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Experimental investigation on pyrolysis products and pore structure characteristics of organic-rich shale heated by supercritical carbon dioxide



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ABSTRACT

The efficient pyrolysis and conversion of organic matter in organic-rich shale, as well as the effective recovery of pyrolysis shale oil and gas, play a vital role in alleviating energy pressure. The state of carbon dioxide (CO_2) in the pyrolysis environment of shale reservoirs is the supercritical state. Its unique supercritical fluid properties not only effectively heat organic matter, displace pyrolysis products and change shale pore structure, but also achieve carbon storage to a certain extent. Shale samples were made into powder and three sizes of cores, and nitrogen (N_2) and supercritical carbon dioxide (ScCO₂) pyrolysis experiments were performed at different final pyrolysis temperatures. The properties and mineral characteristics of the pyrolysis products were studied based on gas chromatography analysis, Xray diffraction tests, and mass spectrometry analysis. Besides, the pore structure characteristics at different regions of cores before and after pyrolysis were analyzed using N₂ adsorption tests to clarify the impact of fracturing degree on the pyrolysis effect. The results indicate that the optimal pyrolysis temperature of Longkou shale is about 430 °C. Compared with N₂, the oil yield of ScCO₂ pyrolysis is higher. The pyrolysis oil obtained by ScCO₂ extraction has more intermediate fractions and higher relative molecular weight. The ScCO₂ can effectively improve the pore diameter of shale and its effect is better than that of N_2 . The micropores are produced in shale after pyrolysis, and the macropores only are generated in ScCO₂ pyrolysis environments with temperatures greater than 430 °C. The pore structure has different development characteristics at different pyrolysis temperatures, which are mainly affected by the pressure holding of volatile matter and products blocking. Compared to the surface of the core, the pore development effect inside the core is better. With the decrease in core size, the pore diameter, specific surface area, and pore volume of cores all increase after pyrolysis.

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1. Introduction

With the in-depth development of conventional oil reservoirs, their extraction process has entered the middle and late stages, and the difficulty is increasing (Qiu et al., 2012). Unconventional oil reservoirs have gradually become a focus of oil energy research. As a vital replacement or supplementary resource for conventional oil

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reservoirs, organic-rich shale reservoirs play an increasingly important role in global resource strategies (Liu et al., 2017; Zhao et al., 2018). Organic-rich shale is a sedimentary rock with high ash content, which is rich in combustible organic matter, and the main hydrocarbon-generating organic matter is kerogen (Han et al., 2014; Hu et al., 2014; Zhao et al., 2017). But kerogen is a solid and cannot be directly developed. Only after dry distillation (pyrolysis) can it be converted to shale oil and gas (Golubev, 2003; Pan et al., 2016). Therefore, efficient and environmentally friendly conversion of kerogen is a key issue in promoting the development of the organic-rich shale industry.

At present, organic-rich shale oil reservoirs are mainly

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developed through on-ground pyrolysis technology and in-situ conversion technology (Crawford and Killen, 2010; Wang et al., 2012). The on-ground pyrolysis technology is the process of crushing and transporting underground shale to the ground for heating development, which not only has low efficiency but also produces a large amount of residue to pollute the environment (He, 2004; Li et al., 2015; Nei et al., 2009). The underground in-situ conversion technology usually generates fractures underground through hydraulic fracturing. Then the kerogen is heated and transformed by different heating methods such as heat conduction and convection. Eventually, the transformed oil and gas are recovered to the surface (Kang et al., 2020a, 2020b). This technology not only improves production efficiency but also buries the produced residues and gases such as carbon dioxide (CO₂) underground, thereby protecting the environment and ensuring the integrity of the geological structure (Zhang et al., 2021). Therefore, in-situ conversion technology has become an inevitable option for the commercial and scale development of organic-rich shale in the future

The pyrolysis development of organic-rich shale by injecting CO₂ has received widespread attention (Allawzi et al., 2011). When the formation temperature is greater than 31.26 °C and the formation pressure is greater than 7.38 MPa, carbon dioxide presents a supercritical state, which can be easily achieved in organic-rich shale formations (Reverchon and De, 2006; Kurz et al., 2018). Supercritical carbon dioxide (ScCO₂) has the properties of supercritical fluids, such as low viscosity, low surface tension, high diffusion ability, and high solubility (Hawthorne et al., 2014; Wu et al., 2016; Alfarge et al., 2017). The ScCO₂ has the density of the liquid phase and the viscosity of the gas phase, which can be used as a displacement medium for in-situ shale oil extraction and can also solve the problem of CO₂ storage in some measure (Gamadi et al., 2014; Liu et al., 2019). In the past several years, different researchers have studied the effect of ScCO₂ on the pyrolysis of organic-rich shale. Injecting nitrogen (N₂) can also promote pyrolysis and it is also easy to obtain. Injecting N₂ has been widely studied in the field of in-situ pyrolysis shale, the N₂ pyrolysis experiment can provide the same temperature, pressure and heating time as CO₂ pyrolysis, so N₂ pyrolysis experiments are often used as a comparison (Han et al., 2015; Guo et al., 2022). Tang et al. (2019) investigated the activation energy of shale pyrolysis under CO2 and N2 conditions, which demonstrated that the reaction activity of long-chain organic compounds increased under the CO₂ condition. The lighter hydrocarbons were produced and the activation energy also decreased, CO₂ can promote the pyrolysis process. Xie et al. (2010) studied the properties of pyrolysis oil under CO₂ and N₂ conditions and found that shale oil produced by CO₂ pyrolysis had longer chain hydrocarbons than nitrogen. Mozaffari et al. (2021) conducted an infrared spectroscopy analysis of pyrolysis oil under CO₂ and N₂ conditions. The experiments found that the properties of pyrolysis oil are similar but CO₂ can promote the cleavage of hydroxyl groups and convert them into volatile substances, while the content of aliphatic compounds is higher. The process of extracting kerogen by ScCO₂ was simulated by Wu et al. (2016) using molecular dynamics methods and found that ScCO₂ can effectively dissolve the kerogen portion on the shale surface. Besides, the extraction of kerogen by ScCO₂ can be facilitated by the hydroxyl functional groups modified on the surface of shale. Zhao et al. (2022) conducted ScCO₂ and N₂ pyrolysis experiments on organic-rich shales in a controlled-pressure pyrolysis fluidized bed. The results showed that the shale oil and gas were released when the pressure difference between the original pores in which the kerogen resides exceeds the minimum principal stress of pores rupture. The extraction-assisted pyrolysis characteristics of ScCO₂ can timely extract shale oil (Bondar and Koel, 1998; Yu et al., 2021).

These results indicate that ScCO₂ can effectively facilitate the pyrolysis and extraction of organic-rich shale. However, many studies of the pyrolysis characteristics of ScCO₂ were mostly based on lower pressure conditions and organic pyrolysis, and relatively few studies focused on the characteristics of inorganic pyrolysis, especially on pore structure. On the one hand, the migration and retention of organic matter and products after pyrolysis can affect the pore structure, thereby affecting the production of shale oil and gases. On the other hand, ScCO₂ also can undergo chemical reactions with shale and influence the decomposition and formation of minerals to change the pore characteristics (Xie et al., 2010). In addition, shale was broken into small pieces after fracturing, and the pore structure characteristics after pyrolysis of different rock block sizes and locations vary greatly. Hence, it is meaningful to analyze the pore structure characteristics of organic-rich shale for clarifying the pyrolysis mechanism of ScCO₂.

In addition, due to high organic matter content and wide lateral range, organic-rich shale has become an important alternative reservoir for CO₂ storage. The pore structure characteristics of reservoirs are key factors affecting the effectiveness of carbon capture, utilization and storage (CCUS) (Shulakova et al., 2017; Liu et al., 2019). Ozotta et al. (2022) found that ScCO₂ can alter the mechanical properties and mineral composition of shale, promoting the expansion of fractures. Ao et al. (2017) indicated that prolonged contact between ScCO₂ and shale can lead to a decrease in shale strength and alter its mineral composition. Yin et al. (2017) studied the effects of ScCO₂ and subcritical CO₂ on the mechanical performance of organic-rich shale at 38 °C and found that they can significantly alter the fracture propagation process and mechanical characteristics of shale. However, these studies focus on shale exposure to the ScCO₂ environment, without considering the high-temperature and high-pressure (HTHP) environment and the impact of the ScCO₂ pyrolysis process on shale properties. Hence, it is urgent to research the pore structure characteristics of organicrich shale before and after ScCO₂ pyrolysis, which also can explain the displacement mechanism of oil and gas.

In this study, organic-rich shale samples were made into shale powders and different sizes of cores, and experiments by ScCO₂ and N₂ pyrolysis of organic-rich shale were performed at five final temperatures using a HTHP in-situ pyrolysis experimental device. The influences of pyrolysis temperature and heating gases on the organic-rich shale pyrolysis process were studied, and the pyrolysis mechanism of organic-rich shale and the production characteristics of shale oil were illuminated. Based on gas chromatography analysis, X-ray diffraction (XRD) analysis, mass spectrometry analysis, and N₂ adsorption tests, the properties and mineral characteristics of the pyrolysis products were analyzed, and the pore structure characteristics in different regions of different sizes cores after pyrolysis were studied. This study provides theoretical guidance for the implementation and application of ScCO₂ in in-situ pyrolysis of organic-rich shale reservoirs, and also provides theoretical support for the implementation of the CCUS process in organic-rich shale reservoirs.

2. Experimental

2.1. Experimental materials

The organic-rich shale samples were drilled from the Longkou area of Shandong, China, and were made into shale cores and shale powders. The shale powders were mainly used to test the basic properties of shale and to study its pyrolysis product composition, pyrolysis oil and gas properties, and mineral changes after pyrolysis. This is because the pyrolysis degree of powder is more complete and the oil yield is higher, which can better reflect the

pyrolysis characteristics of organic-rich shale. Shale cores were mainly used to study the changes in pore structure, which can better clarify the actual pyrolysis situation of the reservoir after fracturing. Two shale powder samples (LK1 and LK2) were evaluated for their basic properties, including proximate analysis, elemental analysis, and oil content analysis. The analysis results are displayed in Table 1. The ash content of Longkou shale accounts for about 50%, and the volatile content is relatively high, indicating the content of organic matter is rich. The oil content of Longkou shale is higher than 19.0%, with high oil content and organic carbon content, indicating a relatively large proportion of organic matter and high development potential. In addition, the kerogen of organicrich shale was extracted and analyzed for its elemental composition, with C, H, and O accounting for 68.63%, 8.66%, and 18.38%, respectively. Further, the atomic ratios of O/C and H/C were calculated (Fig. 1) and the results showed that the type of shale kerogen is type II (Hutton et al., 1994).

The block-shaped oil shale samples were cut into shale cores for studying the effects of heating gas and temperature on pore structure, in which the diameter of these cores is 25 mm and the length is 40 mm (Φ 25 mm × 40 mm). Besides, the small core (Φ 20 mm × 30 mm) and large cores (Φ 30 mm × 50 mm) also were made and used to study the effect of core size. In addition, the permeability of the core parallel to the bedding direction is much higher than that perpendicular to the bedding direction. The parallel direction is usually the main flow channel for heat injection fluids. Therefore, the cores parallel to the bedding direction were selected for all experiments.

2.2. Experimental devices and steps

The flowchart of experimental devices for organic-rich shale pyrolysis under ScCO₂ is displaced in Fig. 2. The experimental devices mainly include a pyrolysis reactor, a temperature and pressure control collection system, and a product collection system. The pyrolysis reactor is a self-designed high-temperature and highpressure reactor (TCWCF-1), which can withstand maximum temperatures and pressures of 600 °C and 35 MPa, respectively, with measurement accuracy of 0.1 °C and 0.01 MPa. The pyrolysis reactor can achieve the in-situ pyrolysis conditions of ScCO₂. The ice water bath device is used to cool and collect liquid products, and two conical bottles can better collect the cooled liquid. In addition, before the experiment, the injection gas pressure needs to be determined based on the ideal gas state equation and the volume of the reactor chamber. The injected gas expands and pressurizes in the reaction system as the temperature increases, ultimately reaching a supercritical state. The injection pressure of ScCO₂ and N₂ is the same. The detailed experimental procedures are as follows.

- (1) The sample cup containing the shale samples (cores or 30 g powders) was placed on the holder of the reactor chamber.
- (2) The lid of the reactor chamber was covered, the fastening bolts were tightened, and then all valves were closed.
- (3) The pressure of the reactor chamber was vacuumed to -0.1 MPa using a vacuum pump, after this the vacuum

Table	1			
Basic	properties	of	Longkou	shales

T-1-1- 4



Fig. 1. The classification diagram of kerogen type.

pump was shut down to observe the pressure change for checking the airtightness of the device.

- (4) The gas cylinder of CO₂ or N₂ was connected to the reactor, and a pressure-reducing valve was used to adjust the inlet pressure of the pyrolysis reactor to the experimental pressure.
- (5) The computer was connected to the reactor by a sensor for collecting pressure and temperature data.
- (6) The reactor started heating to the setting temperature and remained at a constant temperature for 2 h.
- (7) After the constant-temperature pyrolysis was completed, the outlet valve of the reactor was slowly opened to release and collect oil and gas products. The pyrolysis oil was cooled and lodged at the bottom of the conical flasks, and the pyrolysis gas was collected in the gas collection bag.
- (8) After collection, the reactor was quickly cooled down to below 100 °C. Then, the reactor lid was removed, and the sample was taken out, weighed, and stored.
- (9) The 2–5 g semi-cokes at the bottom of the sampling cup were collected and ground to 400 mesh for the different tests. The oil was weighed and placed in the sample bottle in the refrigerator to prevent evaporation.
- (10) The pyrolysis reactor and pipeline were cleaned and dried.

The pyrolysis oil obtained from the pyrolysis experiment was analyzed by a gas chromatography-mass spectrometer (GC-MS). The pyrolysis gas was evaluated using gas chromatography analysis. The shale samples before and after pyrolysis were quantitatively mineral characterized using an X-ray diffractometer. In addition, 3-5 g of powders were scraped from the surface and center of the core sample (the core was cut). According to test requirements, the powder was broken and sieved to 20-30 mesh for N₂ adsorption experiments. The ASAP2460 full-automatic fast specific surface area and microporous physical adsorption analyzer was used for low-temperature N₂ adsorption and desorption experiments. The

Sample	Proximate analysis, wt%			Elemental analysis, wt%			Oil content analysis, wt%					
	Water	Ash	Volatile matter	Fixed carbon	N	С	Н	S	Shale oil	Water	Residue	Gas
LK 1	0.36	50.88	44.16	4.60	0.87	36.84	5.90	1.14	19.7	3.5	67.5	9.3
LK 2	0.35	51.21	43.97	4.47	0.71	36.65	5.81	1.06	19.0	3.2	68.2	9.6



Fig. 2. The schematic chart of experimental devices for pyrolysis.



Fig. 3. The TG and DTG curves of samples.

experimental samples were placed in a clean sample tube and first dried under vacuum at 180 °C for 3 h. Degassing was conducted under a N₂ atmosphere to reduce the impact of impurities on the test. Subsequently, N₂ adsorption and desorption tests were performed in liquid nitrogen at 77.30 K. The data with relative pressure ranging from 0.10 to 0.99 were used for Brunauer Emmett Teller (BET) analysis. The pore diameter distributions were calculated using the desorption branch of the isotherm based on the Barrett Joyner Halenda (BJH) model. The specific surface area and cumulative pore volume of the samples also were calculated using the BJH model. The residue was crushed and then cleaned in dichloromethane for 12 h, and the proportion of thermal bitumen

Table 2
Experimental scheme of pyrolysis experiments.

could be obtained by determining the mass of residue before and after pyrolysis. In addition, based on the thermogravimetric (TG) analysis results of Longkou organic-rich shale (Fig. 3), the shale shows a significant weight loss in the temperature range of 380-490 °C, indicating that this temperature range is the main pyrolysis reaction period of kerogen. Therefore, the temperature range of 380-490 °C was selected for pyrolysis experiments. In addition, when the temperature is around 700 °C, the main reason for weight loss is the decomposition of rock minerals rather than the pyrolysis of organic matter (Meng et al., 2023). The experimental scheme can be seen in Table 2.

3. Results and discussion

3.1. Analysis of organic-rich shale pyrolysis products

3.1.1. Compositions of pyrolysis products

Pyrolysis experiments of organic-rich shale powders were conducted at different final temperatures under ScCO₂ and N₂ conditions. The relationship between shale oil yield and semi-cokes yield with temperature is displaced in Fig. 4. The results demonstrate that the pyrolysis effect under ScCO₂ conditions is significantly better than that under N₂ conditions, resulting in less semicokes and more complete pyrolysis. Compared with N₂, the unique extraction effect of ScCO₂ can effectively promote the recovery of shale oil. The solvation effect and some surface properties of CO₂ can also effectively recover shale oil with better quality. In addition, the study (de Lara et al., 2012) also shows that compared to N₂, ScCO₂ has a stronger interaction with aromatic molecules and can also promote the recovery of shale oil.

The increase in oil yield by ScCO₂ pyrolysis is significant when the temperature is below 430 °C. As the temperature increases, the

Experimental No.	Gas type	Final temperature, °C	Core size (diameter \times length), mm \times mm
1	ScCO ₂	430	$\begin{array}{c} 25 \times 40 \\ 25 \times 40 \end{array}$
2	N ₂	430	
3	ScCO ₂	380	$\begin{array}{l} 25 \times 40 \\ 25 \times 40 \\ 25 \times 40 \\ 25 \times 40 \\ 25 \times 40 \end{array}$
4	ScCO ₂	400	
5	ScCO ₂	460	
6	ScCO ₂	490	
7	ScCO ₂	430	$\begin{array}{c} 20\times 30\\ 30\times 50 \end{array}$
8	ScCO ₂	430	



Fig. 4. The contents of pyrolysis products at different gases and temperatures: (a) Shale oil; (b) Semi-cokes.



Fig. 5. Contents of pyrolysis products of different sizes of cores.

irregular thermal movement of CO₂ molecules intensifies, which can effectively penetrate the nanoscale micropores of organic-rich shale. At the same time, the pyrolysis reaction of kerogen advances inward, reducing the temperature and pressure difference between inside and outside, improving the pyrolysis efficiency, and promoting the information of pyrolysis oil. Besides, the fluidity of N₂ contributes to the carrying and production of oil and gas, but it is not significant in heat conduction, resulting in a consistently lower oil production rate under N₂ conditions than under ScCO₂ conditions.

In the range of 430 to 460 °C, the shale oil yield of $ScCO_2$ pyrolysis is relatively high, but the shale oil and gas carried by $ScCO_2$ cannot be timely displaced and recovered. Instead, the semi-cokes and gas were produced from shale oil through coking reactions during the constant temperature process, resulting in rapid consumption of pyrolysis shale oil after the peak. Besides, due to the high extraction degree of shale oil in the initial stage, the secondary cracking loss of pyrolysis oil is also higher. However, the diffusion and extraction ability of N₂ is weaker than that of $ScCO_2$, so its pyrolysis process is slightly delayed. When the temperature range

is 430-460 °C, the organic-rich shale still can continuously absorb heat to promote pyrolysis reactions. The pressure of the pyrolysis gas also gradually increases with the cracking of kerogen and the decomposition of shale oil. Therefore, the oil yield reaches its peak at this temperature. In this temperature range, the degree of weight loss of organic-rich shale remains almost unchanged (Fig. 3), meaning that the organic matter has almost completely reacted within this temperature range, and the oil yield is mainly affected by the degree of secondary cracking. Under N₂ conditions, the shale oil and gas escape slowly and continue to crack inside the shale. Therefore, secondary cracking had been very severe before pyrolvsis oil and gas were recovered, and the pyrolysis oil yield rapidly decreased after reaching the peak at 460 °C. In the meantime, a lot of oil and gas that diffuses into the chamber space of the reactor also decomposes, resulting in lower shale oil yield than under ScCO₂ conditions at the same temperature. Therefore, when the other pyrolysis conditions are the same, supercritical carbon dioxide can increase the peak of oil yield and effectively reduce the temperature required to reach the peak, making it a more efficient heating gas medium.

The pyrolysis products of different sizes of cores at 430 °C are shown in Fig. 5, and 430 °C is a relatively sufficient temperature for the pyrolysis of kerogen. Different sizes of cores can reflect the pyrolysis characteristics of reservoir rock blocks after fracturing, as well as the pyrolysis differences of shale blocks under different gas encapsulation conditions. The data demonstrate that a smaller volume is more beneficial to the full pyrolysis of the core and increases the yield of pyrolysis oil and gas. On the one hand, gas more easily enters the interior of small cores and heats up, thereby fully pyrolyzing kerogen. On the other hand, pyrolysis oil and gas generated inside the core are easier to discharge and less likely to block pores. Therefore, the fracturing of organic-rich shale reservoirs can not only improve the gas injection capacity but also effectively promote the pyrolysis of shale. The smaller the size of shale fragment produced by fracturing, the more beneficial to the pyrolysis of organic matter and the increase in pyrolysis oil and gas yield. However, the size of the rock produced by fracturing is uncertain, so the core sizes are widely distributed under actual geological conditions. During pyrolysis, the size distribution range of the overall organic-rich shale reservoir should be fully considered, and the pyrolysis time should be appropriately adjusted to improve oil and gas yield.

3.1.2. Property analysis of pyrolysis oil and gas

The properties of pyrolysis oil and gas collected at 430 °C were analyzed to study the influence of ScCO₂ and N₂ in the pyrolysis process. The GC-MS analysis results of pyrolysis oil under two gas conditions are shown in Fig. 6(a). The components of pyrolysis oil mainly include alkanes, olefins, aromatic hydrocarbons, and heteroatomic compounds. Compared with N₂ conditions, the spectrum under ScCO₂ conditions is closer to the right, indicating that the pyrolysis oil obtained by ScCO₂ extraction has more intermediate fractions and higher relative molecular weight. Among them, the intermediate fractions can regenerate a large amount of light oil through a reforming reaction, which has a high utilization value. On the one hand, due to the solvation effect of ScCO₂, pyrolysis oil is easily dissolved in ScCO₂ of the same polarity. The dissolution of pyrolysis oil makes the heat conduction between the heat-carrying fluid and organic-rich shale more uniform, and also reduces gas secondary cracking. On the other hand, the ScCO₂ has a strong extraction capacity on long-chain alkanes, causing a portion of short-chain hydrocarbons to remain in the semi-cokes. The olefins produced under both gas pyrolysis conditions are mainly small molecule olefins, while the olefin vibration peak in the ScCO₂ pyrolysis oil chromatogram is slightly weak. The result indicates that ScCO₂ has an inhibitory effect on the cracking of polycyclic aromatic hydrocarbons, resulting in a lower olefin content in the shale oil. The carbon number distribution in Fig. 6(b) was obtained by GC-MS analysis. The data indicates that ScCO₂ can timely extract alkanes and aromatic hydrocarbons. The components of the pyrolysis oil change due to the extraction process, with more intermediate and heavy components above C_{15} retained in the shale oil.

The gas chromatographic analysis results of pyrolysis gases under two gas conditions are shown in Fig. 7, and the gas component results of different pyrolysis gases (see Fig. 8) were statistically analyzed based on experimental data. The gas-phase products released from the pyrolysis of organic-rich shale are mainly alkanes such as methane, ethane, and propane, followed by olefins and their isomers such as propylene and ethylene. In addition, small amounts of carbon monoxide (CO), CO₂ and hydrogen (H₂) are released. The CO of pyrolysis gas is primarily generated from the cleavage of carboxyl and hydroxyl groups in oxygen-containing functional groups, with a portion reacting with residual O₂ to produce CO₂. Besides, the ScCO₂ undergoes a gasification reaction with residual carbon in pyrolysis semi-cokes to produce CO, resulting in a higher CO content (Tiwari and Deo, 2012). The CO_2 mainly comes from carboxyl, carboxylate, and methoxy groups, and a small amount of CO_2 is also generated by the combustion reaction between kerogen and unexhausted air. The main source of H_2 is the cleavage and recombination of C–H and H–H bonds. The high content of small molecular hydrocarbons and H_2 in the pyrolysis gas under N₂ conditions further indicates that the organic-rich shale undergoes strong secondary cracking. All in all, the diffusion, extraction and other functions of ScCO₂ can promote mass transfer between kerogen and the outside world, dissolve some organic matter, accelerate gas release, and reduce the degree of secondary cracking.

3.1.3. Analysis of mineral properties after pyrolysis

Compared to N₂, carbon dioxide can undergo chemical reactions with some mineral materials, while the organic matter of organicrich shale mainly exists in the mineral skeleton and primary pores. The composition and content of minerals have a strong impact on the pyrolysis process of organic-rich shale. For this purpose, XRD experiments were conducted on the pyrolysis semi-coke obtained from the initial organic-rich shale sample and different pyrolysis environments, and the experimental data is performed in Fig. 9. Compared with the initial sample, minerals such as guartz (26.66 and 36.02 cm⁻¹), calcite (29.48 and 31.68 cm⁻¹), pyrite (27.68, 40.05, and 56.22 cm⁻¹), and analcite (26.48 cm⁻¹) in the pyrolysis semi-coke all decrease. Among them, the characteristic peaks of quartz and calcite have significantly decreased, indicating that both silicate and carbonate minerals have undergone preliminary decomposition. The decomposition degree of calcite under ScCO₂ conditions is lower than that under N₂ conditions at the same temperature, indicating that ScCO₂ can delay the decomposition of carbonate minerals compared to N2 conditions at 430 °C (Xie et al., 2010). During the pyrolysis process, pyrite is mainly decomposed into iron sulfide and elemental sulfur substances. The presence of elemental sulfur substance can promote the depolymerization and cracking reactions of kerogen macromolecules, while also inhibiting aromatization reactions (Gai et al., 2014). The decomposition degree of pyrite by ScCO₂ pyrolysis at 430 °C is higher than that by N₂ pyrolysis, indicating that ScCO₂ can promote the release of sulfur elemental substances, thereby accelerating the formation rate of free radicals in kerogen and improving the yield of pyrolysis oil.





Fig. 6. Properties of pyrolysis oil under different gas conditions. (a) GC-MS results; (b) Carbon number distribution.



Fig. 7. Chromatograms of pyrolysis gas under different gas conditions. (a) ScCO₂ condition; (b) N₂ condition.



Fig. 8. Gas component distribution of pyrolysis gas under different gas conditions.

3.2. Analysis of pore structure characteristics before and after pyrolysis

3.2.1. The effect of different gas pyrolysis on the pore structure of organic-rich shale

The adsorption and desorption isotherms by different gas pyrolysis are displaced in Fig. 10. On the basis of the isotherm classification standard of the International Union of Pure and Applied Chemistry (IUPAC), the adsorption isotherm of the initial sample appears to concave at the initial stage, belonging to type III isotherm (Sing, 1985). After the action of ScCO₂, the adsorption isotherm of the core center shows an inverse "S" shape, belonging to type II isotherm. The adsorption curve under N₂ conditions and the three curves of the core surface also belong to type III isotherms. The results demonstrate that the adsorption capacity of organic-rich shale was significantly increased after ScCO₂ pyrolysis. Compared to N₂, the ScCO₂ can significantly influence the pore structure distribution of organic-rich shale. For the adsorption curve of the core center by ScCO₂ pyrolysis, a hysteresis loop is



Fig. 9. XRD spectra of organic-rich shale samples and pyrolysis semi-cokes.

formed by the adsorption and desorption isotherms. The formation of a hysteresis loop is caused by the phenomenon of capillary condensation. During adsorption, the capillary condensation starts from the liquid surface of the annular adsorption membrane on the pore wall, while desorption starts from the spherical meniscus liquid surface at the pore opening, resulting in non-overlapping curves. The hysteresis loop is relevant to the shape and size of the hole. According to IUPAC's classification of hysteresis loops, the hysteresis loop of this curve is H3 type, indicating that the narrow pores were formed in the core.

The two curves under the initial sample and N₂ pyrolysis conditions almost overlap, without producing a significant hysteresis loop. It could be determined that the pore type of organic-rich shale was mostly a closed pore structure such as cylindrical pores closed at one end. The evolution mechanism of pore structure in organicrich shale by ScCO₂ pyrolysis is a comprehensive result of factors such as diffusion heat transfer of CO₂, thermal expansion of shale, and kerogen transformation. The porosity and adsorption capacity inside the core are higher than those outside the core. This is due to the thermal stress induced by the shale matrix and the pore



Fig. 10. N₂ adsorption/desorption isotherms of cores by ScCO₂ and N₂ pyrolysis. (a) Core center; (b) Core surface.

pressure caused by volatiles, which leads to the expansion of internal pores (Zhu et al., 2018). At the same time, the bedding gaps continue to expand and the cores expand along the vertical bedding direction. The external part of the core is compressed from the inside out, which leads to a lower development degree of pore space. Besides, asphalt and shale oil also adhere to the surface of the core during outward migration. Therefore, after the final thermal fracture of organic-rich shale was undergone, the development degree of the internal pores was higher than that of external pores, and the pore size distribution was more uniform.

IUPAC divides the types of porous materials into three types: macropores (> 50 nm), mesopores (2–50 nm), and micropores (< 2 nm). The pore size distribution of the semi-cokes inside and outside the core under different heating gases was obtained using the BJH calculation model and method. The data is shown in Fig. 11, where dV/dD is the pore size distribution in 10^{-4} cm³/(g nm), V is the pore volume in cm³/g, and *D* is the pore diameter in nm. It could be seen that the core pores before pyrolysis were principally mesopores, micropores appeared in cores after pyrolysis under both two gas conditions, and macropores appeared inside the core after ScCO₂ pyrolysis. The pore diameter of semi-cokes after ScCO₂

pyrolysis is significantly larger than that after N₂ pyrolysis. Besides, the pore diameter of the core center area is obviously larger than the surface of the core. The pore distribution at the center of the core after pyrolysis of the two gases has a significant difference, while the difference at the core surface is not significant. The curve values of the core center under ScCO₂ conditions are significantly higher than the other five curves. On the one hand, the diffusion of ScCO₂ internally promotes heat transfer inside and outside the core, and sufficient heat exchange can also occur inside the core. The thermal stress induced within the shale matrix and the increase in pore pressure caused by volatile substances lead to pore expansion. The outer part of the shale core is compressed from the inside out, resulting in a lower development degree of pore space. In addition, asphalt and shale oil also adhere to the surface of the rock core during outward migration. Therefore, when the final oil shale undergoes thermal fracture, the degree of pore development inside is higher than that outside, and the pore distribution is more uniform. On the other hand, some volatile substances generated inside the core are dissolved into the ScCO₂ phase and continuously dispersed to the outside, resulting in a shorter retention time for asphalt and oil inside. The pyrolysis of organic matter and the flow of pyrolysis



Fig. 11. Pore diameter distribution of cores under different heating gases. (a) Core center; (b) Core surface.

products increase the pore volume of the center area of the core. The pores of the core surface are mainly affected by the direct heat transfer of gases, so the pore size distribution is not significantly different under the two gases.

Besides, the specific surface area and pore volume data of different experimental schemes were statistically analyzed, as shown in Fig. 12. The experimental results are similar to the pore diameter distribution results. The specific surface area and pore volume of semi-cokes by ScCO₂ pyrolysis are higher than those by N_2 pyrolysis, and these two parameters at the surface of the core by ScCO₂ pyrolysis can even be greater than those at the center of the core by N₂ pyrolysis. On the one hand, the strong diffusion of ScCO₂ increases the temperature inside the core and promotes the expansion of internal pores, resulting in a larger volume of internal pores and superior to N₂ conditions. The pores at the surface of the core come into direct contact with the gas environment, which is influenced by the heat and mass transfer of gases, without significant pore thermal expansion. However, the product retention and internal compression are obvious, so the degree of pore development on the surface is poor. On the other hand, the delayed discharge of volatile substances such as water and organic matter can lead to coking inside, part of the pore space is occupied, which also causes the reduction of pore volume. This is consistent with the product composition results of different heating gases. Under N₂ conditions, the proportion of pyrolysis asphalt and semi-cokes is higher, and the pyrolysis of organic matter is inadequate. In the early stage of pyrolysis, the high pressure caused by internal volatiles promotes pore expansion. However, the internal pore connectivity is poor because the temperature gradient is large. The aggregation of shale oil within the core is more prone to secondary cracking reactions, this also leads to smaller pore volume.

3.2.2. The effect of pyrolysis temperature on the pore structure of organic-rich shale

The N₂ adsorption/desorption isotherms of semi-cokes at five pyrolysis final temperatures are displaced in Fig. 13. The results demonstrate that the isotherms curves of semi-cokes under different pyrolysis final temperatures have similar characteristics. When the temperature is above 430 °C, the curve belongs to the inverse "S" II isotherms, indicating that the pore distribution of pyrolysis semi-cokes is continuous and complex. As shown in Fig. 13(a), with the increase in pyrolysis temperature, the hysteresis loop first increases and then decreases, and is most obvious at 430 °C. This indicates that the capillary condensation occurs within

the core at this time, which first increases and then weakens with the increase in temperature. The adsorption isotherms of pyrolysis semi-cokes at 380 and 400 °C have no obvious inflection points during the low-pressure stage, indicating a type III isotherm. Besides, the adsorption isotherms of pyrolysis semi-cokes at 430, 460, and 490 °C are type II isotherms. The adsorption capacity of the pyrolysis semi-cokes at 380 °C is weaker than that of the initial sample, meaning a decrease in adsorption capacity due to pore blockage at this temperature. For the pyrolysis semi-cokes at the surface of the core, there is also a phenomenon of low-temperature pore plugging and an increase in high-temperature adsorption capacity. The curve also shows significant changes at 430 °C, and the adsorption capacity has a significant increase.

The pore diameter distribution results of semi-cokes at five different pyrolysis temperatures are displaced in Fig. 14. Based on this result, the specific surface area and pore volume data at the center and surface of the core were calculated, as shown in Fig. 15. The initial pores of organic-rich shale are mainly mesopores, and after pyrolysis, micropores and macropores begin to appear. After pyrolysis, the pore diameters at the center of cores are generally larger than those at the surface of cores. The pore diameter of the core center has a wider distribution range, while the pores at the surface of the core are mainly concentrated in micropores and mesopores of 1.5–3.5 nm. Apart from the compression caused by core expansion, it also can be attributed to the condensation and attachment of pyrolysis asphalt and shale oil to the surface of the core during their migration along pore spaces and bedding fractures, resulting in less distribution of macropores and relatively large mesopores at the surface of the core.

At 380 °C, the difference in specific surface area and pore volume between the center and surface of the core is relatively small, while the surface of the core is slightly higher than the center due to thermal expansion. This is due to the low development degree of internal pore and limited pore space in organic-rich shale itself. Apart from the initial pyrolysis of kerogen at this temperature, the seepage conditions of shale cores are poor, so the diffusion of ScCO₂ and the migration resistance of asphalt are relatively high. The hot asphalt produced by pyrolysis in the organic-rich core gradually blocks the micropores generated by water evaporation at low temperatures in a liquid or solid form. Afterward, as the temperature increases, the proportion of micropores by water evaporation increases. The temperature also causes the rock to expand, and eventually the pore space continues to increase. Besides, after the migration of oil and gas, the pore diameter begins to significantly



Fig. 12. Pore structure results of cores under different heating gases. (a) Specific surface area; (b) Pore volume.



Fig. 13. N₂ adsorption/desorption isotherms of cores at different pyrolysis temperatures. (a) Core center; (b) Core surface.



Fig. 14. Pore diameter distribution of cores at different pyrolysis temperatures. (a) Core center; (b) Core surface.



Fig. 15. Pore structure results of cores at different final pyrolysis temperatures. (a) Specific surface area; (b) Pore volume.

increase, which is conducive to the diffusion of ScCO₂, thereby promoting further pyrolysis of organic matter.

As the temperature increases, the pore volume and specific surface area change significantly, especially in the core center. During the heating process from 380 to 430 °C, microcracks are generated and pore connectivity is enhanced due to thermal expansion in organic-rich shales, resulting in an increase in pore volume. Besides, the retained hot asphalt decomposes with the increase in temperature, and the generation of shale oil and gas clears the previously blocked pores. Therefore, the pore structure gradually becomes complex, as well as the specific surface area of semi-cokes also increases. When the temperature is 430 °C, the pore volume value reaches its peak, indicating that at this temperature, the shale oil and gas generated by pyrolysis have broken through the fracture stress of its existing pores and are released into the reactor. At this temperature, the Longkou organic-rich shale was in the oil generation window, and the pyrolysis oil and pyrolysis asphalt generated inside the core were partially discharged and connected to local pores, causing rapid development of pores. When the temperature is between 430 and 460 °C, the processes of decomposition of residual asphalt, secondary cracking and coking of shale oil, and fracture of rock skeleton coexist inside the shale core. The decrease in pore volume indicates that the shale oil produced in the previous stage has coking, and the residual asphalt has gradually carbonized. The coke first adheres to the mesopores and macropores, which causes a decrease in pore volume, but the impact on micropores is slightly small. In addition, shale oil and asphalt gradually adhered to the pore surface during their outward migration. During the pyrolysis process at temperatures ranging from 460 to 490 °C, the coking reaction gradually weakened with the consumption of shale oil, and the expansion process of pores was mainly affected by temperature rise. At this point, the pore volume raised again, the reason was that under the action of thermal stress, hard mineral particles cracked along the edges and connected the pores. Besides, the pressure of shale oil and gas generated by the ScCO₂ pyrolysis could be greater than the core fracture pressure, causing the organic-rich shale to form layered fractures along the bedding direction. During this process, effects such as collapse, merging, and structural damage of adjacent pores also may occur. Some micropores connected and transformed into transition pores, causing the pore volume to continue to expand (Liu et al., 2022).

The variation law of specific surface area and pore volume in Fig. 15 is not highly consistent. When the pore volume of the pyrolysis semi-cokes decreases, the specific surface area may increase slightly. The reason is that the specific surface area characterizes the properties of micropores, which are mainly influenced by the number of micropores. The pore volume characterizes the total internal volume, which is mainly influenced by macropores and mesopores.

3.2.3. Pore structure characteristics of different sizes of cores and different core regions after pyrolysis

When the organic-rich shale was pyrolyzed and developed insitu by using ScCO₂, the shale is usually broken into rock fragments of varying sizes after fracturing. Studying the pore structure characteristics of organic-rich shale with different sizes after pyrolysis is important to clarify the pyrolysis mechanism and the effect of ScCO₂. As shown in Fig. 16, the adsorption isotherms of both central and surface semi-cokes of the cores (Φ 30 mm × 50 mm) are all Type III isotherms. The adsorption isotherms of the other two sizes of cores are all inverse "S" shape, which belongs to type II isotherms, indicating the occurrence of capillary condensation phenomenon in these cores. Due to the difference in core size, their adsorption capacity has a significant difference, which is most evident between cores of ϕ 30 mm \times 50 mm and ϕ 25 mm \times 40 mm. In addition, the adsorption curves of different sizes of cores have not shown inflection points, indicating that the changes in core size have not changed their pore morphology. The pores are still dominated by cylindrical pores closed at one end. The less quantity adsorbed and small pore diameter of the large core are still due to the presence of a large amount of retained pyrolysis asphalt inside. With the diffusion and migration of ScCO₂, the internal temperature of the core began to rise, and at the same time, the evaporated crystalline water by heating and the shale oil and gas generated by kerogen pyrolysis began to escape. As the core size decreases, the temperature difference between the center and surface of the core decreases, resulting in more uniform heating and easier recovery of pyrolysis products. Therefore, small shale cores are less affected by pore expansion and thermal stress. The pore development degree is more uniform, which is more conducive to the diffusion and migration of ScCO₂. In addition, the difference in quantity adsorbed between the surface of different semi-cokes is small and is significantly smaller than the quantity adsorbed of the semi-coke center. The main reasons are the increase in internal pore pressure and the retention of pyrolysis products. Moreover, due to the maximum distance between the center and the surface, this phenomenon is more significant in the large core.

The pore diameter distribution of different-sized cores after pyrolysis is shown in Fig. 17. The pore diameter at the center of the cores after pyrolysis is still greater than that at the surface of the cores, which also can be explained by the previous analysis. The micropores and macropores also appear in all three types of cores after pyrolysis, and as the core size decreases, the proportion of micropores gradually increases. In addition, as the core size decreases, the numerical value of the pore size distribution curve generally increases, indicating that the number of pores with different sizes increases and the distribution is more uniform. However, the results also demonstrate that the proportion of macropores in the central area of large cores is relatively high, this is because products that cannot be discharged are blocked inside the core to form high pressure. The existence of resistance leads to the retention of volatile matter inside for a long time, exacerbating the expansion effect. The high internal pressure formed by volatile matter inside the core can open and connect adjacent pores, thereby increasing the pore volume. The pyrolysis of the small cores by ScCO₂ can promote the uniform development of pores inside and outside the core, improving pore connectivity. Therefore, injecting CO₂ for pyrolysis after fracturing can not only effectively improve the pyrolysis effect, but also promote the migration and recovery of pyrolysis oil and gas.

Fig. 18 shows the specific surface area and pore volume results of different sized cores after pyrolysis. These two parameters also decrease with the increase in core size, but the numerical changes are not significant. This is because the pyrolysis effect of small cores is better, generating more micropores, but large cores have a larger volume and more space for developing pores. Besides, the specific surface area and pore volume in the central region of the core are also obviously larger than those in the surface region of the core. With the increase in core volume, the difference between the two parameters becomes larger. The main reason is that the distance between the center and surface regions of the large core is the largest, and the temperature difference during pyrolysis is the highest, which is more significantly affected by pore pressure and product retention. The above results also indicate that the smaller the volume of rock blocks after fracturing, the more favorable it is for the pyrolysis development of organic-rich shales and the recovery of pyrolysis oil and gas.



Fig. 16. N₂ adsorption/desorption isotherms of different sized cores. (a) Core center; (b) Core surface.



Fig. 17. Pore size distribution of different sized cores after pyrolysis. (a) Core center; (b) Core surface.



Fig. 18. Pore structure results of different sized cores after pyrolysis. (a) Specific surface area; (b) Pore volume.

4. Conclusions

In the paper, pyrolysis experiments were conducted on organicrich shale powders and different sizes of cores using a hightemperature and high-pressure reactor under different gases and final temperatures. The characteristics of pyrolysis products, mineral composition, and pore structure changes were analyzed based on testing methods such as XRD analysis, gas chromatography analysis, and N₂ adsorption tests. The main conclusions are as follows.

- (1) There is an optimal pyrolysis temperature range for Longkou shale near 430 °C, and the pyrolysis effect of supercritical carbon dioxide (ScCO₂) is better than N₂, with higher shale oil yield and lower semi-cokes yield. The pyrolysis oil obtained by ScCO₂ pyrolysis has more intermediate fractions and higher relative molecular weight. The ScCO₂ has an inhibitory effect on the cracking of polycyclic aromatic hydrocarbons, thereby reducing the olefin content in the oil. Shale oil undergoes strong secondary cracking under N₂ pyrolysis, and more small molecule hydrocarbons and H₂ are produced.
- (2) The decomposition degree of calcite by $ScCO_2$ pyrolysis is lower than that by N₂ pyrolysis at the same temperature, and $ScCO_2$ can delay the decomposition of carbonate minerals. The $ScCO_2$ can promote the release of elemental sulfur, thereby accelerating the formation of free radicals in kerogen and increasing the yield of pyrolysis oil.
- (3) At 430 °C, the development degree of pore structure after ScCO₂ pyrolysis is higher than after N₂ pyrolysis, whether at the center or surface of the core. After pyrolysis, micropores are generated in cores. The macropores only are generated in ScCO₂ pyrolysis environments with temperatures greater than 430 °C. Besides, the development of pores at the center of the core is always better than that at the core surface.
- (4) The increase in ScCO₂ pyrolysis temperature leads to an increase in the specific surface area of shale cores, and the pore volume increases first, then decreases, and then increases. This reason is that shale oil can coking and block pores, but then microcracks expand under high temperatures, resulting in an increase in pore volume.
- (5) The smaller the core volume, the better the degree of pore development and more uniform pore size distribution after pyrolysis. The ScCO₂ pyrolysis can effectively improve pore connectivity and contribute to the flow of pyrolysis oil and gas.

CRediT authorship contribution statement

Bai-Shuo Liu: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Chuan-Jin Yao:** Writing – review & editing, Supervision, Formal analysis. **Jia-Long Qi:** Methodology, Investigation, Data curation, Conceptualization. **Ya-Qian Liu:** Writing – review & editing, Validation, Methodology. **Liang Xu:** Writing – review & editing, Supervision, Methodology. **Jing-Xuan Hou:** Writing – review & editing, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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