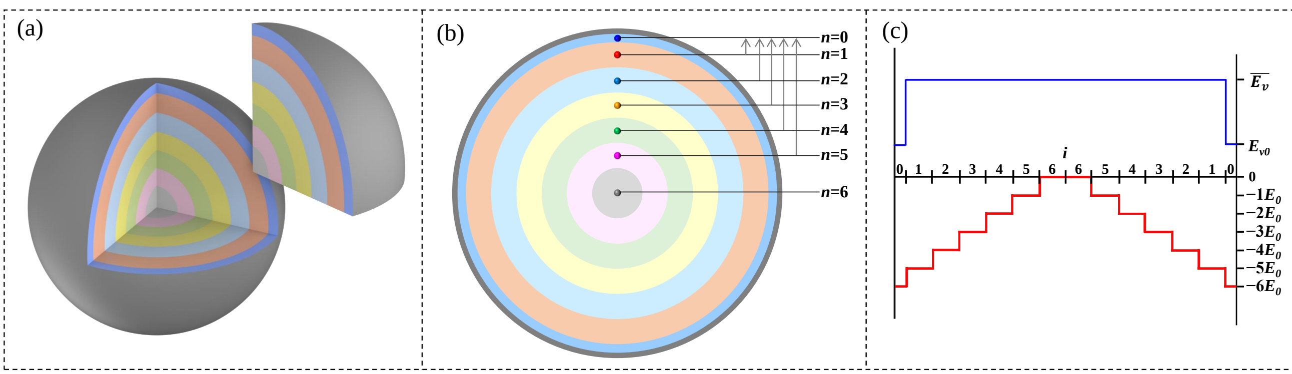

Fig. 2. Conceptually model of quantum physisorption of gas (a case of n = 6) (Modified from Li, 2023). (a) Spatial distribution of quantized energy field within nanopore; (b) An ideal pattern of energy level transition of molecules (a profile in (a)); (c) Energy distribution within a nanopore (a straight line in (b)).

high gas-adsorbed amount and shallow burial depth, while these methods have large errors for shale gas reservoirs with a high free gas amount and deep burial depth. In addition, the direct method cannot distinguish free gas from adsorbed gas, and thus cannot determine the free gas amount.

The indirect method is a method to evaluate the amounts of gas in different occurrence states (adsorbed, free and dissolved gas) (Li et al., 2018b; Gou and Xu, 2019). The main error source of this method is the estimation of gas-adsorbed amount. The calculated value using the isothermal adsorption equation is a theoretical maximum of gas adsorption. Adsorbed gas is one of the main gas storage forms, in order to accurately evaluate the gas-adsorbed amount, it is necessary to reveal the gas adsorption mechanism. For more than 100 years, researchers have been exploring the mechanism of gas physisorption, and have put forward a variety of possible explanations (Mudoi et al., 2022; Babatunde et al., 2022). Among them, Langmuir monolayer adsorption theory and Polanyi adsorption potential theory have a far-reaching influence on later generations. Different from the gas adsorption on an open flat surface (Langmuir theory), when the gas is in a narrow and confined nanoscale space, the gas molecules are attracted by the pore surface from all directions. This leads to a possibility that the gravitational potential energy of the interaction between gas-solid surfaces may no longer be a continuous distribution, but a quantized distribution (Fig. 2). Based on this consideration, Li (2023) proposed a quantized gas physisorption behavior in nanoporous media, that is, gas physisorption in nanoporous media shows a quantum effect. Gas adsorption is the result of energy level transition, and the uneven spatial distribution of gas in the nanoporous pores controls the gas physisorption behavior. This point of view provides a new way for us to evaluate the gas-adsorbed capacity of shale, and may also be a new research direction

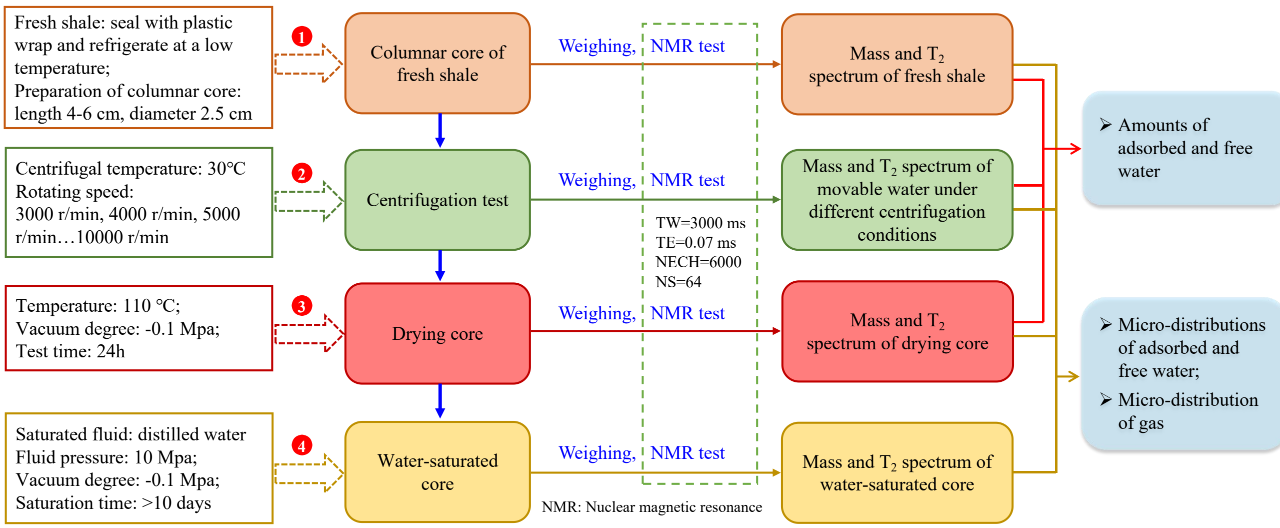

Fig. 3. Quantitative evaluation procedure for the amounts and micro-distributions of adsorbed and free water in shales.

in gas physisorption field.

Recently, two quantitative methods of estimating in situ gas amount were proposed by combining both the advantages of direct and indirect methods, that is the process analysis method (Li et al., 2020b) and the isotope fractionation method (Li et al., 2021b). The process analysis method divides the whole process of drilling coring and field analysis into five stages and evaluates the released amounts of adsorbed and free gas in different stages. After obtaining the data of drilling coring, reservoir physical properties, adsorption/diffusion parameters, gas characteristics and core field analysis, this method can be used to calculate the whole process of gas desorption and then obtain in situ the amounts of total, adsorbed and free gas. The isotope fractionation method is based on the four stages of CH_4 carbon isotope fractionation in the shale gas transport process. The isotope fractionation model coupled with multiple transport mechanisms in the multi-scale pore and fracture system is constructed. Further, the evaluation method is established to obtain in situ the gas-bearing characteristics. These two methods provide effective solutions for the gas-bearing characteristic evaluation of shale.

3. Shale pore water

A certain amount of water generally remains in shale matrix pores during the process of oil and gas evolution, which is called connate water. The connate water that bound in the pores occupies the space for oil and gas accumulation, and thus weakens the storage capacity of oil and gas. Moreover, as an obstacle on the migration channel of oil and gas, connate water makes shale pore-throats smaller and their connectivity worse, causing a more difficult flow of oil and gas (Cai et al., 2019a, 2019b; Tian et al., 2022; Lin et al., 2022). Previous studies (theory, experiment and molecular simulation) on the occurrence of shale pore water mainly focus on the evaluation of water distribution characteristics in shale or mineral pores by water vapor adsorption method (e.g., Zolfaghari et al., 2017a, 2017b; Yang et al., 2020a, 2020b, 2021; Zhang et al., 2021; Gao et al., 2022). Although many understandings have been obtained, the analysis results may be different from the characteristics of the liquid water occurrence under geological conditions. In addition, the difference in pore water occurrence state (mainly adsorbed and free) is not considered, which will lead to a distortion of water saturation calculation result (Li et al., 2019). In recent years, by defining the classification scheme of shale pore water and combining the saturation-centrifugation test, the relationship among the movable amount, free amount and centrifugal pressure difference was proposed (Li et al., 2019). Further, experimental evaluation on the amounts of adsorbed and free water in the shale matrix was established. By combining the adsorption ratio equation with classical nuclear magnetic resonance theory, a quantitative evaluation procedure for the microscopic distributions of adsorbed and free water in shales under laboratory conditions was established (Li et al., 2019, Li, 2021a). It can be used to quantitatively evaluate the amounts and microscopic distributions of water in different states in shale pores (Fig. 3).

The results of molecular simulation show that the occurrence characteristics of water in shale organic/inorganic pores are obviously different. For example, Xu et al. (2020) analyzed the occurrence state of water in hydrophilic and hydrophobic pores through molecular simulation, and appeared in the form of water film in hydrophilic pores, while in the form of water clusters in hydrophobic pores. In addition, the organic/inorganic pore structure and surface properties of shale also have important effects on pore water storage (Bai et al., 2020; Zhang et al., 2022). In future, considering the characteristics of high temperature and high pressure (overpressure) in deep marine shale gas reservoirs in south China (Wei et al., 2019; He et al., 2023), it is necessary to explore the occurrence characteristics of in situ pore water under high temperature and pressure conditions by analyzing the transformation law of adsorbed and free water. In essence, the key is characterizing water-rock interaction, which needs to be strengthened in future work.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (No. 41972123).

Conflict of interest

The authors declare no competing interest.

References

Ahsani, T., Tamsilian, Y., Rezaei, A. Molecular dynamic simulation and experimental study of wettability alteration by hydrolyzed polyacrylamide for enhanced oil recovery: A new finding for polymer flooding process. Journal of Petroleum Science and Engineering, 2021, 196: 108029.

Babatunde, K. A., Negash, B. M., Jufar, S. R., et al. Adsorption of gases on heterogeneous shale surfaces: A review. Journal of Petroleum Science and Engineering, 2022, 208: 109466.

Bai, J., Kang, Y., Chen, M., et al. Impact of surface chemistry and pore structure on water vapor adsorption behavior in gas shale. Chemical Engineering Journal, 2020, 402: 126238.

Cai, J., Lin, D., Singh, H., et al. A simple permeability model for shale gas and key insights on relative importance of various transport mechanisms. Fuel, 2019a, 252: 210-219.

Cai, J., Zhang, Z., Wei, W., et al. The critical factors for permeability-formation factor relation in reservoir rocks: Pore-throat ratio, tortuosity and connectivity. Energy, 2019b, 188: 116051.

Dang, W., Nie, H., Zhang, J., et al. Pore-scale mechanisms and characterization of light oil storage in shale nanopores: New method and insights. Geoscience Frontiers, 2022,13: 101424.

Tian, S., Xue, H., Lu, S., et al. Molecular simulation of oil mixture adsorption character in shale system. Journal of Nanoscience and Nanotechnology, 2017, 17(9): 6198-6209.

Fei, J., Wang, M., Li, J., et al. Molecular dynamics simulation of adsorption and absorption behavior of shale oil in realistic kerogen slits. Energy & Fuels, 2023, 37: 3654-3671.

Gao, Z., Xiong, S., Wei, L. The new multistage water adsorption model of Longmaxi Formation shale considering the spatial configuration relationship between organic matter and clay minerals. Petroleum Science, 2022, 19: 1950-1963.

Gou, Q., Xu, S. Quantitative evaluation of free gas and adsorbed gas content of Wufeng-Longmaxi shales in the Jiaoshiba area, Sichuan Basin, China. Advances in Geo-Energy Research, 2019, 3(3): 258-267.

He, X., Chen, G., Wu, J., et al. Deep shale gas exploration and development in the southern Sichuan Basin: New progress and challenges. Natural Gas Industry B, 2023, 10: 32-43.

Hu, T., Pang, X., Jiang, F., et al. Movable oil content evaluation of lacustrine organic-rich shales: Methods and a novel quantitative evaluation model. Earth-Science Reviews, 2021, 214: 103545.

Jarvie, D. M. Shale resource systems for oil and gas: Part 2—shale-oil resource systems. Shale reservoirs-giant resources for the 21^{st} century: AAPG Memory, 2012, 97: 89-119.

Jin, Z. Hydrocarbon accumulation and resources evaluation: Recent advances and current challenges. Advances in Geo-Energy Research, 2023, 8(1): 1-4.

Li, J. Development of adsorption ratio equation and state equation of liquid and their geological significance. Capillarity, 2021a, 4(4): 63-65.

Li, J. Quantum physisorption of gas in nanoporous media: A new perspective. Processes, 2023, 11(3): 758.

Li, W., Lu, S., Li, J., et al. Geochemical modeling of carbon isotope fractionation during methane transport in tight sedimentary rocks. Chemical Geology, 2021b, 566: 120033.

Li, J., Jiang, C., Wang, M., et al. Adsorbed and free hydrocarbons in unconventional shale reservoir: A new insight from NMR T_1-T_2 maps. Marine and Petroleum Geology, 2020a, 116: 104311.

Li, J., Lu, S., Cai, J., et al. Adsorbed and free oil in lacustrine nanoporous shale: A theoretical model and a case study. Energy & Fuels, 2018a, 32(12): 12247-12258.

Li, J., Lu, S., Zhang, P., et al. Estimation of gas-in-place content in coal and shale reservoirs: A process analysis method and its preliminary application. Fuel, 2020b, 259: 116266.

Li, J., Wang, M., Jiang, C., et al. Sorption model of lacustrine shale oil: Insights from the contribution of organic matter and clay minerals. Energy, 2022, 260: 125011.

Li, J., Wang, S., Lu, S., et al. Microdistribution and mobility of water in gas shale: A theoretical and experimental study. Marine and Petroleum Geology, 2019, 102: 496-507.

Li, Q., Pang, X., Tang, L., et al. Occurrence features and gas content analysis of marine and continental shales: A comparative study of Longmaxi Formation and Yanchang Formation. Journal of Natural Gas Science & Engineering, 2018b, 56: 504-522.

Li, Z., Zou, Y., Xu, X., et al. Adsorption of mudstone source rock for shale oil-experiments, model and a case study. Organic Geochemistry, 2016, 92: 55-62.

Lin, Z., Li, J., Wang, M., et al. Organic fluid migration in low permeability reservoirs restricted by pore structure parameters. Journal of Petroleum Science and Engineering, 2022, 218: 111028.

Mudoi, M. P., Sharma, P., Khichi, A.S. A review of gas adsorption on shale and the influencing factors of CH_4 and CO_2 adsorption. Journal of Petroleum Science and Engineering, 2022, 217: 110897.

Mukhametdinova, A., Kazak, A., Habina-Skrzyniarz, I., et al. NMR relaxometry interpretation of source rock liquid saturation-A holistic approach. Marine and Petroleum Geology, 2021, 132: 105165.

Pang, X., Li, M., Li, B., et al. Main controlling factors and movability evaluation of continental shale oil. Earth-Science Reviews, 2023, 243: 104472.

Shen, W., Li, X., Cihan, A., et al. Experimental and numerical simulation of water adsorption and diffusion in shale gas reservoir rocks. Advances in Geo-Energy Research, 2019, 3(2): 165-174.

Tazikeh, S., Shafiei, A., Yerkenov, T., et al. A systematic and critical review of asphaltene adsorption from macroscopic to microscopic scale: Theoretical, experimental, statistical, intelligent, and molecular dynamics simulation approaches. Fuel, 2022, 329: 125379.

Tian, Z., Wei, W., Zhou, S., et al. Impacts of gas properties and transport mechanisms on the permeability of shale at pore and core scale. Energy, 2022, 244: 122707.

Wang, X., Li, J., Jiang, W., et al. Characteristics, current exploration practices, and prospects of continental shale oil in China. Advances in Geo-Energy Research, 2022, 6(6): 454-459.

Wei, S., He, S., Pan, Z., et al. Models of shale gas storage capacity during burial and uplift: Application to Wufeng-Longmaxi shales in the Fuling shale gas field. Marine and Petroleum Geology, 2019, 109: 233-244.

Xu, H., Yu, H., Fan, J., et al. Two-phase transport characteristic of shale gas and water through hydrophilic and hydrophobic nanopores. Energy & Fuels, 2020, 34: 4407-4420.

Yang, R., Jia, A., He, S., et al. Water adsorption characteristics of organic-rich Wufeng and Longmaxi Shales, Sichuan Basin (China). Journal of Petroleum Science and Engineering, 2020a, 193: 107387.

Yang, R., Jia, A., He, S., et al. Experimental investigation of water vapor adsorption isotherm on gas-producing Longmaxi shale: Mathematical modeling and implication for water distribution in shale reservoirs. Chemical Engineering Journal, 2021, 406: 125982.

Yang, R., Jia, A., Hu, Q., et al. Particle size effect on water vapor sorption measurement of organic shale: One example from Dongyuemiao Member of Lower Jurassic Ziliujing Formation in Jiannan Area of China. Advances in Geo-Energy Research, 2020b, 4(2): 207-218.

Zhang, L., Li, Q., Liu, Y., et al. Molecular insight of flow property for gas-water mixture (CO_2/CH_4-H_2O) in shale organic matrix. Fuel, 2021, 288: 119720.

Zhang, P., Lu, S., Li, J., et al. Evaluating microdistribution of adsorbed and free oil in a lacustrine shale using nuclear magnetic resonance: A theoretical and experimental study. Journal of Petroleum Science and Engineering, 2022, 212: 110208.

Zhao, W., Hu, S., Hou, L., et al. Types and resource potential of continental shale oil in China and its boundary with tight oil. Petroleum Exploration and Development, 2020, 47(1): 1-11.

Zolfaghari, A., Dehghanpour, H., Holyk, J. Water sorption behaviour of gas shales: I. Role of clays. International Journal of Coal Geology, 2017a, 179: 130-138.

Zolfaghari, A., Dehghanpour, H., Xu, M. Water sorption behaviour of gas shales: II. Pore size distribution. International Journal of Coal Geology, 2017b, 179: 187-195.

Zou, C., Yang, Z., Zhang, G., et al. Conventional and unconventional petroleum "orderly accumulation": Concept and practical significance. Petroleum Exploration and Development, 2014, 41(1): 14-30.

Zou, C., Zhu, R., Dong, D., et al. Scientific and technological progress, development strategy and policy suggestion regarding shale oil and gas. Acta Petrolei Sinica, 2022, 43(12): 1675-1686.