Oil Shale, 2025, Vol. 42, No. 1, pp. 115–128
doi: https://doi.org/10.3176/oil.2025.1.05

ISSN 0208-189X

Study on the influence of the water-shale mass ratio on organic carbon migration and pore evolution during hydrocarbon generation by pyrolysis of medium- and low-maturity organic-rich shale in supercritical water conversion

Tian Xie[(a)]*, Yue Li[(a)], Qiuyang Zhao[(b)]*, Hui Jin[(b)], Yechun Wang[(b)], Liejin Guo[(b)]

[(a)] Xi'an Shiyou University, Xi'an 710065, China
[(b)] State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

Received 10 September 2024, accepted 10 January 2025, available online 14 January 2025

Abstract. *Oil reservoirs contain significant amounts of water. Therefore, the role of water in the in situ hydrocarbon generation of medium- and low-maturity organic-rich shale cannot be ignored. In this study, a self-developed reaction system was used to simulate hydrocarbon generation under supercritical water in situ conversion, examining the influence of water-shale mass ratio changes on organic carbon migration and pore evolution. The results showed that higher water-shale mass ratios were conducive to the conversion of organic carbon in shale and the migration of organic carbon to gas-phase products. As the water-shale mass ratio increased, the proportion of carbon elements in carbon dioxide from organic sources gradually decreased, while that of carbon elements from inorganic sources gradually increased. Increasing the water-shale mass ratio from 0.5 to 5, the porosity and permeability of shale were greatly improved, with porosity increasing more than threefold and permeability more than fivefold.*

Keywords: *supercritical water, organic-rich shale, conversion, water-shale mass ratio.*

1. Introduction

It is well known that oil is stored in porous media, which contains not only oil but also large amounts of water [1]. For the specific reservoir system of medium- and low-maturity organic-rich shale, thermal conversion is necessary to convert internal kerogen into mobile oil and gas products to access its oil resources [2–7]. In recent years, supercritical water in situ conversion

---

* Corresponding authors, xietian@xsyu.edu.cn, qyzhao@xjtu.edu.cn

technology for organic-rich shale pyrolysis and hydrocarbon generation has gained considerable attention [8, 9]. The unique properties of supercritical water, compared to those of ordinary water, greatly affect the conversion process. Therefore, regardless of the presence of original water inside the reservoir or external water injected into the reservoir to provide heat, its influence on the pyrolysis of organic-rich shale to generate hydrocarbons cannot be ignored [10].

Recently, many researchers have explored the influence of water closure on the pyrolysis of macromolecular organic matter from both micro and macro aspects. Microscopic studies show that when temperature and water pressure reach the supercritical state (374 °C, 22.1 MPa), water can be used as a green solvent to dissolve organic matter and as an in situ hydrogen supplier in the upgrading reaction. The hydrogen isotope tracer method is essential in studying water's mechanism in the pyrolysis of macromolecular organic matter. Dong Yu et al. [11] applied this method, combined with Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy analysis, to determine the hydrogen supply mechanism during supercritical water extraction of asphaltene. Dutta et al. [12] studied the pyrolysis of asphalt in steam (350–530 °C) using nuclear magnetic resonance (NMR) and stable isotope analysis, finding that about 16% of the hydrogen produced was deuterium. Gao et al. [13] determined the deuteration degree of water molecules in heavy oil refining (415 °C, H_2/D_2O mixture, catalyzed) through NMR. Hosseinpour et al. [14] examined the upgrading of polycyclic aromatic hydrocarbons (PAH) by adding formic acid and Fe_2O_3 catalyst in compressed hot water (400–500 °C, 0.2 g/cm^3, 0.5 h), noting significant =CH deuteration in FTIR, while –CH deuteration was insignificant. Hosseinpour et al. [15] also studied the upgrading of vacuum residue in supercritical water and proposed a method to distinguish between hydrogen supply by water and hydrogen supply by condensation reaction, using FTIR. Al-Muntaser et al. [16] carried out a well-designed upgrading of heavy oil in hot water (300 °C, 9/7.2 MPa, 24 h) and reported that adding a Ni-tallate catalyst during upgrading could deuterate –CH and =CH.

Deuterium is derived from catalyst and water dissociation reaction in the water-gas shift reaction. Macroscopic studies show that the mass ratio of water to macromolecular organic matter in the pyrolysis system affects the composition distribution of the pyrolysis products. Liang et al. [17] found that, in supercritical water gasification of organic-rich shale to produce hydrogen-rich syngas, an increased water-shale mass ratio improves gasification efficiency and the proportion of hydrogen in gas production. Wang et al. [18] observed that in subcritical water extraction of oil shale, extraction efficiency initially increases and then decreases with the rising water-shale mass ratio.

Overall, under high-temperature conditions, water can be used as a hydrogen donor in the pyrolysis of macromolecular organic matter, and the mass ratio of water to macromolecular organic matter affects the conversion reaction process. However, there are few reports on the influence of the water-shale mass ratio on organic carbon migration and pore evolution during supercritical water conversion for hydrocarbon generation in medium- and low-maturity organic-rich shale. This study uses a high-temperature and pressure reaction system to simulate the hydrocarbon generation process of medium- and low-maturity organic-rich shale under supercritical water in situ conversion, investigating the influence of the water-shale mass ratio on organic carbon migration and pore evolution. Hopefully, these findings can guide the efficient development of medium- and low-maturity organic-rich shale.

2. Experiment

2.1. Experimental system

The reaction equipment used in this experiment is a high-temperature and high-pressure reactor developed in-house, with its composition and characteristics detailed in the previous work of our team [19]. The chamber volume of the reactor is about 60 mL, the maximum temperature is 700 °C, and the maximum pressure is 35 MPa.

2.2. Experimental procedure

The experimental procedure has been described in detail in our previous work [20]. This paper briefly outlines the steps of the experiment. First, shale and deionized water were added to the reactor, which was then sealed for leak detection. After confirming that the seal was intact, heating was started. Once the target heating time was reached, the heating system was turned off for cooling. When the temperature dropped to room temperature, the reactor was turned on to collect the products for testing and analysis [20].

The focus of this study was to examine the influence of the water-shale mass ratio on the hydrocarbon generation of medium- and low-maturity organic-rich shale under supercritical water in situ conversion. The variable in the study was the water-shale mass ratio, with other working conditions remaining unchanged. The closed reactor setup required stable water quality to maintain constant pressure under specified temperature conditions. Therefore, the water-shale mass ratio adjustments could only be achieved by changing the quality of the shale added to the reactor. It was assumed that any volume change caused by varying shale quality would have no influence on the hydrocarbon generation process.

In this experiment, it took about 1.5 h to reach the target temperature. To avoid the influence of the heating stage as much as possible, some researchers use electromagnetic heating devices to make the reactor rise to the target temperature in a very short time. However, this study avoided using electromagnetic heating for the following reasons. In the process of in situ conversion of the reservoir, heat transfers from the injection point to the surrounding areas, and the heating process of the edge region is slow, just as simulated in this experiment. Therefore, the experiment represents heating and hydrocarbon generation at the shale reservoir's edge, aligning with the conditions of supercritical water in situ conversion and development.

3. Results and discussion

3.1. Organic carbon migration

The importance of organic carbon migration during hydrocarbon generation by pyrolysis of medium- and low-maturity organic-rich shale is reflected in the following aspects.

(1) Hydrocarbon generation potential assessment: Understanding organic carbon migration patterns is helpful in evaluating oil shale's hydrocarbon generation potential. By analyzing the transformation and migration behavior of organic matter at different maturity stages, it is possible to estimate the volume of hydrocarbons that oil shale can generate under specific geological conditions.

(2) Pyrolysis process control: Organic carbon migration patterns are crucial to controlling the pyrolysis process. During pyrolysis, the conversion and migration of organic matter directly affect hydrocarbon generation efficiency and product composition. Understanding these patterns can help optimize pyrolysis conditions and improve the efficiency of hydrocarbon generation.

(3) Resource exploration and development: Understanding organic carbon migration patterns has guiding significance for resource exploration and development of medium- and low-maturity organic-rich shale. By studying these patterns, the location and size of oil and gas reservoirs can be predicted more accurately, thus guiding exploration and development activities.

(4) Environmental impact assessment: In the process of pyrolysis hydrocarbon generation, the migration of organic carbon may release environmental pollutants, such as volatile organic compounds and greenhouse gases. Understanding these migration patterns can help assess and manage potential environmental risks.

(5) Improving resource utilization rate: Studying organic carbon migration patterns is conducive to improving the resource utilization rate of shale gas and shale oil. By optimizing pyrolysis conditions and processes, organic carbon loss can be minimized and the recovery rate of resources can be improved.

(6) Understanding chemical reaction mechanism: Studying organic carbon migration patterns helps further understand the chemical reactions of organic matter in the pyrolysis process. This is of great significance for developing new pyrolysis techniques and improving hydrocarbon generation efficiency.

(7) Geological model construction: Organic carbon migration patterns are

a key factor in constructing geological models. Through these patterns, the migration and conversion processes of organic matter over geological history can be more accurately simulated, which provides important information for geological research.

(8) Economic evaluation: Organic carbon migration patterns play an important role in assessing the economic viability of shale gas and shale oil projects. By understanding the migration and conversion efficiency of organic carbon, project costs and benefits can be more accurately predicted.

In conclusion, organic carbon migration patterns play a crucial role in hydrocarbon generation by pyrolysis of medium- and low-maturity organic-rich shale. It impacts not only the efficiency of hydrocarbon generation and resource exploration and development but also influences environmental impact and economic evaluations.

3.1.1. Effects of water-shale mass ratio on products and organic carbon utilization

Under the conditions of 400 °C, 25 MPa, and a 1-hour reaction time, the effects of the water-shale mass ratio (0.5–5) on organic carbon migration during hydrocarbon generation were investigated. Figure 1 shows the oil production rate variation with the increasing water-shale mass ratio. As the ratio increased from 0.5 to 5, the oil production rate rose from 2.02 to 4.11 kg oil$\cdot$t^{-1} shale. Figure 2 shows the gas production rate variation with the increasing water-shale mass ratio. As the ratio increased from 0.5 to 5, the gas production rate rose from 14.1 to 25.4 m^3 gas$\cdot$t^{-1} shale. Figure 3 shows the changes in organic and inorganic carbon quality and yield in wastewater with the increasing water-shale mass ratio. As the ratio increased from 0.5 to 5, both organic and inorganic carbon quality in wastewater showed a downward trend, while the organic carbon yield in wastewater showed an upward trend.

It is important to note that the control variable method was strictly applied in this study to control temperature, pressure, and reaction time. As described in Section 2 of this paper, the reaction system was a closed system with a fixed volume, where pressure was provided by the steam pressure from water evaporation. To maintain constant pressure at the same temperature, the mass of water added was kept unchanged. Thus, changes to the water-shale mass ratio were achieved by controlling the mass of shale added to the reactor, with negligible pressure fluctuation due to variations in shale volume.

From the above, it can be concluded that as the water-shale mass ratio increases, the quality of organic and inorganic carbon in wastewater gradually decreases, while the organic carbon yield in wastewater gradually increases. Figure 4 shows the variation in the organic carbon conversion rate with the increasing water-shale mass ratio. As the ratio increased from 0.5 to 5, the organic carbon conversion rate rose from 4.86% to 6.25%. This increase in organic carbon conversion is attributed to the simultaneous rise in both oil and gas production, as illustrated in Figures 1, 2, and 4.

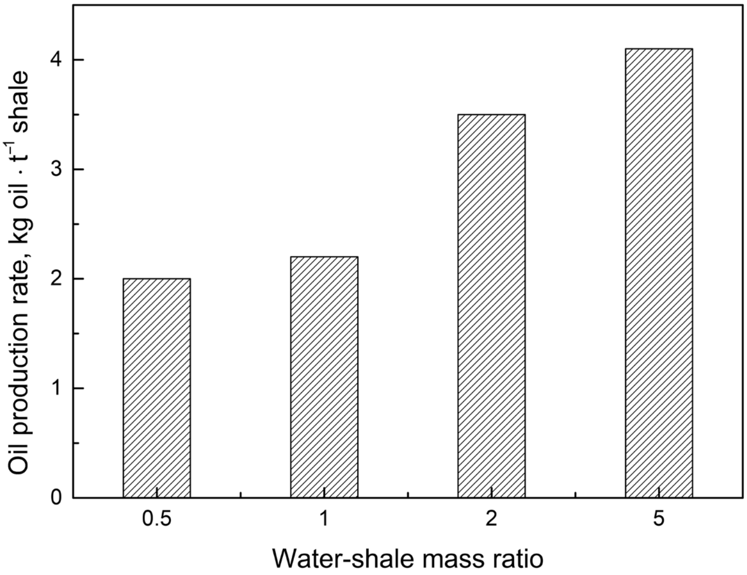

Fig. 1. Oil production rate variation with increasing water-shale mass ratio.

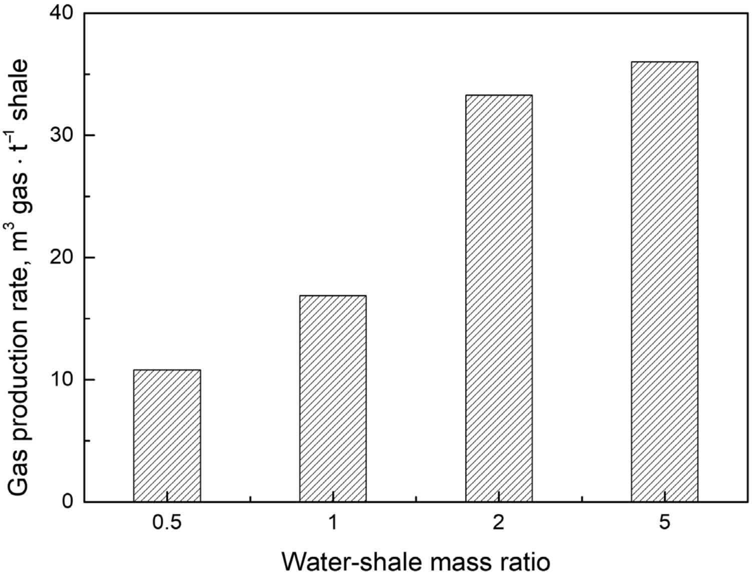

Fig. 2. Gas production rate variation with increasing water-shale mass ratio.

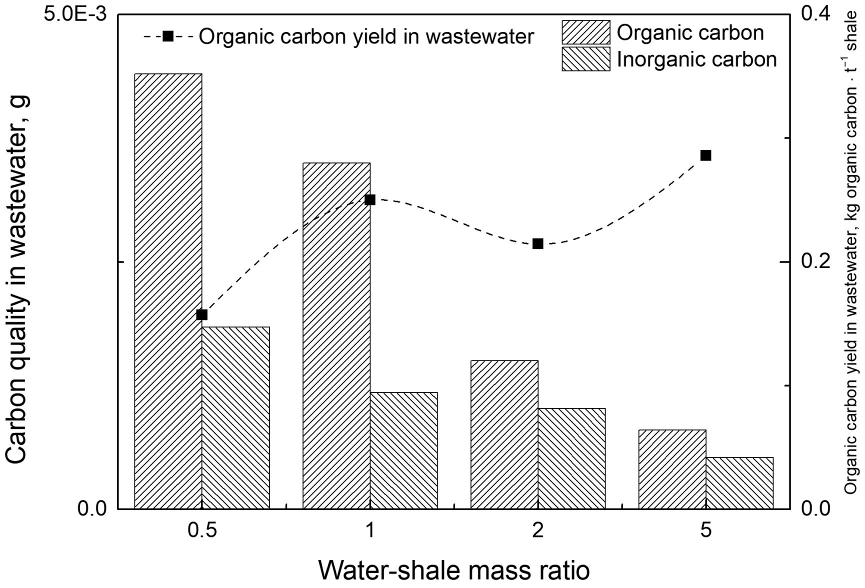

Fig. 3. Influence of the water-shale mass ratio on organic and inorganic carbon quality and yield in wastewater.

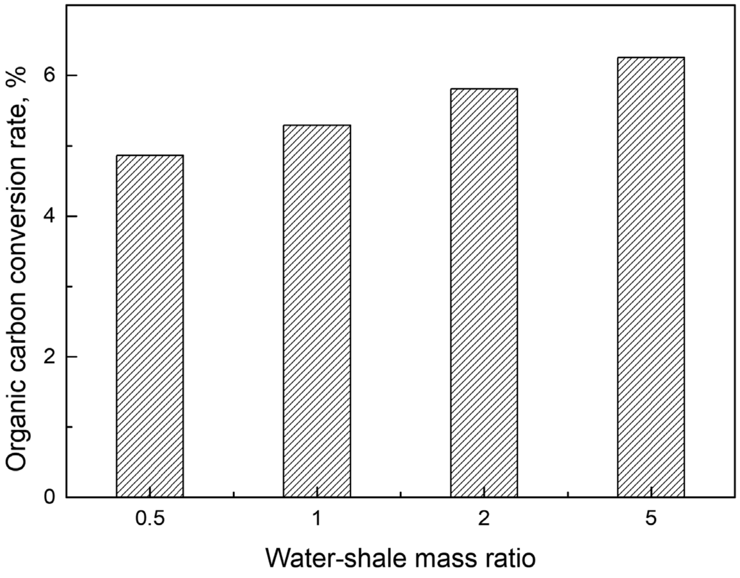

Fig. 4. Organic carbon conversion rate variation with increasing water-shale mass ratio.

3.1.2. Influence of the water-shale mass ratio on carbon sources in CO_2 products

Our previous research results show that the relative content of carbon dioxide (CO_2) in gas-phase products from medium- and low-maturity organic-rich shale in supercritical water has always maintained a high level [9]. From the perspective of whether it can be burned to provide energy, the presence of CO_2 prevents the proportion of combustible components in gas-phase products from reaching 100%. Therefore, exploring the carbon sources of CO_2 is helpful to further grasp the effective conversion rate of organic carbon converted in the initial shale. Figure 5 shows the distribution of carbon sources in CO_2, as affected by the water-shale mass ratio. With the increasing water-shale mass ratio, the proportion of carbon elements in CO_2 derived from organic sources gradually decreases, while that of carbon elements from inorganic sources gradually increases. To obtain the results shown in Figure 5, this study assumed that the mass of inorganic carbon converted from the initial shale after supercritical water reaction was equal to the mass of inorganic carbon in the shale before the reaction minus the mass of inorganic carbon in the residue after the reaction. Since no carbon monoxide was detected in this study, this likely indicates a complete water-gas shift reaction in the supercritical water environment. Therefore, it is assumed that all converted inorganic carbon is released as CO_2.

Accordingly, the amount of inorganic carbon in CO_2 is equal to that of inorganic carbon converted from the initial shale minus the amount of inorganic carbon in the wastewater. Similarly, the carbon mass of CO_2 from

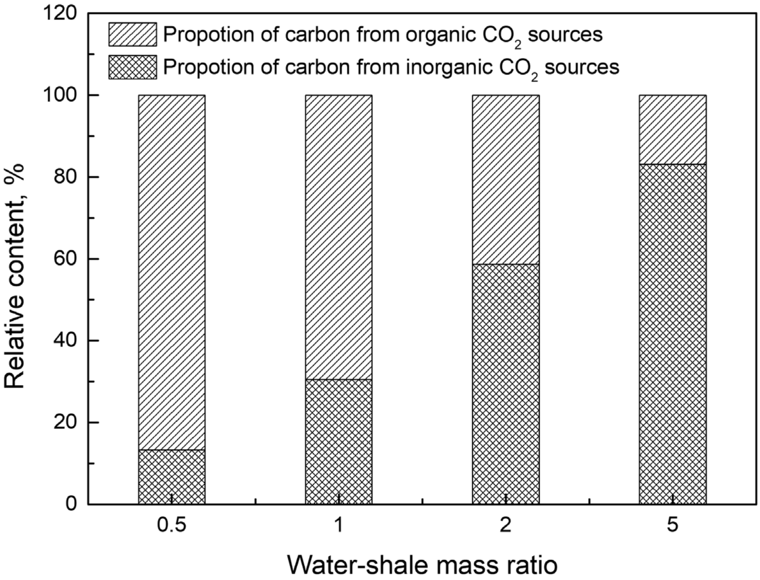

Fig. 5. Influence of the water-shale mass ratio on carbon sources in carbon dioxide.

organic carbon sources is equal to the total carbon mass of CO_2 minus the carbon element mass of CO_2 from inorganic carbon. It is assumed that, in the supercritical water environment, CO_2 does not reconvert to inorganic minerals, though it may convert to organic matter. Additionally, the CO_2 produced by the conversion of inorganic carbon does not undergo subsequent reactions, such as methanation, to synthesize organic matter. Therefore, the proportion of carbon from inorganic CO_2 sources in Figure 5 is greater than the actual value, while that of carbon from organic CO_2 sources is lower than the actual value.

3.1.3. Influence of the water-shale mass ratio on organic carbon migration ratio during pyrolysis

Figure 6 shows the distribution of converted organic carbon in the three-phase products of oil, gas, and water during the hydrocarbon generation of medium- and low-maturity organic-rich shale in supercritical water co-heated conditions with a changing water-shale mass ratio. As evident, the distribution ratio of organic carbon in oil-phase products and wastewater decreases with the increase in the water-shale mass ratio, while the distribution ratio of organic carbon in gas-phase products rises with the increase in the water-shale mass ratio. This indicates that a higher water-shale mass ratio is conducive to the migration of organic carbon into gas-phase products, suggesting that although it can promote both oil and gas production, it has a stronger effect on the latter.

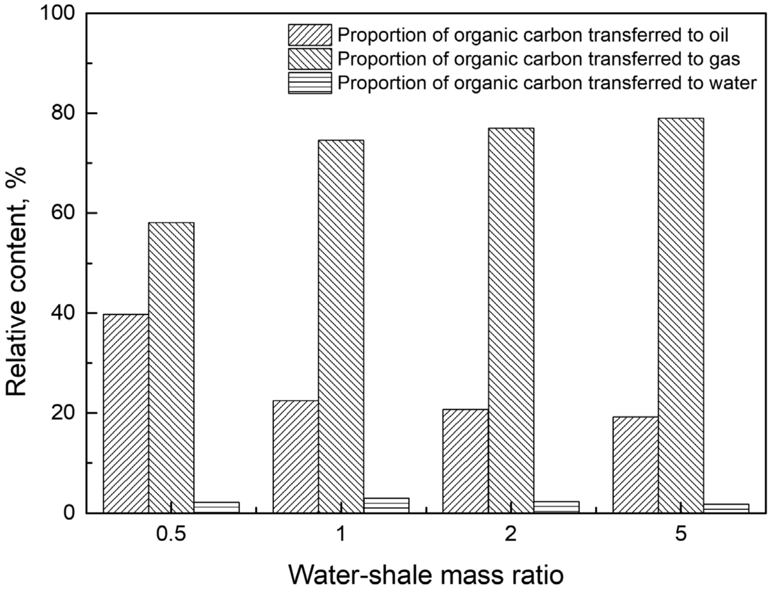

Fig. 6. Distribution ratio of converted organic carbon with changing water-shale mass ratio.

3.2. Influence of the water-shale mass ratio on pore evolution

Figures 7, 8, and 9 respectively show changes in the porosity, permeability, and specific surface area of medium- and low-maturity organic-rich shale with the increasing water-shale mass ratio after supercritical water conversion. Evidently, porosity, permeability, and specific surface area all increased gradually with a higher water-shale mass ratio, indicating enhanced pore expansion. This can be mainly attributed to the homogeneous reaction environment and hydrogen supply, further promoting the pyrolysis of solid organic matter.

Figure 10 shows the gradual increases in mean, mode, and median pore diameters with a higher water-shale mass ratio. Greater water-shale interaction during hydrocarbon generation appears to significantly affect porosity and permeability, having an important impact on the hydrocarbon generation of medium- and low-maturity organic-rich shale. It promotes the dissolution and precipitation of minerals in the rock, changing the porosity and permeability of the reservoir. The increasing water-shale mass ratio may also affect the shale pyrolysis reaction by promoting ring-opening reactions of kerogen macromolecules and the cleavage of kerogen side chains, leading to the maturation of kerogen. As kerogen, initially occupying pore spaces, undergoes pyrolysis to form oil and gas, it improves the shale's porosity and permeability.

In conclusion, the increasing water-shale mass ratio promotes the hydrocarbon generation of medium- and low-maturity organic-rich shale to a certain extent. Therefore, the effect of hydrocarbon generation can be optimized by adjusting the water-shale ratio and reaction conditions in the actual process of in situ hydrocarbon generation in supercritical water.

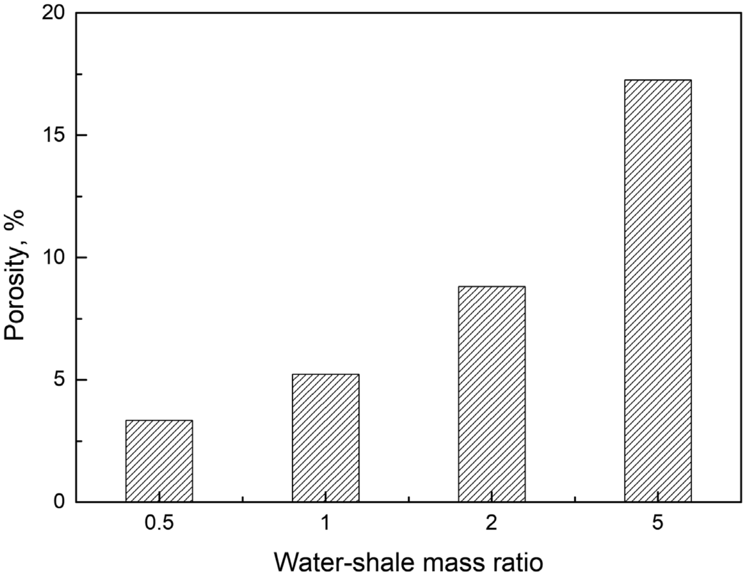

Fig. 7. Influence of the water-shale mass ratio on shale porosity.

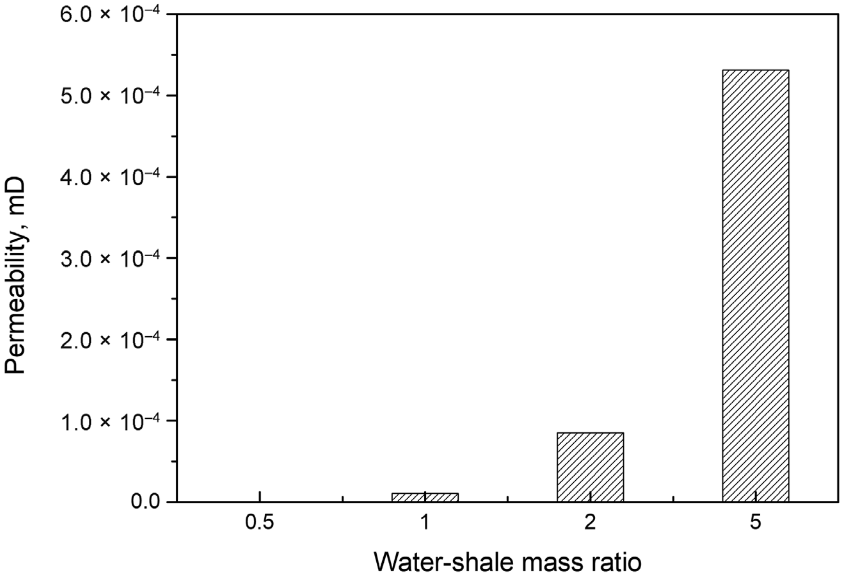

Fig. 8. Influence of the water-shale mass ratio on shale permeability.

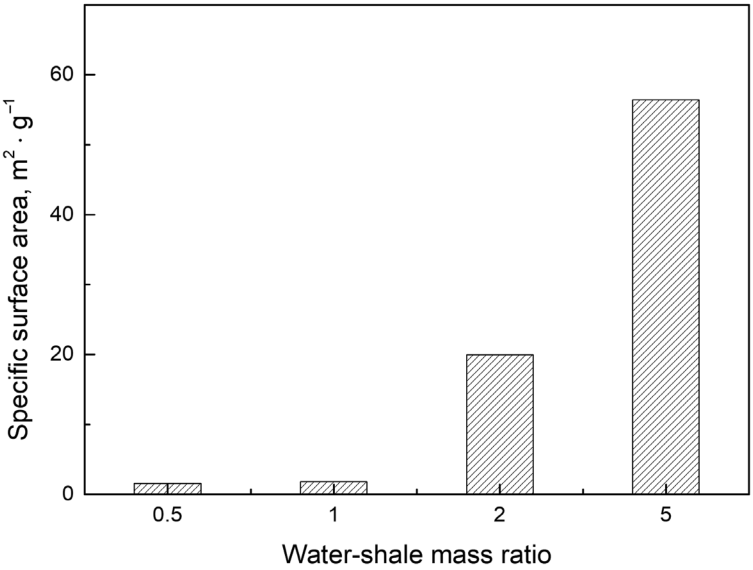

Fig. 9. Influence of the water-shale mass ratio on the specific surface area of shale pores.

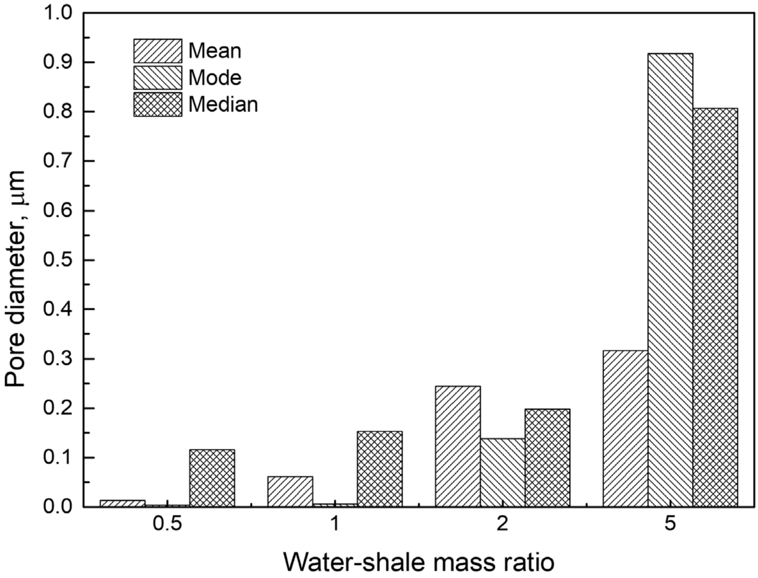

Fig. 10. Influence of the water-shale mass ratio on the pore diameter distribution of shale.

4. Conclusions

In this study, a self-developed high-temperature and high-pressure reaction system was used to simulate the hydrocarbon generation of medium- and low-maturity organic-rich shale under supercritical water in situ conversion, with a focus on the influence of the water-shale mass ratio (0.5–5) on organic carbon migration and pore evolution. The following conclusions were made:

1. As the water-shale ratio increases, the distribution ratio of organic carbon in oil-phase products and wastewater decreases, while it increases in gas-phase products.
2. With a higher water-shale mass ratio, the proportion of carbon elements in carbon dioxide from organic sources gradually decreases, while that of carbon elements from inorganic sources gradually increases.
3. Porosity, permeability, and specific surface area, along with pore diameter, gradually increase with a higher water-shale mass ratio.

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

Acknowledgments

Financial support from the Basic Science Center Program for Ordered Energy Conversion of the National Nature Science Foundation of China (grant No. 52488201) is gratefully acknowledged. The authors are thankful to the reviewers and editors for their work on this article. The publication costs of this article were partially covered by the Estonian Academy of Sciences.

References

1. Lewan, M. D. Water as a source of hydrogen and oxygen in petroleum formation by hydrous pyrolysis. *Am. Chem. Soc., Div. Fuel Chem.*, 1992, **37**, 1643−1649.
2. Deng, S., Wang, Z., Gao, Y., Gu, Q., Cui, X., Wang, H. Subcritical water extraction of bitumen from Huadian oil shale lumps. *J. Anal. Appl. Pyrolysis*, 2012, **98**, 151−158. https://doi.org/10.1016/j.jaap.2012.07.011
3. Akiya, N., Savage, P. E. Roles of water for chemical reactions in high-temperature water. *Chem. Rev.*, 2002, **102**(8), 2725−2750. https://doi.org/10.1021/cr000668w
4. Bake, K. D., Pomerantz, A. E. Optical analysis of pyrolysis products of Green River oil shale. *Energy Fuels*, 2017, **31**(12), 13345−13352. https://doi.org/10.1021/acs.energyfuels.7b01020
5. Kang, Z., Zhao, Y., Yang, D. Review of oil shale in-situ conversion technology. *Appl. Energy*, 2020, **269**, 115121. https://doi.org/10.1016/j.apenergy.2020.115121
6. Tang, X., Li, S., Yue, C., He, J., Hou, J. Lumping kinetics of hydrodesulfurization and hydrodenitrogenation of the middle distillate from Chinese shale oil. *Oil Shale*, 2013, **30**(4), 517−535. http://dx.doi.org/10.3176/oil.2013.4.05
7. Hou, L., Ma, W., Luo, X., Liu, J. Characteristics and quantitative models for hydrocarbon generation-retention-production of shale under ICP conditions: example from the Chang 7 member in the Ordos Basin. *Fuel*, 2020, **279**, 118497. https://doi.org/10.1016/j.fuel.2020.118497
8. Xie, T., Zhao, Q., Jin, H., Wang, Y., Guo, L. Reaction kinetics study on hydrocarbon generation of medium- and low-maturity organic-rich shale in supercritical water. *Energy Fuels*, 2023, **37**(18), 14192–14201. https://doi.org/10.1021/acs.energyfuels.3c02494
9. Xie, T., Zhao, Q., Jin, H., Wang, Y., Guo, L. Experimental investigation on the organic carbon migration path and pore evolution during co-thermal hydrocarbon generation of low maturity organic-rich shale and supercritical water. *Energy Fuels*, 2022, **36**(24), 15047–15054. https://doi.org/10.1021/acs.energyfuels.2c02932
10. Xie, T., Zhao, Q., Dong, Y., Jin, H., Wang, Y., Guo, L. Experimental investigation on the hydrocarbon generation of low maturity organic-rich shale in supercritical water. *Oil Shale*, 2022, **39**(3), 169–188. https://doi.org/10.3176/oil.2022.3.02
11. Dong, Y., Zhao, Q., Jin, H., Miao, Y., Zhang, Y., Wang, X., Guo, L. Hydrogen donation of supercritical water in asphaltenes upgrading by deuterium tracing method. *J. Supercrit. Fluids*, 2024, **205**, 106137. https://doi.org/10.1016/j.supflu.2023.106137

12. Dutta, R. P., Mccaffrey, W. C., Gray, M. R., Muehlenbachs, K. Thermal cracking of Athabasca bitumen: influence of steam on reaction chemistry. *Energy Fuels*, 2000, **14**(3), 671–676. https://doi.org/10.1021/ef990223e
13. Gao, L., Liu, Y., Wen, L., Huang, W., Mu, X., Zong, B., Fan, H., Han, B. The effect of supercritical water on the hydroconversion of Tahe residue. *AIChE J.*, 2010, **56**(12), 3236–3242. https://doi.org/10.1002/aic.12227
14. Hosseinpour, M., Akizuki, M., Oshima, Y., Soltani, M. Influence of formic acid and iron oxide nanoparticles on active hydrogenation of PAHs by hot compressed water. Isotope tracing study. *Fuel*, 2019, **254**, 115675. https://doi.org/10.1016/j.fuel.2019.115675
15. Hosseinpour, M., Fatemi, S., Ahmadi, S. J., Oshima, Y., Morimoto, M., Akizuki, M. Isotope tracing study on hydrogen donating capability of supercritical water assisted by formic acid to upgrade heavy oil: computer simulation vs. experiment. *Fuel*, 2018, **225**, 161–173. https://doi.org/10.1016/j.fuel.2018.03.098
16. Al-Muntaser, A. A., Varfolomeev, M. A., Suwaid, M. A., Saleh, M. M., Djimasbe, R., Yuan, C., Zairov, R. R., Ancheyta, J. Effect of decalin as hydrogen-donor for in-situ upgrading of heavy crude oil in presence of nickel-based catalyst. *Fuel*, 2022, **313**, 122652. https://doi.org/10.1016/j.fuel.2021.122652
17. Liang, X., Zhao, Q., Dong, Y., Guo, L., Jin, Z., Liu, Q. Experimental investigation on supercritical water gasification of organic-rich shale with low maturity for syngas production. *Energy Fuels*, 2021, **35**(9), 7657–7665. https://doi.org/10.1021/acs.energyfuels.0c04140
18. Wang, Z., Deng, S., Gu, Q., Cui, X., Zhang, Y., Wang, H. Subcritical water extraction of Huadian oil shale under isothermal condition and pyrolysate analysis. *Energy Fuels*, 2014, **28**(4), 2305–2313. https://doi.org/10.1021/ef5000062
19. Xie, T., Zhao, Q., Dong, Y., Jin, H., Wang, Y., Guo, L. Experimental investigation on hydrocarbon generation of organic-rich shale with low maturity in sub- and supercritical water. *Geoenergy Sci. Eng.*, 2023, **223**, 211553. https://doi.org/10.1016/j.geoen.2023.211553
20. Xie, T., Zhao, Q., Jin, H., Wang, Y., Guo, L. Study on the influence of non-temperature factors on the migration path of organic carbon and evolution characteristics of pore permeability parameters of organic-rich shale under supercritical water in situ conversion. *Oil Shale*, 2024, **41**(3), 189–207. http://dx.doi.org/10.3176/oil.2024.3.03