
This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Zhao, Shuai; Su, Jianzheng; Wu, Junwen; Xiaoshu, Lü

Release Mechanism of Volatile Products from Oil Shale Pressure-Controlled Pyrolysis Induced by Supercritical Carbon Dioxide

Published in:
ACS Omega

DOI:
[10.1021/acsomega.2c06693](https://doi.org/10.1021/acsomega.2c06693)

Published: 01/01/2022

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY-NC-ND

Please cite the original version:
Zhao, S., Su, J., Wu, J., & Xiaoshu, L. (2022). Release Mechanism of Volatile Products from Oil Shale Pressure-Controlled Pyrolysis Induced by Supercritical Carbon Dioxide. *ACS Omega*, 7(50), 47330-47340.
<https://doi.org/10.1021/acsomega.2c06693>

Release Mechanism of Volatile Products from Oil Shale Pressure-Controlled Pyrolysis Induced by Supercritical Carbon Dioxide

Shuai Zhao, Jianzheng Su, Junwen Wu,* and Lü Xiaoshu

Cite This: *ACS Omega* 2022, 7, 47330–47340

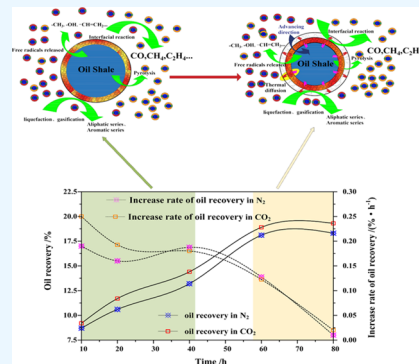
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The compactness of the oil shale reservoir and the complexity of the pore structure lead to the secondary reaction of kerogen in the process of hydrocarbon expulsion, which reduces the effective recovery of shale oil. In this paper, supercritical carbon dioxide was used as a heat carrier and a displacement medium. In a self-designed fluidized bed experimental system for pressure-controlled pyrolysis of oil shale, the experiments of oil shale pyrolysis under standard atmospheric pressure and 7.8–8.0 MPa pressure in nitrogen and carbon dioxide atmospheres were completed. The extraction efficiency of supercritical carbon dioxide at low temperature is obvious, but with the increase of temperature, the effect of extraction on pyrolysis is lower than that of temperature. Under a nitrogen atmosphere, the secondary reaction of shale oil is mainly secondary pyrolysis and aromatization. However, in a supercritical carbon dioxide atmosphere, the main reactions are secondary addition and aromatization. In addition, compared with that in the standard atmospheric pressure, it was found that the olefin synthesis reaction was obviously inhibited under a high-pressure nitrogen or supercritical carbon dioxide atmosphere.



1. INTRODUCTION

The oil shale resource is a condensate shale oil resource rich in immature organic matter, and it is also the most promising alternative resource of oil resource. After being heated, kerogen pyrolysis will release shale oil and shale gas.¹ The common pyrolysis methods of oil shale include ground retorting and an underground in situ pyrolysis process.^{2,3} Because the ground retorting process covers a large area, slag accumulates on the ground and dust and tail gas will also result in serious pollution to the environment, and all these factors limit its development. The in situ pyrolysis process of oil shale avoids the above defects. However, compared with the ground retorting process, in the in situ pyrolysis process of oil shale, the cracking, diffusion, and release of kerogen in pores, and the migration of oil and gas products in porous media are very complex, which also has an impact on oil and gas recovery.⁴

At present, the research direction of oil shale pyrolysis is mainly focused on the improvement of pyrolysis methods and processes to improve the efficiency of heat and mass transfer and effective oil recovery⁵ and to improve the quality of oil.⁶ Wang et al. used superheated steam to pyrolysis Fushun oil shale, used the 3D CT scanning technology to study the pore characteristics of pyrolysis residue, and calculated the permeability. The results show that the effective porosity of all parts along the bedding plane is greater than 19.41%, and the proportion of the ore bed with the permeability ranging from 1.8×10^{-17} to 3.0×10^{-17} m² is 63.51%.⁷ Mu et al. found that the addition of plastics (polypropylene and low-density polyethylene) can improve the yield of the light fraction, heavy

fraction, and total content of oil and reduce the content of aromatics and olefins in the oil. A small amount of 10–25% plastic is conducive to the formation of light components.⁸ In addition, some scholars have devoted themselves to the study of the pyrolysis mechanism of the complex physical–chemical coupling process, mostly focusing on the analysis of the first-order kinetic model.^{9,10} In a non-isothermal thermogravimetric thermal analyzer system, Bai et al. studied the effects of the particle size, heating rate, and sample mass on mass and heat transfer, as well as on the pyrolysis behavior and kinetic parameters. The results show that the second stage of oil shale pyrolysis can be simulated by the Avrami–Erofeev AE2 equation, the influence of the particle size on the release rate of products is the least, and the influence of the sample mass on the average activation energy is the least.¹¹ According to Foltin et al., kinetic parameters calculated by the Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose methods become more accurate at a higher conversion, when the reaction rate was lower. Isothermal kerogen pyrolysis approached an incomplete conversion limit that could be increased only by increasing the temperature. This type of behavior was predicted by the

Received: October 17, 2022

Accepted: December 1, 2022

Published: December 9, 2022



conversion dependence of the activation energy.¹² You et al. simplified the model of kerogen without considering the heat transfer and secondary reaction and predicted that the pyrolysis process of kerogen includes four processes: initial pyrolysis, aliphatic chain reaction, aromatization, and condensation.¹³ Kuang et al. studied the pyrolysis process of kerogen with Luhe oil shale as the sample and considered that the early pyrolysis of oil shale was controlled by the first-order reaction model and the later by the second-order reaction model.¹⁴

In conclusion, researchers pay more attention to the pyrolysis kinetics, heat and mass transfer performance of the pyrolysis process, and quantitative analysis of pyrolysis products. However, this cannot provide the key information that affects the product release during the pyrolysis of oil shale. Under different properties, the release process, release form, and influencing factors of oil shale pyrolysis products are less studied by researchers. The release process of condensate shale oil at high temperature is affected by many factors, especially pressure, temperature, and pyrolysis atmosphere. To explore the release characteristics and control mechanism of condensate shale oil, in situ pyrolysis is of great significance to improve the shale oil production efficiency and reduce production costs.

In the process of studying the automatic pyrolysis in situ conversion process (ATS) of oil shale, Guo et al. selected high-pressure nitrogen as the heat carrier gas to preheat oil shale. The results show that when the temperature at the end face of the sample (50 mm) reaches 300 °C, the ATS of oil shale is successfully triggered.¹⁵ Liu et al. studied the thermal expansion of the oil shale in situ pyrolysis process and found that after heating, the oil shale under a high-temperature and high-pressure nitrogen atmosphere, the estimated potential decreased by nearly 52%.¹⁶ Wang et al. found that the apparent viscosity of supercritical carbon dioxide (SC-CO₂) in shale organic pores was 4.76 $\mu\text{Pa}\cdot\text{s}$ when studying the transport mechanism of liquid through organic pores, greater than that of CH₄ (1.6 $\mu\text{Pa}\cdot\text{s}$) and C₈H₁₈ (2.6 $\mu\text{Pa}\cdot\text{s}$), but the viscosity is 13 times smaller than the volume viscosity, indicating that the SC-CO₂ in the shale organic pores has a rapid mass transfer effect.¹⁷ Wu et al. simulated the extraction of organic matter from oil shale by SC-CO₂, and the results showed that the solubility of SC-CO₂ effectively increased with the increase of pressure before the pressure reached the critical value (about 50 MPa), which can effectively dissolve the kerogen adsorbed on the shale surface.¹⁸ Shuai et al. studied the displacement mechanism of oil shale pyrolyzed by heat carrying SC-CO₂. The results showed that when the temperature was 350–400 °C and the injection rate of SC-CO₂ was 9 mL/s, the effective recovery of shale oil increased from 36 to 97.4% with the increase of temperature and pyrolysis time.¹

In this paper, a self-designed pressure-controlled fluidized bed for oil shale pyrolysis is used as the experimental device. Using supercritical carbon dioxide and high-pressure nitrogen as the pyrolysis atmosphere, the effects of standard atmospheric pressure and high-pressure conditions on the effective oil recovery and product composition of oil shale pyrolysis were studied. Combined with the pressure fluctuation characteristics of the reactor, the effective recovery factor and component content of shale oil, the pyrolysis and volatile product release mechanism of oil shale under different pyrolysis atmospheres were discussed, which can be used as

a guidance for optimizing the process parameters of oil shale in situ pyrolysis.

2. EXPERIMENTAL SAMPLES AND METHODS

2.1. Experimental Samples. The oil shale samples are brown and dark brown, which were obtained from Dachengzi mining area, Huadian City, Jilin Province. Before the experiment, the oil shale samples were broken into small pieces of 1.2–1.5 cm³. After mixing evenly, two samples were randomly selected and ground into powder. The samples with a 40–60 mesh were selected by screening. The samples were dried in an oven at 60 °C for 12 h, and then, the powder samples were subjected to proximate analysis, Fisher analysis, and element analysis. The results are shown in Tables 1–3.

Table 1. Industrial Analysis of the Huadian Oil Shale

attribute	proximate analysis			
samples	moisture wt %	ash wt %	volatiles wt %	fixed carbon wt %
HD1	4.23	52.61	31.32	11.84
HD2	3.98	53.26	30.24	12.52

Table 2. Fisher Analysis of the Huadian Oil Shale

attribute	Fisher analysis			
samples	oil wt %	water wt %	residue wt %	gas wt %
HD1	22.31	4.67	62.32	10.70
HD2	21.19	4.49	64.23	10.09

Table 3. Element Analysis of the Huadian Oil Shale

attribute	element analysis			
samples	H wt %	C wt %	N wt %	S wt %
HD1	4.37	30.96	0.67	2.191
HD2	4.02	29.26	0.63	2.112

The results of proximate analysis show that the free water content of the dried Huadian oil shale is low, only about 4%, and the average volatile content is about 40%. In addition, Fisher analysis shows that the oil content of the Huadian oil shale is about 21.75%, and the gas content is between 10 and 11%.

2.2. Experimental Methods. This experiment is carried out in a self-designed experimental device for pressure-controlled pyrolysis of oil shale with supercritical carbon dioxide. As shown in Figure 1, the whole experimental system consists of five modules: a gas supply module, a heating and boosting module, an oil and gas collection module, a data collection module, and a product analysis module. The gas supply module uses a cylinder with stable pressure to provide carbon dioxide. After passing through the pressure reducing valve and high-temperature and high-pressure valve, the carbon dioxide gas enters the heating and boosting module. The pressure is directly controlled by temperature. A pressure relief valve is installed at the outlet of the reactor to maintain the pressure of the reactor at 7.8–8.0 MPa.

The oil and gas collection module is implemented in the way of ice-water bath condensation. The pyrolysis product flows into the condenser tube through the high-temperature and high-pressure valve at the outlet of the reactor. The oil is enriched in the condensing tube, and then, it flows to the round-bottom flask for collection. The flow channel of gas products is the same as that of shale oil. It then flows from the

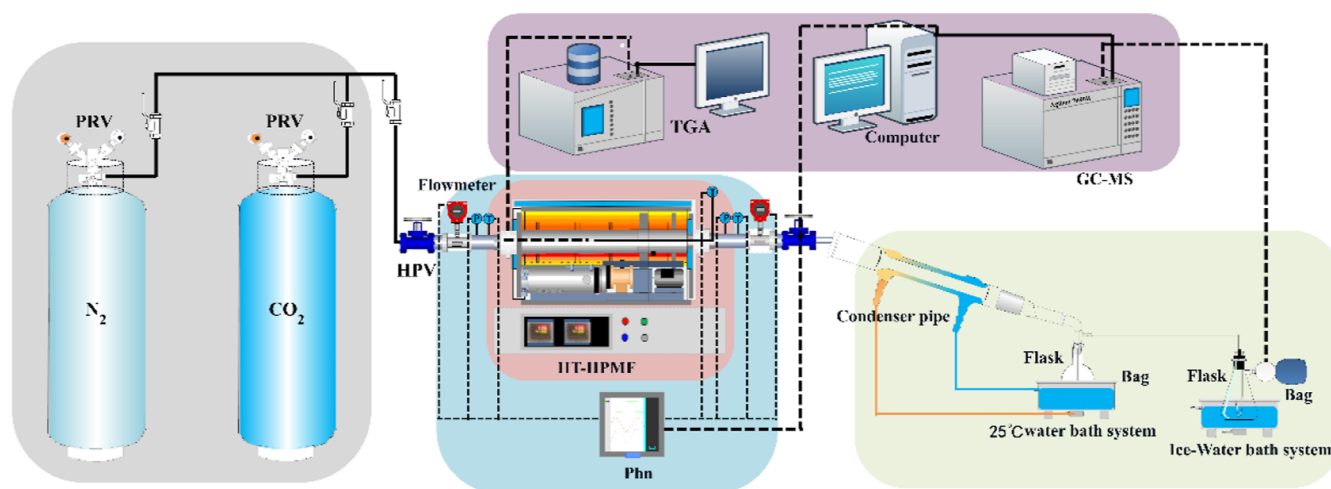


Figure 1. Experimental system for oil shale pressure-controlled pyrolysis.

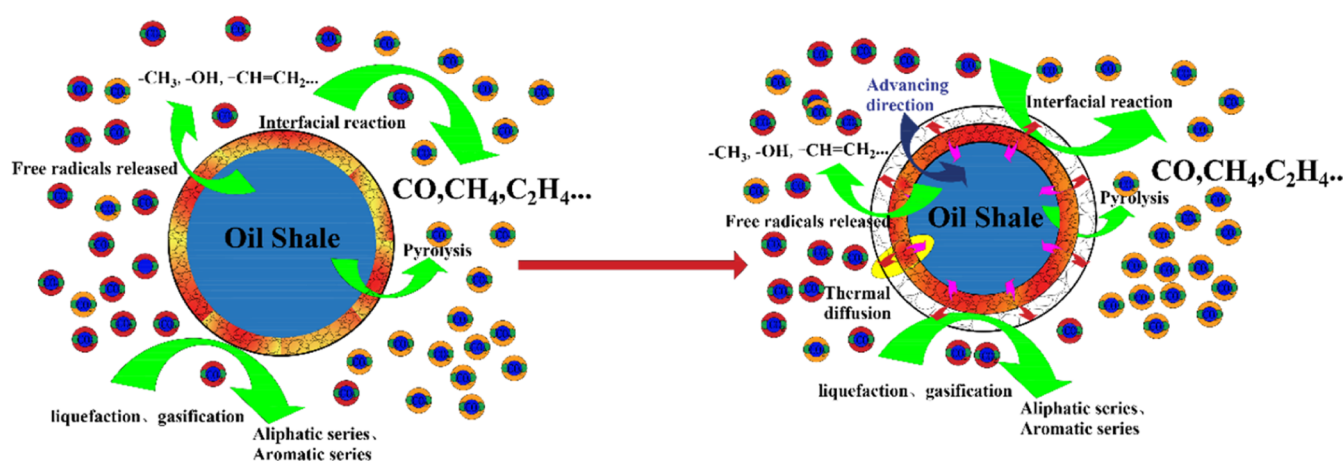


Figure 2. Schematic diagram of the interfacial reaction advancement during oil shale pyrolysis.

outlet at the upper end of the round-bottom flask into the gas sampling bag. The data collection module is mainly composed of a temperature sensor (0–500 °C), a pressure sensor (0–10 MPa), and a flow sensor (0–100 mL/s) set at the inlet and outlet of the reactor to collect the relevant data and display them in a paperless recorder. After the pyrolysis experiment, the effective recovery of shale oil and gas was calculated, and the gas chromatography and mass spectrometry of products were performed.

To reflect the difference between the standard atmospheric pressure and supercritical state of oil shale pyrolysis, the extraction experiments under atmospheric pressure and the supercritical state were set up, respectively. The experiment duration was set as 10, 20, 40, and 80 h, respectively. The temperature gradient of the experiment was 10 °C between 350 and 400 °C. The extraction experiment was conducted every 10 °C.

3. RESULTS AND DISCUSSION

3.1. Pressure Fluctuation Characteristics of the Pyrolysis Process. The pyrolysis process of oil shale in a nitrogen atmosphere is more severe than that in a carbon dioxide atmosphere, and the pressure fluctuation is relatively stable in a carbon dioxide atmosphere. There is no pressure fluctuation in the pyrolysis process of 10 and 20 h, and the

pressure fluctuation is more obvious when the pyrolysis time is more than 40 h.

The pyrolysis process of oil shale is controlled by the interfacial reaction mechanism, as shown in Figure 2, and there is an obvious entrance effect.¹

The pyrolysis of kerogen is the main reaction of oil shale heated in a nitrogen atmosphere. However, the release process of kerogen is complex. At the initial stage of the reaction, kerogen exists in the primary pores of oil shale. With the increase of temperature, kerogen gradually undergoes liquefaction and gasification in the pores. At the same time, the pressure difference between the oil shale pores and reactor environment also increases gradually. When the pressure difference increases to the minimum principal stress of pore fracture, the pore will fracture. When the real channel is opened, the gasified kerogen will immediately release oil and gas products, and the release of oil and gas products will lead to the instantaneous increase of reactor pressure.¹⁹ When the pressure is higher than the set value of the relief valve, an active pressure relief process will occur. In addition, the oil and gas products released in the reactor are exposed to high temperature for a long time, which leads to the break and recombination of chemical bonds. The unsaturated hydrocarbons generated easily undergo an addition reaction and consume free methyl and hydrogen free radicals. In addition, the condensation reaction and aromatization reaction will form

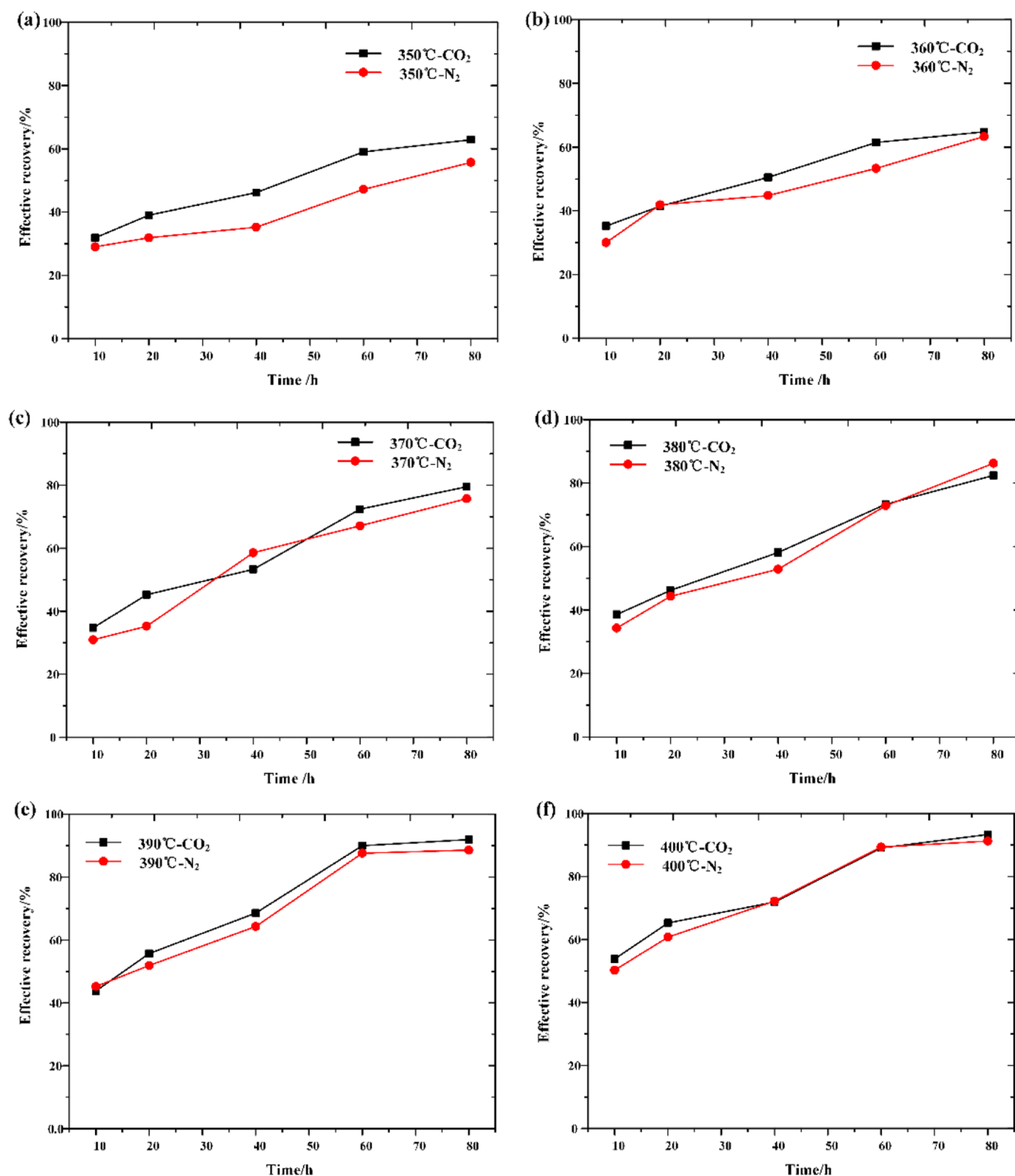


Figure 3. Effective recovery of shale oil varies with time in the two atmospheres: (a) 350, (b) 360, (c) 370, (d) 380, (e) 390, and (f) 400 °C.

cycloalkanes, branched alkanes, and aromatic byproducts.^{20,21} Thus, the pressure will also be reduced. In the process of oil shale pyrolysis, semi coke will be formed, and carbon dioxide will react with semi coke, which will promote the porosity of the oil shale skeleton, leading to the entrance effect more easily, so the release of oil and gas products is relatively easy. The reaction of carbon dioxide and semi coke will lead to the decrease of tensile strength of the pore wall, thus reducing the

minimum principal stress of fracture. Therefore, the shale oil and gas produced by kerogen pyrolysis can be released when the pressure of pore is low, which reduces the intensity of the reaction.

3.2. Analysis of the Effective Oil Recovery. We define the effective recovery as the ratio of the shale oil recovery of oil produced by oil shale pyrolysis to the oil content of undisturbed oil shale samples, which is also expressed as a

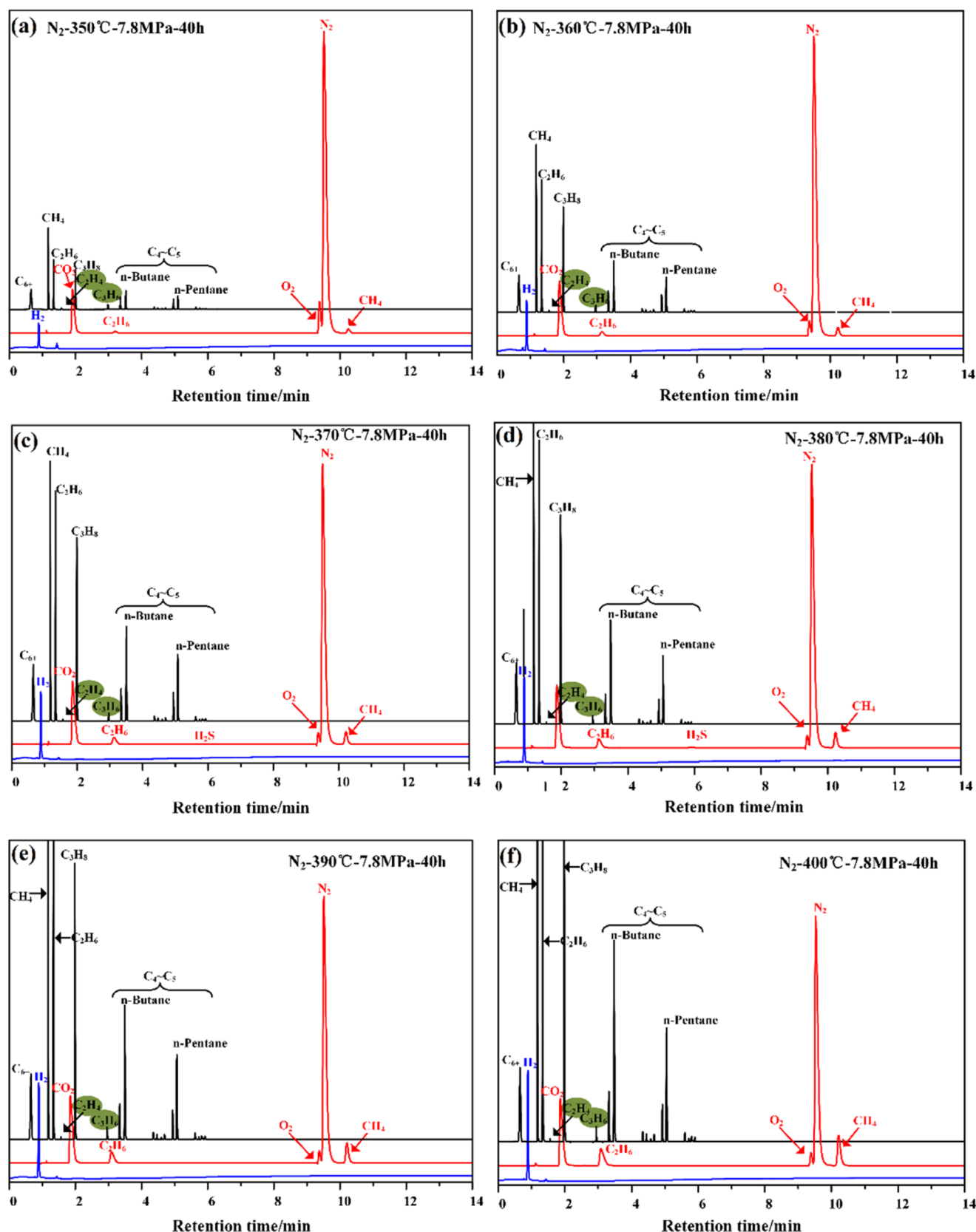


Figure 4. Gas chromatographic analysis of gas products from oil shale pyrolysis 40 h by high-temperature and high-pressure nitrogen: (a) 350, (b) 360, (c) 370, (d) 380, (e) 390, and (f) 400 °C.

percentage. The oil produced by oil shale pyrolysis belongs to condensate type oil, whose viscosity is greatly affected by temperature, and it exists as an approximately paste solid from

low temperature to room temperature. If only a one-stage condensing system is used, a part of shale oil will condense and adhere to the condensation pipeline. During the experiment, a

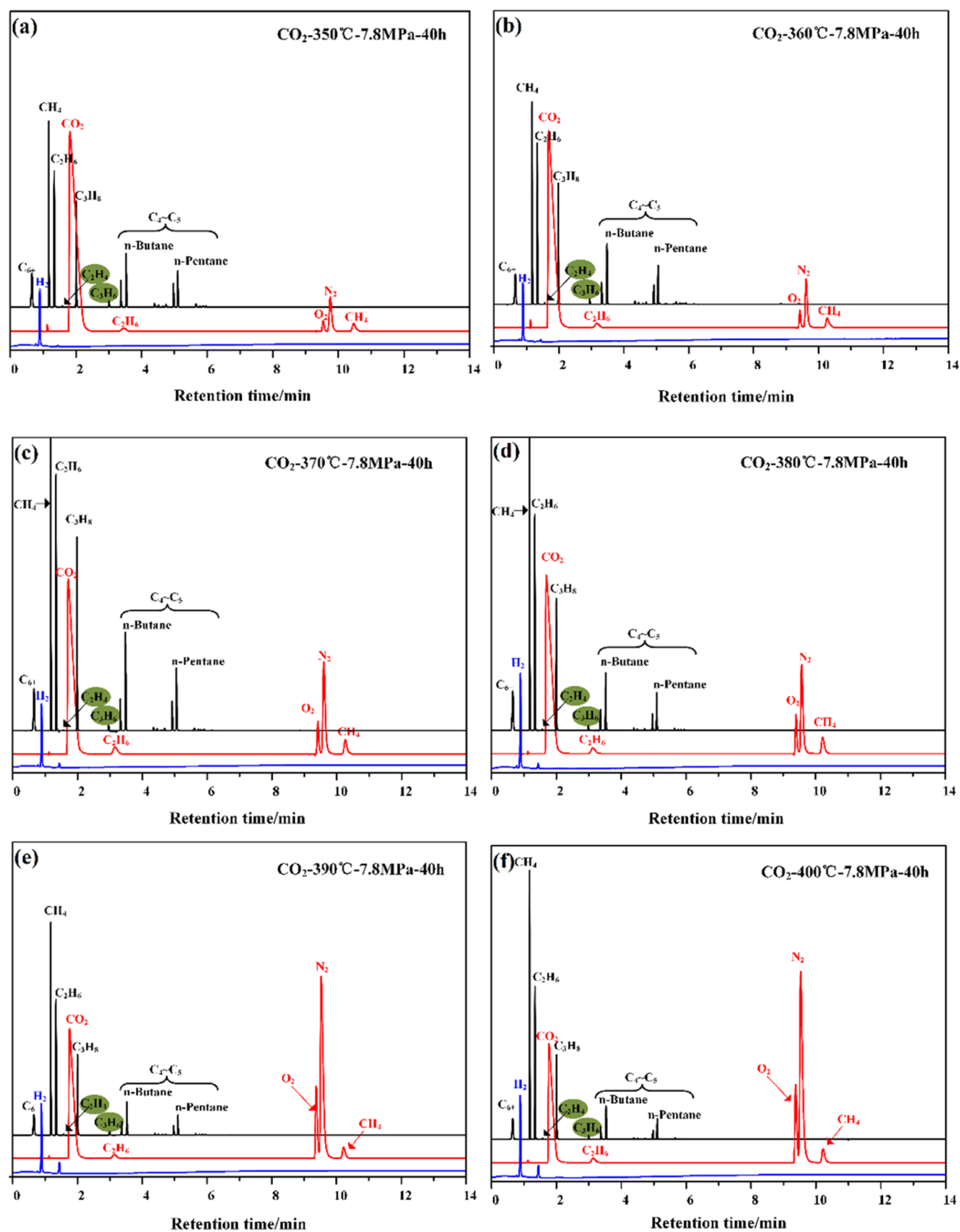


Figure 5. Gas chromatography analysis of oil shale pyrolysis 40 h in a supercritical carbon dioxide atmosphere: (a) 350, (b) 360, (c) 370, (d) 380, (e) 390, and (f) 400 °C.

two-stage collection system was used. The first level of the collection system was also the main collection system, which was the room-temperature collection in a small distillation flask (50 mL). The second level of the collection system is ice-water bath low-temperature collection in a large distillation flask (150 mL).

The temperature and environmental atmosphere have different effects on the pyrolysis of oil shale. For the same pyrolysis time, when the temperature is increased, the enhanced effective recovery of shale oil is more obvious. The oil content of Huadian oil shale is 21.19–22.31%. During the experiment, as shown in Figure 3, the recovery rate of shale oil obtained under different atmosphere and temperature conditions ranged from 6.1 to 19.7%, and the effective recovery rate reached 28.05–90.57% of the average oil content. In the same pyrolysis time, the oil recovery in a high-temperature and high-pressure nitrogen atmosphere is 3.23–12.15% lower than that in a supercritical carbon dioxide atmosphere at 350–370 °C. This indicates that supercritical carbon dioxide has a positive extraction effect on the organic matter generated by pyrolysis of oil shale at the low-temperature stage. However, under the high-temperature and high-pressure nitrogen atmosphere, shale oil escapes from the primary pores mainly by spontaneous volatilization and diffusion. With the increase of temperature, after 400 °C, the effect of extraction is weakened by the temperature, displacement efficiency, and secondary reaction. The effective recovery of shale oil in a nitrogen atmosphere is basically consistent with that in a supercritical carbon dioxide atmosphere. This is because with the extension of pyrolysis time, the interfacial reaction of oil shale pyrolysis gradually advances to the interior of the closed system, and the conductivity and displacement efficiency of the heat carrying fluid decrease. The oil and gas products produced by oil shale pyrolysis cannot escape in time, which leads to the aggravation of the secondary reaction. At a high temperature, the branched chain and some active functions of macromolecular organic matter that are not displaced in time are broken, and a small-molecule gas is formed. Therefore, with the extension of pyrolysis time, the increase degree of shale oil effective recovery decreases gradually. At a low temperature, the recovery efficiency of supercritical carbon dioxide is higher than that of nitrogen, but this trend gradually decreases with the increase of temperature. The results show that the entrance effect and extraction efficiency of supercritical carbon dioxide are obvious at the low-temperature stage. With the increase of temperature, the influence of the temperature and displacement efficiency on oil shale pyrolysis becomes more and more important. Especially, when the temperature reaches 400 °C, the recovery efficiency of the high-pressure nitrogen atmosphere is similar to that of the supercritical carbon dioxide atmosphere, and the superiority of the supercritical carbon dioxide extraction-assisted pyrolysis disappears.

3.3. Gas Chromatography and Mass Spectrometry Analyses of Gas Products. The pyrolysis products of oil shale under the condition of high temperature and high-pressure nitrogen and supercritical carbon dioxide were analyzed by gas chromatography and mass spectrometry.

In order to ensure the accuracy of the test results, before the gas chromatography and mass spectrometry analyses, first, 25 mL of air is injected into the gas chromatography analyzer to detect the normal working properties of the instrument. Then, the shale gas samples collected from each experiment were

connected with the inlet of the gas chromatograph. Taking the gas collected during pyrolysis for 40 h as an example, 25 mL of gas is slowly injected, followed by waiting for the pressure and temperature of the instrument to be ready, and then, the test is started. The results are shown in Figure 4. Methane, ethane, and propane are the main gas products of oil shale pyrolysis under a high-temperature and high-pressure nitrogen atmosphere. With the increase of temperature, butane, pentane, and their isomers also appear. In addition, it also contains a small amount of hydrogen and ethylene, propylene, and so forth.

Figure 5 shows that the pyrolysis products of oil shale in a supercritical carbon dioxide atmosphere are consistent with those in a nitrogen atmosphere. Long time and a high-temperature pyrolysis environment can promote the secondary pyrolysis of oil and gas products,²⁰ which can be obtained from the change of characteristic peaks of alkanes. The secondary pyrolysis is more serious with the increase of temperature and time in the high-temperature and high-pressure nitrogen atmosphere, which can be verified by the characteristic peaks of C₆⁺, methane, ethane, propane, and hydrogen. In addition, it also contains a small number of olefins. Propylene is the main component of olefins, but butene also appears with the increase of temperature. However, alkenes will decrease during long-term pyrolysis at high temperature, which indicates that the C=C double bond breaks and reacts with free methyl and hydrogen-free radicals, which promotes the production of ethane, propane, butane and its isomers, and pentane and its isomers to a certain extent. Zhao et al. (2020) showed that the pyrolysis of oil shale is the cracking of the covalent bond to form free radical fragments. Then, the free radical fragments randomly collide and couple to form volatile compounds (shale oil and natural gas) and semi coke. The reaction of free radicals determines the distribution, composition, and quality of pyrolysis products.²¹

3.4. Gas Chromatography and Mass Spectrometry Analyses of Shale Oil. Before analyzing the pyrolysis products (shale oil) by gas chromatography and mass spectrometry, it is necessary to mix the shale oil and toluene at the ratio of 0.8:60 mL. After heating in a water bath at 70 °C for 6 h, as shown in Figure 6, 3 mL of water bath samples are

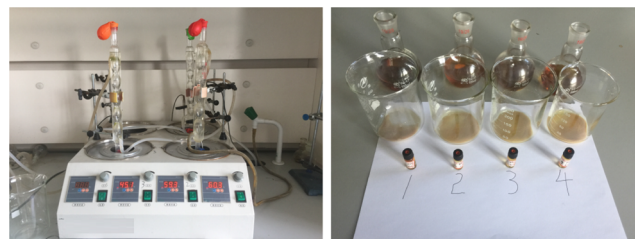


Figure 6. Shale oil sample refining process. Photograph courtesy of “Shuai Zhao”. Copyright 2022.

collected, and anhydrous sodium sulfate is used to remove water so as to prevent the water in the oil sample from affecting the adsorption properties of the chromatographic column during the gas chromatography test. Then, the oil samples were analyzed by gas chromatography and mass spectrometry. The test results are shown in Figures 7 and 8.

The components of shale oil from oil shale pyrolysis are complex, including *n*-alkanes, ISO alkanes, cycloalkanes, olefins, aromatic hydrocarbons, branched alkanes, acids, and ketones. In the process of oil shale pyrolysis and interpretation

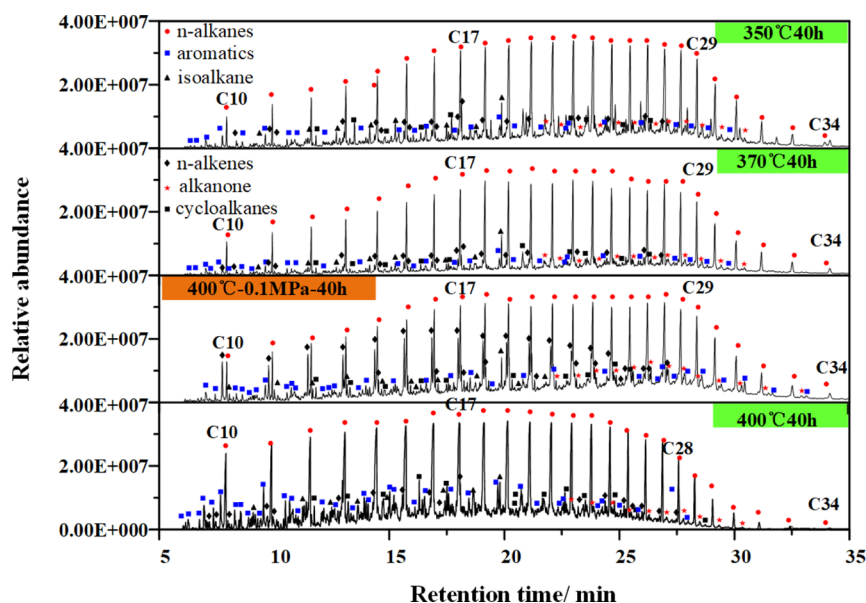


Figure 7. Chromatographic analysis of shale oil under HPHT-N₂.

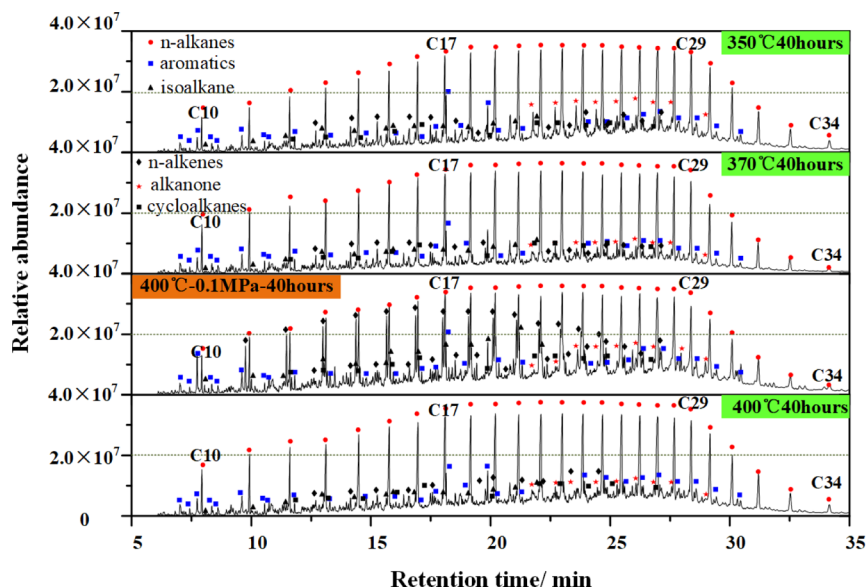


Figure 8. Chromatographic analysis of shale oil under SC-CO₂.

of oil and gas products, the synergistic mechanism of temperature and pressure promotes and accelerates the process of oil shale releasing oil and gas products and promotes the development and expansion of effective diversion channels.²² The main components of shale oil are C16–C28 in a nitrogen atmosphere and C16–C29 in a supercritical carbon dioxide atmosphere. With the increase of pyrolysis temperature, the relative abundances of C28–C34 decrease gradually. Combined with the analysis results of gas-phase products, the relative abundance of C10–C15, methane, ethane, and propane, is gradually increased. This is mainly related to the secondary pyrolysis of macromolecular alkanes caused by the temperature increase.²³

Figure 9 shows the effect of temperature on the pyrolysis of oil shale with an ambient pressure of 7.8 MPa for 40 h. Under a nitrogen atmosphere, the content of *n*-alkanes in shale oil increased from 60% at 350 °C to 75% at 380 °C and then gradually decreased to 53% at 400 °C. This is because when

the pyrolysis time is 40 h, 370–380 °C is the temperature at which 100 g of oil shale can be completely pyrolyzed in the fluidized bed. When the temperature increases, the shale oil will undergo a secondary pyrolysis reaction in a closed reactor. The main types of secondary reactions are condensation and aromatization of aliphatic hydrocarbons.^{24,25} At 360 °C, the contents of olefins and aromatic products in shale oil are 8 and 12%, respectively. When the temperature is increased to 400 °C, the contents of olefins and aromatic products reached 13 and 21%, respectively.

Compared with that in a nitrogen atmosphere, temperature has little effect on the secondary reaction of shale oil in a supercritical carbon dioxide atmosphere. The content of *n*-alkanes remained stable, but it also increased from 64% at 350 °C to 69% at 390 °C and then decreased to 66% at 400 °C. The content of olefins decreased from 16 to 4%, and the content of aromatic products increased from 10 to 17%. This shows that the secondary reaction of shale oil also takes place

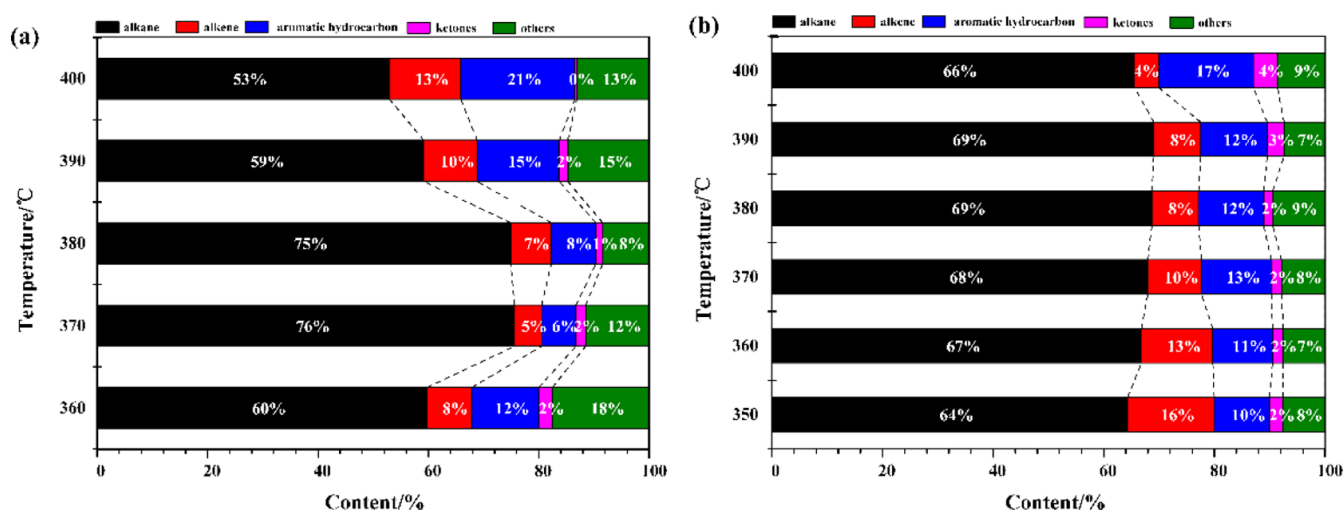


Figure 9. Shale oil component in 40 h pyrolysis at 350–400 °C under (a) HPHT-N₂ and (b) SC-CO₂.

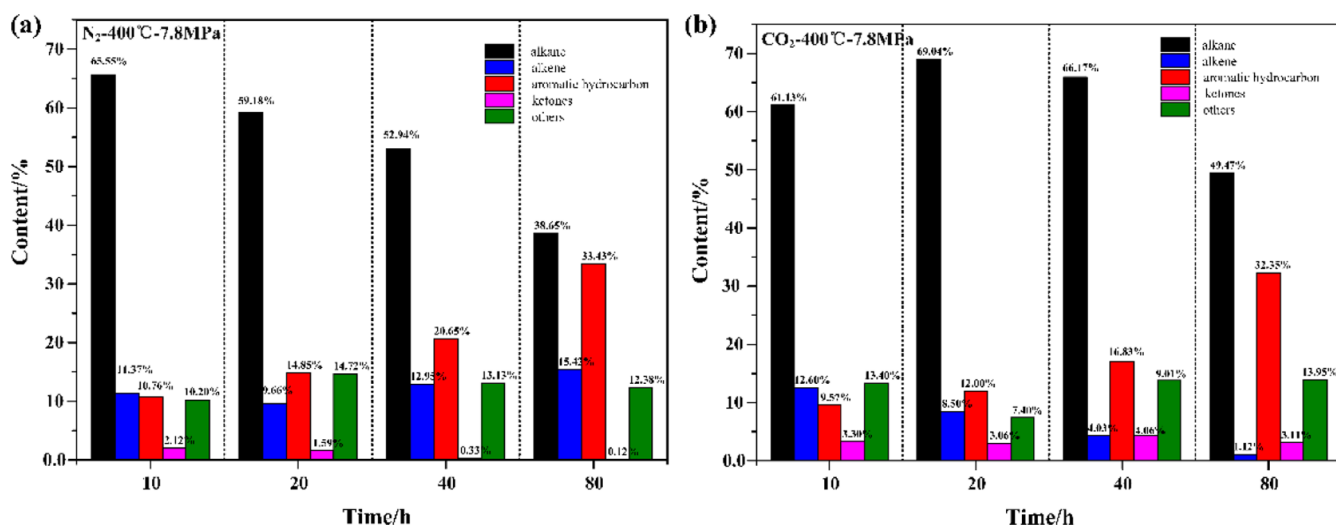


Figure 10. Shale oil component at 400 °C and 7.8 MPa after 10–80 h under (a) HPHT-N₂ and (b) SC-CO₂.

with the increase of temperature in a supercritical carbon dioxide atmosphere in a closed reactor. However, compared with that in a nitrogen atmosphere, the secondary reaction of shale oil in a supercritical carbon dioxide atmosphere is mainly the addition reaction and aromatization reaction. By comparing the contents of *n*-alkanes, olefins, and aromatic products, it is found that the advance degree of the addition reaction is higher than that of the condensation reaction. However, the degree of aromatization in a supercritical carbon dioxide atmosphere is lower than that in a nitrogen atmosphere.

To explore the influence of induction time under different atmospheres on the pyrolysis products of oil shale, pyrolysis experiments were carried out at 400 °C for 10–80 h. The results are shown in Figure 10. Under a high-temperature and high-pressure nitrogen atmosphere, with the increase of pyrolysis time, the content of *n*-alkane decreased from 65.55 to 38.65%, the content of olefin increased from 11.37 to 15.41%, and the content of aromatic products increased from 10.76 to 33.43%. Under a supercritical carbon dioxide atmosphere, with the prolongation of induction time, the content of *n*-alkanes increased from 66.13 to 69.04% at the induction time of 20 h and then gradually decreased to 49.47%.

The content of olefins decreased from 12.60 to 1.12%, and the content of aromatic products increased from 9.57 to 32.35%. With the extension of pyrolysis time, the pressure of the reaction system gradually stabilized, and the opening frequency of the pressure relief valve decreased, so the flow bed gradually evolved into a closed reactor, resulting in the degree of the secondary reaction gradually increasing.

In the volatilization process of oil and gas products at standard atmospheric pressure, the pressure around the pores where the oil and gas products exist is lower than the saturated vapor pressure, so the resistance in the escape process is small.²⁶ In the high-pressure system, the pressure around the pores where oil and gas products occur is higher than the saturated steam pressure. Only higher temperatures can increase the saturated vapor pressure. At this time, the oil and gas products are in a constant temperature state, so part of the escaped oil and gas products will be condensed and re-adsorbed in the pores of the oil shale, resulting in the intensification of the secondary reaction. The inlet effect on the secondary reaction in nitrogen is lower than extraction in supercritical carbon dioxide. In this process, the content of olefins has no obvious change in the nitrogen atmosphere, which indicates that the main types of secondary reactions are

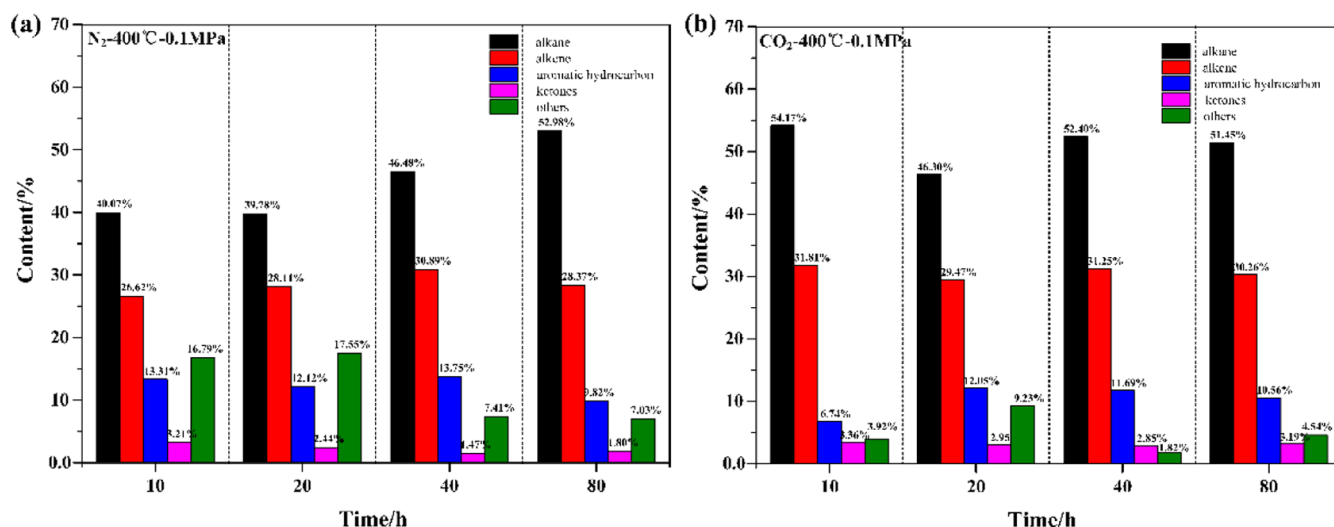


Figure 11. Shale oil component at 400 °C and standard atmospheric pressure after 10–80 h under (a) HPHT-N₂ and (b) SC-CO₂.

condensation and aromatization of aliphatic hydrocarbons. The content of alkanes and alkenes decreased while the content of aromatic products increased under a supercritical carbon dioxide atmosphere, indicating that the secondary reactions were mainly the addition reaction and aromatization reaction.

Figure 11 shows the effect of pressure on oil shale pyrolysis. Compared with that in the high-pressure state, the content of olefins under standard atmospheric pressure is about 30%, which is much higher than the value of about 10% under high pressure. This shows that high pressure inhibits the release of unsaturated hydrocarbons and promotes the addition reaction of unsaturated bonds and free radicals. When the pyrolysis time is less than 40 h, the content of alkanes in the standard atmospheric pressure state is lower than that in the high-pressure state. When the pyrolysis time is increased to 80 h, the degree of the secondary reaction under high pressure is intensified, and the content of alkanes is lower than that of standard atmospheric pressure. In addition, under standard atmospheric pressure, the components of shale oil obtained by oil shale pyrolysis in the carbon dioxide atmosphere are basically stable, while the contents of *n*-alkanes, aromatic products, and other products (fatty acids, branched chain alkanes, and cycloalkanes) vary greatly under a nitrogen atmosphere, indicating that the stability of oil shale pyrolysis in the nitrogen atmosphere is relatively low.

4. CONCLUSIONS

- (1) The extraction efficiency of supercritical carbon dioxide at low temperature is obvious, but with the increase of temperature, the effect of extraction on pyrolysis is lower than that of temperature.
- (2) With the increase of temperature and time, the secondary pyrolysis becomes more serious, while the olefins decrease during long-term pyrolysis at high temperature, which indicates that C=C breaks and reacts with free methyl and hydrogen-free radicals, which promotes the production of ethane, propane, butane and its isomers, and pentane and its isomers to a certain extent.
- (3) During oil shale pyrolysis, the release process of shale oil and gas is a process in which the internal and external

pressure difference of kerogen primary pore breaks through the minimum principal stress of pore fracture. The process of extraction assisted pyrolysis is also included in the supercritical carbon dioxide atmosphere, which can extract the shale oil in a timelier manner.

- (4) A high-pressure environment can inhibit the olefin synthesis reaction during the pyrolysis of oil shale.

AUTHOR INFORMATION

Corresponding Author

Junwen Wu – State Key Laboratory of Shale Oil and Gas Enrichment Mechanisms and Effective Development, Beijing 1100083, China; State Center Research and Development of Oil Shale Exploitation, Beijing 1100083, China; Email: wujw.syky@sinopec.com

Authors

Shuai Zhao – State Key Laboratory of Shale Oil and Gas Enrichment Mechanisms and Effective Development, Beijing 1100083, China; State Center Research and Development of Oil Shale Exploitation, Beijing 1100083, China; School of Mines, China University of Mining and Technology, XuZhou 221116, China; orcid.org/0000-0001-7735-8949

Jianzheng Su – State Key Laboratory of Shale Oil and Gas Enrichment Mechanisms and Effective Development, Beijing 1100083, China; State Center Research and Development of Oil Shale Exploitation, Beijing 1100083, China

Lü Xiaoshu – Department of Electrical Engineering and Energy Technology, University of Vaasa, Vaasa FIN-65101, Finland; Department of Civil Engineering, Aalto University, Espoo FIN-02130, Finland

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.2c06693>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This experimental work was supported by “the Open Fund for Research on the Control Mechanism of Gas Injection Parameters on the Coking Degree in the Product Migration Process of the National Oil Shale Exploitation Research and

Development Center”, “the Fundamental Research Funds for the Central Universities, grant number 2021QN1002”, “The Natural Science Foundation of Jiangsu Province, grant number BK20221133”, the “China Postdoctoral Science Foundation, grant number 2021M693421”, “Laboratory opening project of China University of Mining and Technology in 2021, grant number 2021SYF97” and “The 2021 Jiangsu Shuangchuang (Mass Innovation and Entrepreneurship) Talent Program, grant number JSSCBS20211238”. The authors also express their appreciation for the technical reviewers for their constructive comments.

REFERENCES

- (1) Shuai, Z.; Xiaoshu, L.; Qiang, L.; Youhong, S. Thermal-fluid coupling analysis of oil shale pyrolysis and displacement by heat-carrying supercritical carbon dioxide. *Chem. Eng. J.* **2020**, *394*, 125037.
- (2) Pan, Y.; Zhang, X.; Liu, S.-H.; Yang, S.; Ren, N. A Review on Technologies for Oil Shale Surface Retort. *J. Chem. Soc. Pak.* **2012**, *34*, 1331–1338.
- (3) 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.
- (4) Sun, J.; Xiao, X.; Cheng, P.; Tian, H. Formation and evolution of nanopores in shales and its impact on retained oil during oil generation and expulsion based on pyrolysis experiments. *J. Petrol. Sci. Eng.* **2019**, *176*, 509–520.
- (5) Youhong, Y.; Shuai, S.; Qiang, Q.; Shichang, S.; Jing, J. Thermoelectric coupling analysis of high-voltage breakdown industrial frequency pyrolysis in Fuyu oil shale. *Int. J. Therm. Sci.* **2018**, *130*, 19–27.
- (6) Amer, A.; Aljariri Alhesan, J.; Marshall, M.; Awwad, A.; Al-Ayed, O. Characterization of Jordanian oil shale and variation in oil properties with pyrolysis temperature. *J. Anal. Appl. Pyrolysis* **2019**, *140*, 219–226.
- (7) Wang, L.; Zhao, Y.; Yang, D.; Kang, Z. J.; Zhao, J. Effect of pyrolysis on oil shale using superheated steam: A case study on the Fushun oil shale, China. *Fuel* **2019**, *253*, 1490–1498.
- (8) Mu, M.; Han, X.; Jiang, X. Interactions between oil shale and hydrogen-rich wastes during co-pyrolysis: 1. Co-pyrolysis of oil shale and polyolefins. *Fuel* **2020**, *265*, 116994.
- (9) Zhao, S.; Sun, Y.; Lü, X.; Li, Q. Energy consumption and product release characteristics evaluation of oil shale non-isothermal pyrolysis based on TG-DSC. *J. Petrol. Sci. Eng.* **2020**, *187*, 106812.
- (10) He, L.; Ma, Y.; Yue, C.; Wu, J.; Li, S. Kinetic modeling of Kukersite oil shale pyrolysis with thermal bitumen as an intermediate. *Fuel* **2020**, *279*, 118371.
- (11) Bai, F.; Sun, Y.; Liu, Y.; Guo, M.; Zhao, J. Characteristics and Kinetics of Huadian Oil Shale Pyrolysis via Non-isothermal Thermogravimetric and Gray Relational Analysis. *Combust. Sci. Technol.* **2020**, *192*, 471–485.
- (12) Foltin, P.; Lisboa, C.; de Klerk, K. Oil Shale Pyrolysis: Conversion Dependence of Kinetic Parameters. *Energy Fuels* **2017**, *31*, 6766–6776.
- (13) You, Y.; Wang, X.; Han, X.; Jiang, X. Kerogen pyrolysis model based on its chemical structure for predicting product evolution. *Fuel* **2019**, *246*, 149–159.
- (14) Kuang, W.; Lu, M.; Yeboah, I.; Qian, G.; Duan, X.; Yang, J.; Chen, D.; Zhou, X. A comprehensive kinetics study on non-isothermal pyrolysis of kerogen from Green River oil shale. *Chem. Eng. J.* **2019**, *377*, 120275.
- (15) Guo, W.; Yang, Q.; Deng, S.; Li, Q.; Sun, Y.; Su, J.; Zhu, C. Experimental study of the autothermic pyrolysis in-situ conversion process (ATS) for oil shale recovery. *Energy* **2022**, *258*, 124878.
- (16) Liu, L.; Sun, Y.; Guo, W.; Li, Q. Reservoir-scale study of oil shale hydration swelling and thermal expansion after hydraulic fracturing. *J. Petrol. Sci. Eng.* **2020**, *195*, 107619.
- (17) Wang, S.; Javadpour, F.; Feng, Q. Fast mass transport of oil and supercritical carbon dioxide through organic nanopores in shale. *Fuel* **2016**, *181*, 741–758.
- (18) Wu, T.; Xue, Q.; Li, X.; Tao, Y.; Jin, Y.; Ling, C.; Lu, S. Extraction of kerogen from oil shale with supercritical carbon dioxide: Molecular dynamics simulations. *J. Supercrit. Fluids* **2016**, *107*, 499–506.
- (19) Saif, T.; Lin, Q.; Bijeljic, B.; Blunt, M. Microstructural imaging and characterization of oil shale before and after pyrolysis. *Fuel* **2017**, *197*, 562–574.
- (20) Chen, B.; Han, X.; Tong, J.; Mu, M.; Jiang, X.; Wang, S.; Shen, J.; Ye, X. Studies of fast co-pyrolysis of oil shale and wood in a bubbling fluidized bed. *Energy Convers. Manag.* **2020**, *205*, 112356.
- (21) Zhao, X.; Liu, Z.; Liu, Q. The bond cleavage and radical coupling during pyrolysis of Huadian oil shale. *Fuel* **2017**, *199*, 169–175.
- (22) Bake, D.B.; Pomerantz, E. P. Optical Analysis of Pyrolysis Products of Green River Oil Shale. *Energy Fuels* **2017**, *31*, 13345–13352.
- (23) Aljariri Alhesan, A.; Fei, F.; Marshall, M.; Jackson, J.; Qi, Q.; Chaffee, L.C.; Cassidy, C. Long time, low temperature pyrolysis of El-Lajjun oil shale. *J. Anal. Appl. Pyrolysis* **2018**, *130*, 135–141.
- (24) Tian, Y.; Li, M.; Lai, D.; Chen, Z.; Gao, S.; Xu, G. Characteristics of oil shale pyrolysis in a two-stage fluidized bed. *Chin. J. Chem. Eng.* **2018**, *26*, 407–414.
- (25) Lai, D.; Zhang, G.; Xu, G. Characterization of oil shale pyrolysis by solid heat carrier in moving bed with internals. *Fuel Process. Technol.* **2017**, *158*, 191–198.
- (26) Corredor, C. M.; Deo, M. D. Effect of vapor liquid equilibrium on product quality and yield in oil shale pyrolysis. *Fuel* **2018**, *234*, 1498–1506.