

Citation: QIAN Menhui, LI Maowen, JIANG Qigui, LI Zhiming, TAO Guoliang, BAO Yunjie. Evaluation of evaporative loss of hydrocarbon in shale samples and its geological implications[J], *Petroleum Geology & Experiment*, 2022 (3): 497–504, 514.

The English version here is roughly translated and has not been reviewed or edited. Please contact us if you need a finely translated and edited version.

Evaluation of evaporative loss of hydrocarbon in shale samples and its geological implications

QIAN Menhui^{1,2,3,4}, LI Maowen^{1,2,3,4}, JIANG Qigui^{1,2,3,4}, LI Zhiming^{1,2,3,4}, TAO Guoliang^{1,2,3,4}, BAO Yunjie^{1,2,3,4}

1. Wuxi Research Institute of Petroleum Geology, SINOPEC Petroleum Exploration and Production Research Institute, Wuxi 214126, Jiangsu;

2. State Key Laboratory of Shale Oil and Gas Enrichment Mechanisms and Effective Development, Wuxi 214126, Jiangsu;

3. State Energy Center for Shale Oil Research and Development, Wuxi 214126, Jiangsu;

4. SINOPEC Key Laboratory of Petroleum Accumulation Mechanisms, Wuxi 214126, Jiangsu

Abstract: Free hydrocarbon content is one of the key parameters for resource assessment of shale oil. However, due to the evaporative loss of hydrocarbon, the measured results from lab analysis differ greatly from real value, which leads to the “distortion” of shale oil resource assessment. To investigate the process of the evaporative loss and obtain the hydrocarbon loss amount and correction coefficient, a time-series of analysis has been carried out on fresh oil-bearing shale samples with similar maturity and different lithofacies for both the amount and the composition of the hydrocarbons retained in shale. Results suggest that there are two processes of early rapid and later slow evaporative loss. The volatile components are mainly light hydrocarbons with carbon numbers smaller than C₁₃–C₁₅, while the medium to heavy components are less affected. Both the amount and processes of hydrocarbon evaporative loss are controlled by the physical properties and original oil content of shale samples. The oil-bearing shale samples with higher original oil content and better physical properties appear to have more evaporative loss of hydrocarbons. Results also indicate that more attention should be exercised on original hydrocarbon content when conducting the shale oil resource assessment of “sweet spot” section with high oil content and good physical properties. **DOI:** 10.11781/sydz202203497-en

Keywords: hydrocarbon evaporative loss; recovery of light hydrocarbons; free hydrocarbon content; evaluation of oil-bearing capacity; shale oil

1 Research status quo

With the breakthrough of shale oil and gas exploration and exploitation in North America, shale oil, an important part of unconventional oil and gas resources, has gradually attracted the attention of domestic explorers^[1–8], which has resulted in the growth of investment in exploration and exploitation of continental shale oil in China^[9]. Different from the relatively stable marine sedimentary strata in North America, continental shale sedimentary strata in China have strong heterogeneity^[10], with quite different oil-bearing properties. Evaluation of oil-bearing properties in shale is the basis for predicting the sweet spot section and sweet spot block of shale oil, and also the core of potential evaluation for shale oil resource. With the progress and perfection of experimental technology and the deepened understanding of the occurrence mechanism of continental shale oil^[11–14], the evaluation of oil-bearing properties of shale oil has gradually

developed from the in-situ retained oil evaluation aiming at the total amount of retained hydrocarbons to the free oil evaluation aiming at free hydrocarbons^[15–20]. However, it is the basic work of evaluation of shale oil resources to obtain and evaluate the original free hydrocarbon content of shale oil.

Free hydrocarbon, as the most realistic movable oil component in retained oil of mud shale^[21], is often characterized by the parameter pyrolysis S_1 (the content of free hydrocarbon released by unit rock heated to 300 °C in a rock pyrolyzer), dominated by liquid light hydrocarbons, which is quite unstable and easily volatilized and lost^[22–24]. Its content increases with the rise of thermal maturity of shale rock stratum series, and varies with different types of organic matter. The free hydrocarbon components retained in mud shale will cause different degrees of loss during the coring, standing at room temperature and crushing at room temperature. The higher the maturity of shale is, the greater the hydrocarbon loss will be. ZHU et al.^[25] treated and analyzed

Received: 2022-01-06

Supported by: National Natural Science Foundation of China (42090022)

First author: QIAN Menhui (1985–), male, master, associate researcher. Research interests: shale geochemistry and petroleum geology study. E-mail: qianmh.syky@sinopec.com

the fresh samples in a frozen and sealed condition, and compared them with the analysis and test data after standing for 30 d under conventional conditions. They believed that the average loss rate of S_1 light hydrocarbon reached about 50% in a mature evolution stage. Moreover, they obtained the C_{14} component content by chromatographic analysis of crude oil produced in natural profile, and developed a light hydrocarbon recovery method of chloroform asphalt “A”—a conventional sample based on the analysis results. They believed that the light hydrocarbon loss was about 30% when R_o was 0.9%. WANG [26] obtained the light hydrocarbon content of rock samples at different mature stages by using low boiling point solvent to extract light hydrocarbon at low temperature using the methods established by previous scholars, and established the recovery coefficient of light hydrocarbon during chloroform extraction in Dongying Depression, which was considered to be consistent with the recovery coefficient of light hydrocarbon obtained by the natural evolution profile method. LI et al [27] simulated and calculated the ratio of light hydrocarbon (C_{6-13}) to heavy hydrocarbon (C_{13+}) of organic matters at different evolution stages by using the kinetics method for hydrocarbon generation, and developed the light hydrocarbon correction method of residual hydrocarbon in Damintun Sag based on the recovery of S_1 heavy hydrocarbons. JARVIE [28] compared S_1 values of samples placed for a long time with those of fresh sidewall coring samples, and believed that the difference of free hydrocarbon content of samples can reach about 5 times after long-term placement. CHEN et al. [29–31] calculated the light hydrocarbon loss ratio of type-I kerogen at different evolution stages by using the hydrogen index material balance method. They believed that the light hydrocarbon loss decreased with the rise of evolution degree after the source rock entered the oil-generating window and before the R_o reached 1.3%, and increased rapidly with the rise of evolution degree after reaching 1.3%.

The current main focus is on the study of the evaluation of the thermal evolution degree of light hydrocarbon loss, while the loss of light free hydrocarbon is a continuous process. The content of free hydrocarbon measured in the laboratory varies greatly with the difference of placement time of core samples. The recovery result of light hydrocarbon loss based on the measured value after the sample placement for a certain time can't really indicate the original oil content information of the samples. Moreover, the migration and accumulation characteristics of shale oil system vary with openness. A short-distance migration is often needed for the development of the sweet spot block of shale oil, while the migration of light hydrocarbons is significantly different from that of medium and heavy hydrocarbons, which leads to the difference of hydrocarbon components in the “source” and “storage” of shale oil. The recovery of light hydrocarbon loss based on hydrocarbon generation thermal simulation may not be quite suitable for open or semi-open shale oil systems. In fact, the content of light free hydrocarbon is not only associated with the composition of hydrocarbon (determined by the

types of bio-precursors and maturity characteristics), but also closely correlated with the storage time of core samples [32], reservoir physical properties [33], sample analysis pretreatment methods [33–36], and the like. Hence, to clarify the loss process of free hydrocarbons, especially light free hydrocarbons, in shale oil is the basis of light hydrocarbon recovery in shale oil, and also the key to objectively evaluate the oil-bearing property of shale oil.

2 Geological samples and experimental methods

In this experiment, fresh oil-bearing core samples from the third member of Paleogene Qianjiang Formation in wells BYY1 and BYY2 in Qianjiang Sag of Jiangnan Basin were selected, and the R_o was about 0.9%. The samples include dolomitic mudstone, argillaceous dolomite, dolomitic mudstone and glauberite-bearing mudstone. The original oil content of samples varies. The pyrolysis S_1 is 2.43–12.60 mg/g and the porosity is 0.7%–13.4%, which represent the distribution situation of samples with different oil content and different porosity and permeability conditions. The geochemical characteristics, mineral composition and physical properties of the samples are shown in Table 1.

The experimental samples were frozen at ultra-low temperature ($-40\text{ }^\circ\text{C}$) immediately after the core was taken out of the barrel. After 48 hours of freezing, 1/3 and 2/3 blocks of the core were cut at low temperature [37], so as to prevent the loss of light hydrocarbons to the greatest extent. In order to avoid the experimental error caused by the heterogeneity of samples, 1/3 blocks of cores were cut longitudinally in this study, and rock blocks with a width of 1 cm or so were cut on the same side by four cycles (original status, after one week, after two months and after five months at room temperature). These blocks were frozen and sealed under the protection of liquid nitrogen, and the rock pyrolysis and pyrolysis chromatographic analysis were carried out, respectively. The porosity and mineral composition of the remaining samples were tested and analyzed, and some of the experimental cycles were conducted at hourly intervals. The national standard *Rock Pyrolysis Analysis (GB/T: 18602–2012)* was adopted for rock pyrolysis, and the thermoluminescence conditions of the pyrolysis chromatography experiment are consistent with S_1 analysis conditions of rock pyrolysis. In this study, the pyrolysis S_1 value was used as the free hydrocarbon content, and the storage temperature is about $24\text{ }^\circ\text{C}$, which facilitates the comparison with the study of other scholars in the industry.

3 Experimental results and discussion

Hydrocarbon evaporative loss is a continuous process, but the processes experienced are obviously different. After the

Table 1 Basic information of experimental samples

Well No.	Sample No.	Lithology	Depth/m	$S_1/$ ($\text{mg} \cdot \text{g}^{-1}$)	$S_2/$ ($\text{mg} \cdot \text{g}^{-1}$)	$\omega(\text{TOC})/$ %	$T_{\text{max}}/$ °C	Content of main minerals/%						Porosity /%	
								Clay	Quartz	Feldspar	Calcite	Dolomite	Plaster		Glauberite
	45	Gray lamellar dolomitic mudstone	3 124.07	4.45	2.96	2.07	408	29.6	14.5	7.4	5.8	28.8	1.1	8.0	1.1
	55	Gray lamellar argillaceous dolomite	3 124.39	5.72	3.91	2.17	414	19.2	9.2	8.1	16.5	40.2	1.4	2.3	8.4
	61	Gray-black lamellar dolomitic mudstone	3 124.70	3.23	2.86	1.46	416	18.7	9.2	8.3	19.6	34.9	2.1	1.2	1.0
	67	Gray-black lamellar dolomitic mudstone	3 124.88	3.66	2.26	1.28	414	38.6	17.8	7.9	18.6	5.0	1.2	2.4	3.1
	143	Gray argillaceous dolomite	3 127.33	5.54	3.36	1.75	407	18.5	10.2	6.5	12.1	47.6	0.9	0.6	7.5
	161	Gray lamellar argillaceous dolomite	3 127.76	7.79	1.55	1.16	402	13.9	9.4	7.8	16.9	43.1	0.8	4.3	2.5
BYY1	192	Gray-yellow glauberite-bearing dolomite	3 129.07	5.34	1.22	0.80	398	17.1	9.0	6.5	6.7	25.4	1.8	27.9	2.8
	205	Gray-yellow lamellar dolomite	3 129.56	12.60	1.21	1.40	393	8.0	7.5	8.1	4.0	54.1	1.0	13.3	1.6
	220	Light gray dolomite	3 130.12	3.93	0.69	0.60	403	7.6	12.6	11.4	3.6	56.7	1.2	1.2	13.4
	224	Gray fine-grained lamellar dolomite	3 130.27	7.60	4.22	1.68	408	34.1	20.3	5.0	5.3	3.7	1.5	24.1	3.8
	197	Gray glauberite-bearing dolomitic mudstone	3 129.29	4.43	1.68	1.04	397	31.3	22.2	10.3	11.3	7.0	1.6	5.1	3.8
	253	Gray-white massive glauberite	3 131.40	2.92	0.77	0.66	391	27.6	15.3	4.0	3.6	1.9	1.8	37.4	0.7
	264	Gray-yellow massive dolomite	3 131.73	4.75	1.18	0.85	405	13.3	8.7	4.4	2.7	58.1	0.6	1.2	8.2
BYY2	1111	Gray-black lamellar dolomitic mudstone	3 400.29	10.88	5.22	4.13	428	15.5	8.6	13.7	21.3	29.0	5.1	0.3	1.3
	1076	Gray-black lamellar dolomitic mudstone	3 399.37	2.43	0.69	2.27	400	12.4	6.1	18.5	8.7	35.3	16.7	0.7	6.0

Note: S_1 , S_2 , TOC, and T_{max} data are the analysis results of the original sample.

separation from the high-temperature and high-pressure environments of the stratum, the temperature and pressure of the oil-bearing core samples varies with the processes of drilling and pulling out of the barrel. With the continuous loss and volatilization of hydrocarbons, the oil concentration of the samples themselves is also decreasing, and there are different volatilization degrees for different hydrocarbon components, which thus results in the different re-volatilization speeds of residual hydrocarbons in different time. The influence of multiple factors leads to the extremely complicated process of hydrocarbon loss.

3.1 Hydrocarbon loss process of shale sample

In order to clarify the early hydrocarbon loss process of shale samples, two samples with different oil contents were studied emphatically. After the cores are taken out of the barrel, they are placed at room temperature, and the hydrocarbon content S_1 value of the cores is measured at 2, 8, 32, 56, 794, 1 394 h respectively after they are taken out of the barrel (Table 2, Fig.1).

The original hydrocarbon content of the high oil-bearing samples (sample 1111) is as high as 10.88 mg/g, and the final

hydrocarbon content is 8.16 mg/g after storing 1 394 h at room temperature, and the final loss ratio is 25% of the original hydrocarbon content. The original hydrocarbon content of the low oil-bearing samples (sample 1076) is 2.43 mg/g, and the final hydrocarbon content after storage is 0.98 mg/g, and the final loss ratio is 59.7% of the original hydrocarbon content (Table 2). The results are iteratively regressed by a nonlinear fitting. The tested data show that there are obviously two processes for the loss of hydrocarbons with the increase of storage time, namely, the early rapid loss stage and the late

Table 2 Rock-Eval S_1 value of shale samples after a time-series of storing in normal conditions

Storing Time/h	$S_1/(\text{mg} \cdot \text{g}^{-1})$	
	Sample 1111	Sample 1076
2	10.88	2.43
8	10.54	1.64
32	9.70	1.45
56	9.41	1.27
794	8.20	1.08
1 394	8.16	0.98

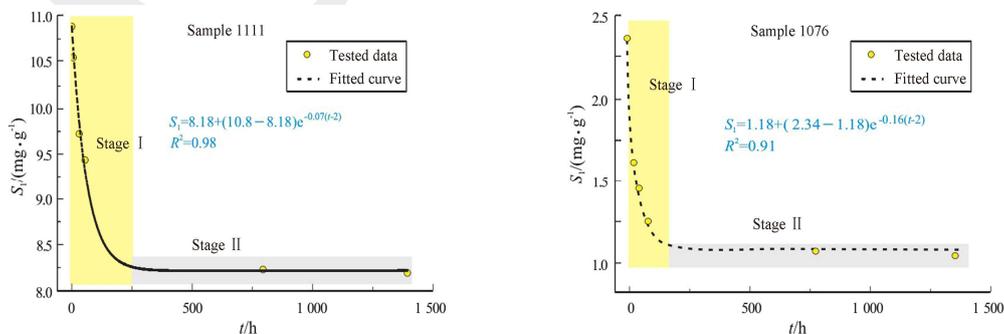


Fig. 1 Relationships between Rock-Eval S_1 value and sample storing time

slow loss stage (Fig. 1). Loss of hydrocarbons mainly occurs at the early stage of rapid loss. During the process of tripping out, taking out of the barrel and storing at room temperature, the temperature and pressure of the core rapidly drop and release, which leads to the precipitation and evaporative loss of a large number of hydrocarbons. Most of the flowable hydrocarbons are completely volatilized at this stage and the evaporative loss amount accounts for more than 90% of the total evaporative loss amount. After entering the late stage of slow evaporative loss, hydrocarbons still continue to lose, but the loss is limited, accounting for less than 10% of the total loss, and the loss rate is very slow. Moreover, the duration of the rapid evaporative loss stage is positively correlated with the original oil content of the sample. In other words, the higher the oil content is, the longer the sample will experience a rapid evaporative loss stage.

In order to further study the hydrocarbon evaporative loss process of shale samples, the author carried out longer period experiments on other samples with different oil contents. After five months of storage, the results reveal that the loss process of samples with different oil abundance manifests three types after long-term storage (Fig. 2). One is the continuous rapid evaporative loss, with representative samples such as 205 and 55. The initial oil content of this type of samples is relatively high, generally more than 5 mg/g, the S_1 value continues to decrease greatly, and it has not yet entered the slow loss stage even after five months. The volatilization amount of hydrocarbons decreased by about 28.5% to 37.14% (32.81% on average) after one week, and it was volatilized by about 39.69% to 57.54% (48.61% on average) after two months, and as high as 67.83% to 81.75% (74.79% on average) after five months. The second one is the early rapid evaporative loss, with the representative samples, such as 224, 161, 264, and 67. A lot of hydrocarbons are volatilized in a short time for this type of samples and remains stable in the later period. The volatilization amount of hydrocarbon decreased by about 24%–47% (average 36.34%) for one week, it was volatilized by about 24%–64% (average 44%) after two months, and it was volatilized by about 25.41%–81.75% (average 55%) after five months. The third one is the slow evaporative loss, with representative samples

such as 143 and 192, etc. The hydrocarbon loss is not obvious after this type of samples is placed, with the slow evaporative loss and small loss volume. After two months, it reached the stage of slow evaporative loss, and the volatilization of hydrocarbons decreased within 10% in one week or so, and by 25%–34% (29.88% on average) or so in two months, and then kept in an equilibrium state.

3.2 Characteristics of hydrocarbon evaporative loss in shale samples

The occurrence states of hydrocarbons in shale samples can be classified into three states, i.e., free state, adsorbed state and kerogen miscible state [20]. Free-state hydrocarbons mainly occur in large pore spaces such as macropores and microcracks. Adsorbed hydrocarbons mainly occur in micropores and rock mineral surfaces [38]. The study results show that the light hydrocarbons with low carbon numbers dissociate and precipitate easily because of their short carbon chains, weak polarity, and small interaction with adsorption media. However, medium/heavy hydrocarbons with high carbon numbers are the main adsorbed hydrocarbons in shale oil because they have relatively long carbon chains, and the interaction between them and the adsorption media is relatively large [39–40]. The comparison result of the residual hydrocarbon components after different storage periods (Fig. 3) reveals that the main peak carbon number of the residual hydrocarbon components gradually increases with the increase of storage time, and the light hydrocarbons in front of C_{13} are retained within one week, and then they are basically dissipated after that time, and the residual hydrocarbon components are mainly dominated by medium/heavy hydrocarbons above C_{15} .

3.3 Influencing factors of hydrocarbon evaporative loss and its geological significance

3.3.1 Influencing factors of hydrocarbon evaporative loss

The relationship between free hydrocarbon content of the samples and the original free hydrocarbon content was regressed (Fig. 4) after different storing time. The analysis

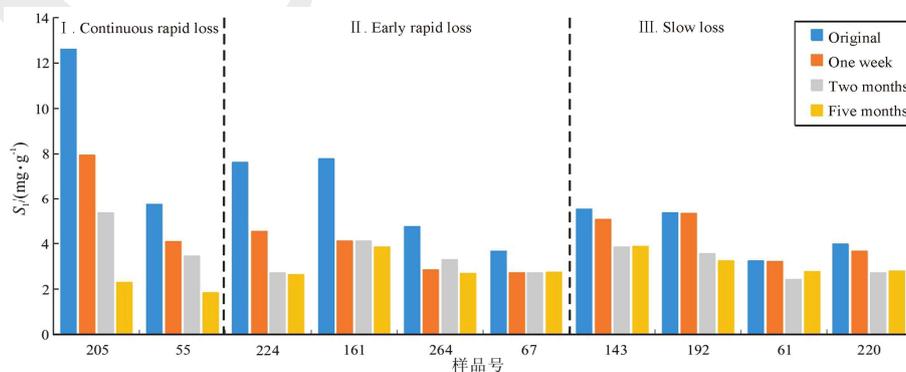


Fig. 2 Rock-Eval S_1 value changes of samples with different oil contents after storing

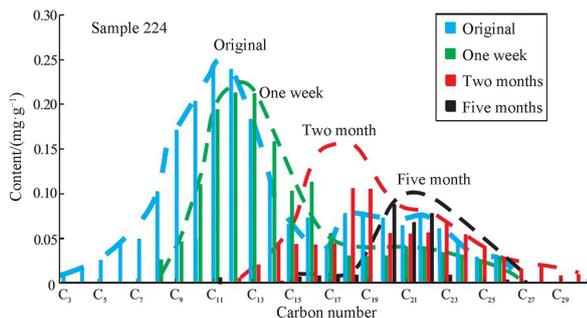


Fig. 3 Characteristics of hydrocarbon component changes of shale core samples with different storing time

result showed a positive correlation on the whole, but the correlation coefficient was extremely low, which indicates that the hydrocarbons of shale samples with different oil contents are continuously dissipated with the rise of storing time. However, it is by no means the single factor influencing the original hydrocarbon content. At the early stage of evaporative loss, the hydrocarbon evaporative loss in samples was mainly correlated with the permeability characteristics of shale and the original oil content in shale (Fig. 5). For example, samples 161 and 224 in this paper have a porosity of less than 5%, but their evaporative loss at the early stage was as high as 3 mg/g, with a relatively high evaporative loss ratio, which is mainly associated with their relatively high permeability and original oil content.

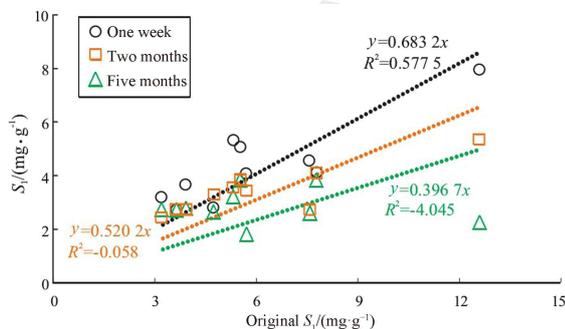


Fig. 4 Free hydrocarbon contents before and after different storing time

CHEN et al. [29] believed that the evaporative loss amount of free hydrocarbons is associated with total organic carbon

(TOC) content. The evaporative loss amount of free hydrocarbons in shale with high TOC is relatively small due to the adsorption effect. NOBLE et al. [41] conducted the storage experiment of crude oil with different API degrees at normal temperature, and studied the quality changes of crude oil after different storing times. They believed that the loss ratio of light hydrocarbons was correlated with the maturity and composition of crude oil, and the loss ratio of light crude oil (API° = 58) after 2 hours' storage could reach 60%. Limited by the sample conditions, the TOC of the samples selected in this paper was generally low (less than 2%), and they were sampled from the same horizon with similar maturity (Table 1). There was little change in the composition of hydrocarbon components, so we failed to discuss the effects of organic matter abundance, maturity and hydrocarbon components of shale samples on the evaporative loss of free hydrocarbons in this paper.

3.3.2 Discussion on correction coefficient of light hydrocarbons

The studies show that the content of light hydrocarbons in shale grows with the increase of maturity, and the content of light hydrocarbons plays an important role in the exploration and resource evaluation of continental shale oil with middle/high maturity. However, it is difficult to directly determine the content of light hydrocarbons due to its easy evaporative loss. Domestic scholars [16, 25] corrected the content of light hydrocarbons in the related studies by using different technical means, and established the corresponding correction recovery coefficient (Fig. 6). The higher the maturity of hydrocarbons is, the greater the light hydrocarbon content and hydrocarbon evaporative loss, and the larger the required correction coefficient will be, and they are in a proportional upward trend (the decrease of correction coefficient before R_0 is 0.9% in Reference [16] may be an illusion). There are different correction coefficients of light hydrocarbons for different evolution stages. The proportion of light hydrocarbons at low evolution stage is small, and the required recovery coefficient will also be small. However, the evaporative loss and recovery coefficient of light hydrocarbons are also larger due to the existence of a large number of light hydrocarbons at middle/high evolution stages. Moreover, unlike marine type-II organic matters, the light hydrocarbon generation stage of lacustrine type-I organic matters

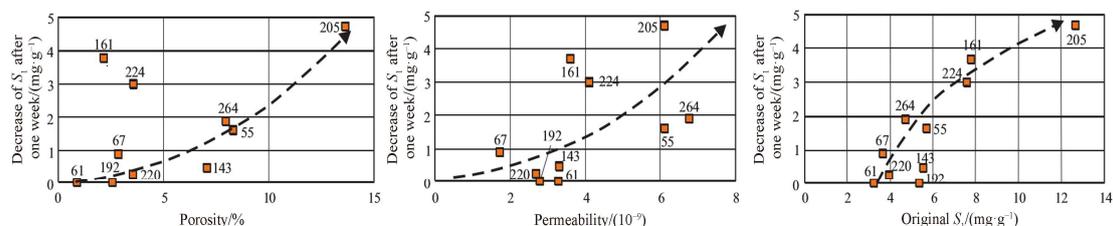


Fig. 5 Early loss vs. porosity, permeability and original oil content of samples

was relatively late and a higher activation energy would be needed [42]. The cracking of a large amount of organic matters into light hydrocarbons or gaseous hydrocarbons mainly occurred at the high evolution stage with $R_o \geq 1.3\%$. For this reason, it shall be more cautious to correct the light hydrocarbon recovery for medium/high maturity hydrocarbons.

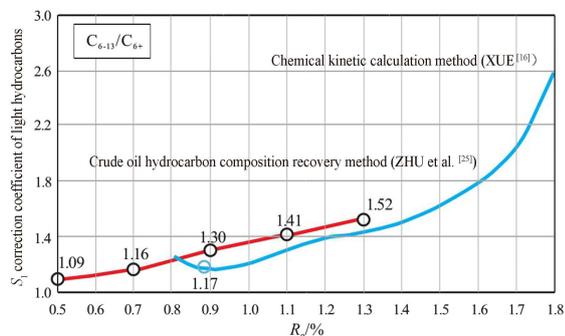


Fig. 6 Correction coefficient of light hydrocarbons commonly used

In this paper, from the early rapid evaporative loss stage to the late slow evaporative loss stage, the S_1 decrease of shale core samples was calculated as evaporative loss of light hydrocarbons, and the ratio of this value to the S_1 value of original fresh sample was the loss ratio. The ratio of this value to the S_1 value at slow loss stage is further calculated as the recovery coefficient of light hydrocarbons. The tested values and calculation results are shown in Table 3. The maturity R_o of the sample used in this paper was approximately 0.9 %, while the correction coefficient interval used by the existing light hydrocarbon correction methods should be 1.17–1.3 (Fig. 6). Based on the calculation, the light hydrocarbon evaporative loss recovery coefficient of the shale samples studied in this paper is actually at least 1.33–2.89 (Table 3), and the light hydrocarbon evaporative loss in the tripping-out process has not been taken into consideration. Hence, the author thinks that the existing recovery and correction coefficient of light hydrocarbons is obviously underestimated, and the objective and reasonable recovery and

correction coefficient of light hydrocarbons shall be further studied.

3.3.3 Discussion on geological significance of hydrocarbon evaporative loss in shale oil

The evaporative loss performance is different for hydrocarbons with different original oil contents. After the core samples are stored for a long time, the higher the original oil content is, the greater the hydrocarbon evaporative loss and the higher the loss ratio will be (Fig. 7). The comparison with the original oil content reveals that the loss ratio of hydrocarbons in high oil content samples is larger (Fig. 8), and the residual hydrocarbon amount after the evaporative loss can be much lower than that of tight shale samples with ordinary initial oil content. For example, the initial oil content S_1 of sample 205 is 12.6 mg/g, while its S_1 value is only 2.3 mg/g and its porosity is 13.4% after five months of storage. However, the initial oil content S_1 of sample 220 is 3.93 mg/g, the measured value of S_1 is 2.73 mg/g and the porosity is 3.84% similarly after five months of storage. If the original oil content is restored according to the relationship between maturity evolution and light hydrocarbon correction, the opposite evaluation results of oil content will inevitably be obtained. Comparatively speaking, the high oil-bearing reservoir, as the “sweet spot block” of shale oil, has better porosity and permeability conditions, and it is easier for its hydrocarbons to be lost. After a long-time storing, the hydrocarbon evaporative loss of core samples with high oil content is much greater than that of the compact shale samples with ordinary porosity and permeability conditions.

The exploration practice of high-yield shale oil regions in North America shows that the “sweet spot blocks” with high yield and enrichment of shale oil are generally the regions with higher thermal evolution of source rocks [43], high light hydrocarbon content, light oiliness, low crude oil viscosity and good mobility. For example, the shale oil in the Bakken Formation, a high shale oil province in the middle of the Williston Basin, is mostly the light crude oil with a density of less than 0.82 g/cm³. This shale oil system includes two sets

Table 3 Calculation results of corrective coefficients of Rock-Eval S_1 for different samples

Sample No.	Original S_1 content/(mg·g ⁻¹)	S_1 content at slow loss stage/(mg·g ⁻¹)	S_1 loss ratio/%	S_1 recovery coefficient
205	12.6			
55	5.72			
224	7.60	2.63	65.39	2.89
161	7.79	4.11	47.24	1.90
264	4.75	2.83	40.42	1.68
67	3.66	2.75	24.86	1.33
143	5.54	3.84	30.69	1.44
192	5.34	3.55	33.52	1.50
61	3.23	2.43	24.77	1.33
220	3.93	2.73	30.53	1.44

Note: Samples 205 and 55 have not yet entered the slow loss phase, so their recovery coefficient is not calculated in this paper.

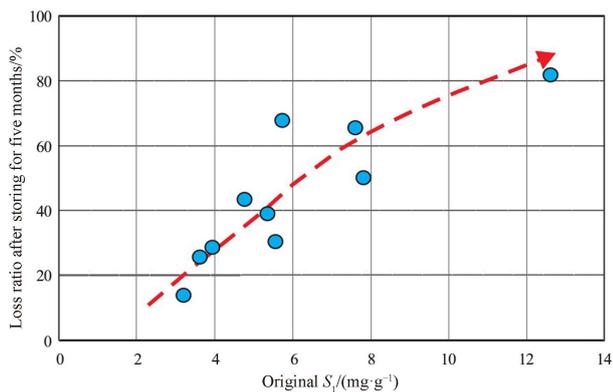


Fig. 7 Hydrocarbon loss ratio vs. original oil content of shale samples after long-time storing

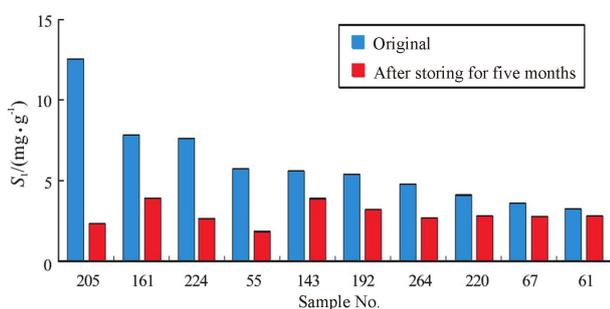


Fig. 8 Original S_1 value vs. S_1 value of different shale samples after storing for five months

of source rocks in the upper and lower members of the Bakken Formation and a high shale oil producing stratum in the middle member. The studies of JARVIE [28] showed that the chromatographic analysis results of crude oil produced in the middle interlayer were very similar to those of shale extracts in the upper member, and all of them were mainly light hydrocarbons with carbon number of lower than 15, while only some relatively heavy hydrocarbon components remained in the interlayer of dolomite sandstone and siltstone in the middle member of Bakken Formation. The studies of ALMANZA [44] showed that the average shale porosity of the upper and lower members of Bakken Formation was 1.7% and 3.1%, respectively, and the average permeability was $0.001 \times 10^{-9} \mu\text{m}^2$; the average porosity and permeability of dolomitic sandstone and siltstone in the middle member of Bakken Formation were 5.0% and $0.04 \times 10^{-3} \mu\text{m}^2$, respectively. The low-porosity tight shale formed the roof and floor of the shale oil system of the Bakken Formation and the sandstone layer with relatively good porosity and permeability in the middle member became the occurrence place of dissipated light hydrocarbons. In other words, the light hydrocarbon loss is not high in the tight shale oil reservoirs with low porosity and permeability, and it mostly lost in the “sweet spot section” of shale oil with better porosity and permeability.

4 Conclusion

The evaporative loss of hydrocarbons from shale oil is a continuous process, and the evaporative loss amount of hydrocarbons varies with the storing time of samples. Hydrocarbons with low carbon number in front of C_{13} – C_{15} are the main volatile components, while medium/heavy components are less affected. The amount and proportion of loss are closely correlated with its original oil content and porosity & permeability conditions. The bigger the original oil content and the better the porosity and permeability conditions, the greater the evaporative loss and the smaller the residual hydrocarbon content will be. Consequently, more attention shall be paid to the recovery of original hydrocarbon content for the oil-bearing property evaluation of “sweet spot sections” with high oil content and better porosity and permeability conditions when evaluating the oil-bearing property of shale. Of course, besides the influencing factors listed in this paper, there are many other factors that affect the hydrocarbon loss of shale oil (such as the type of drill bit and mud, the nature and composition of crude oil, the type of kerogen and evolution degree, the way of sample crushing and preservation, etc. during the drilling). Due to the limitations of the detection method in this paper, it is impossible to discuss them one by one. Hence, more in-depth studies and the solutions of key problems are needed to establish the recovery technology of hydrocarbon evaporative loss of shale oil under the influence of multiple factors.

References

- [1] LI Zhiming, TAO Guoliang, LI Maowen, et al. Discussion on prospecting potential of shale oil in the 3rd sub-member of the Triassic Chang 7 member in Binchang block, southwestern Ordos Basin[J]. *Oil&Gas Geology*, 2019, 40(3):558–570.
- [2] SONG Mingshui. Practice and current status of shale oil exploration in Jiyang Depression[J]. *Petroleum Geology and Recovery Efficiency*, 2019, 26(1):1–12.
- [3] KANG Yuzhu. Significant exploration progress and resource potential of unconventional oil and gas in China[J]. *Oil Forum*, 2018, 37(4):1–7.
- [4] LIN Tiefeng, ZHAO Ying, BAI Yunfeng, et al. Geological conditions and exploration potential for K_2qn (Upper Cretaceous Qingshankou Formation) shale oil reservoir in Gulong Sag[C]//Proceedings of International Field Exploration and Development Conference. Xi'an, China: Xi'an Huaxian Network Information Service Co., Ltd., 2018:767–769.
- [5] YANG Zhi, HOU Lianhua, LIN Senhu, et al. Geologic characteristics and exploration potential of tight oil and shale oil in Lucaogou Formation in Jimsar Sag[J]. *China Petroleum Exploration*, 2018, 23(4):76–85.
- [6] CUI Baowen, MENG Qi'an, BAI Xuefeng, et al. Petroleum exploration progress and suggestions for north Songliao Basin[J]. *Petroleum Geology&Oilfield Development in Daqing*, 2018, 37(3):1–9.
- [7] ZHAO Xianzheng, ZHOU Lihong, PU Xiugang, et al. Geological characteristics of shale rock system and shale oil exploration in a lacustrine basin: a case study from the Paleogene 1st sub-member of Kong 2 member in Cangdong Sag, Bohai Bay Basin, China[J]. *Petroleum Exploration and Development*, 2018, 45(3):361–372.
- [8] ZHOU Lihong, CHEN Changwei, HAN Guomeng, et al. Geological characteristics and shale oil exploration potential of lower first member of Shahejie Formation in Qikou Sag, Bohai Bay Basin[J]. *Earth Science*, 2019, 44(8):2736–2750.
- [9] JIN Zhijun, BAI Zhenrui, GAO Bo, et al. Has China ushered in the shale oil and gas revolution?[J]. *Oil&Gas Geology*, 2019, 40(3):451–458.
- [10] LI Maowen, MA Xiaoxiao, JIANG Qigui, et al. Enlightenment from

- formation conditions and enrichment characteristics of marine shale oil in North America[J]. *Petroleum Geology and Recovery Efficiency*, 2019, 26(1):13–28.
- [11] NING Fangxing, WANG Xuejun, HAO Xuefeng, et al. Occurrence mechanism of shale oil with different lithofacies in Jiyang Depression[J]. *Acta Petrolei Sinica*, 2017, 38(2):185–195.
- [12] KE Si. Discussion on occurrence state and mobility of shale oil in Biyang Depression[J]. *Petroleum Geology and Engineering*, 2017, 31(1):80–83.
- [13] CHEN Xiaohui. Advances in the research on the occurrence state and resources assessment of shale oil[J]. *Science Technology and Engineering*, 2017, 17(3):136–144.
- [14] LI Jijun, SHI Yinglin, HUANG Zhenkai, et al. Pore characteristics of continental shale and its impact on storage of shale oil in northern Songliao Basin[J]. *Journal of China University of Petroleum*, 2015, 39(4):27–34.
- [15] HE Jinyi, CAI Jingong, LEI Tianzhu, et al. Characteristics of soluble organic matter of Paleogene shale in Dongying Sag and prediction of shale oil “sweet spots”[J]. *Petroleum Geology and Recovery Efficiency*, 2019, 26(1):174–182.
- [16] XUE Haitao, TIAN Shansi, WANG Weiming, et al. Correction of oil content: one key parameter in shale oil resource assessment[J]. *Oil & Gas Geology*, 2016, 37(1):15–22.
- [17] LU Shuangfang, XUE Haitao, WANG Min, et al. Several key issues and research trends in evaluation of shale oil[J]. *Acta Petrolei Sinica*, 2016, 37(10):1309–1322.
- [18] NING Fangxing, WANG Xuejun, HAO Xuefeng, et al. Evaluation method of shale oil sweet spots in Jiyang Depression[J]. *Science Technology and Engineering*, 2015, 15(35):11–16.
- [19] WANG Min. Key parameter and calculation in shale oil reservoir evaluation[J]. *Acta Sedimentologica Sinica*, 2014, 32(1):174–181.
- [20] ZOU Caineng, YANG Zhi, CUI Jingwei, et al. Formation mechanism, geological characteristics and development strategy of nonmarine shale oil in China[J]. *Petroleum Exploration and Development*, 2013, 40(1):14–26.
- [21] SONG Guoqi, ZHANG Linye, LU Shuangfang, et al. Resource evaluation method for shale oil and its application[J]. *Earth Science Frontiers*, 2013, 20(4):221–228.
- [22] ENGEL M H, IMBUS S W, ZUMBERGE J E. Organic geochemical correlation of Oklahoma crude oils using R- and Q-mode factor analysis[J]. *Organic Geochemistry*, 1988, 12(2):157–170.
- [23] COOLES G P, MACKENZIE A S, QUIGLEY T M. Calculation of petroleum masses generated and expelled from source rocks[J]. *Organic Geochemistry*, 1986, 10(1/3):235–245.
- [24] HUNT J M, HUC A Y, WHELAN J K. Generation of light hydrocarbons in sedimentary rocks[J]. *Nature*, 1980, 288(5792):688–690.
- [25] ZHU Rifang, ZHANG Linye, LI Juyuan, et al. Quantitative evaluation of residual liquid hydrocarbons in shale[J]. *Acta Petrolei Sinica*, 2015, 36(1):13–18.
- [26] WANG Juan. Low-temperature closed extraction technology of light hydrocarbons and its application in evaluation of shale oil resource[J]. *China Petroleum Exploration*, 2015, 20(3):58–63.
- [27] LI Jinbu, LU Shuangfang, CHEN Guohui, et al. Correction of key parameters S₁ for shale oil resource evaluation in E₂S₂ section of Damintun Depression[C]//2014 China Earth Science Joint Academic Annual Meeting—Session 57: basin dynamics and unconventional energy. Beijing: Chinese Geophysical Society, 2014:2494–2496.
- [28] JARVIE D M. Shale resource systems for oil and gas: part 2: shale-oil resource systems[M]//BREYER J A. Shale reservoirs giant resources for the 21st century. Tulsa: AAPG, 2012:89–119.
- [29] CHEN Junqing, PANG Xiongqi, PANG Hong, et al. Hydrocarbon evaporative loss evaluation of lacustrine shale oil based on mass balance method: Permian Lucaogou Formation in Jimusaer Depression, Junggar Basin[J]. *Marine and Petroleum Geology*, 2018, 91:422–431.
- [30] JIANG Chunqing, CHEN Zhuoheng, MORT A, et al. Hydrocarbon evaporative loss from shale core samples as revealed by Rock-Eval and thermal desorption-gas chromatography analysis: its geochemical and geological implications[J]. *Marine and Petroleum Geology*, 2016, 70:294–303.
- [31] CHEN Zhuoheng, JIANG Chunqing. A data driven model for studying kerogen kinetics with application examples from Canadian sedimentary basins[J]. *Marine and Petroleum Geology*, 2015, 67:795–803.
- [32] LANG Dongsheng, GUO Shusheng, MA Dehua. The correlation method of pyrolysis parameters to evaluated hydrocarbon-bearing samples from reservoirs[J]. *Marine Origin Petroleum Geology*, 1996, 1(1):53–55.
- [33] LI Yuheng, WU Liyan, HUANG Jiushi. Oil storage rock pyrolysis geochemical logging evaluation technology[M]. Beijing: Petroleum Industry Press, 1993:165–171.
- [34] WU Xinsong, HAN Dexin, ZAN Xin, et al. Critical point analysis method for recovering pyrolysis parameters of rock cuttings[J]. *Acta Petrolei Sinica*, 2004, 25(4):46–49.
- [35] GUO Shusheng, LANG Dongsheng. Correction method of pyrolysis parameter S₁[J]. *Logging Technology*, 1997, 8(1):23–26.
- [36] PAN Zhiqing, MEI Bowen, SU Xiufang, et al. Thermolysis assessment method for reservoir oil potential[J]. *Oil & Gas Geology*, 1996, 17(4):353–355.
- [37] JIANG Qigui, LI Maowen, QIAN Menhui, et al. Experimental procedures of well-site geological evaluation for shale oil and related technological progress[J]. *Oil & Gas Geology*, 2019, 40(3):571–582.
- [38] JIANG Qigui, LI Maowen, MA Yuanyuan, et al. Molecular geochemical evaluation of shale oil mobility: a case study of shale oil in Jiyang Depression[J]. *Petroleum Geology & Experiment*, 2018, 40(6):849–854.
- [39] OKAMOTO K, WATANABE N, HAGIMOTO Y, et al. Evaporation characteristics of multi-component liquid[J]. *Journal of Loss Prevention in the Process Industries*, 2010, 23(1):89–97.
- [40] MACKAY D, MATSUGU R S. Evaporation rates of liquid hydrocarbon spills on land and water[J]. *The Canadian Journal of Chemical Engineering*, 1973, 51(4):434–439.
- [41] NOBLE R A, KALDI J G, ATKINSON C D. Oil saturation in shales: applications in seal evaluation[M]//SURDAM R C. Seals, traps, and the petroleum system. Tulsa, Oklahoma: AAPG, 1997:13–29.
- [42] KATZ B, LIN Fang. Lacustrine basin unconventional resource plays: key differences[J]. *Marine and Petroleum Geology*, 2014, 56:255–265.
- [43] LI Zhiming, RUI Xiaoqing, LI Maowen, et al. Characteristics of typical hybrid shale-oil system in North America and its implications[J]. *Journal of Jilin University (Earth Science Edition)*, 2015, 45(4):1060–1072.
- [44] ALMANZA A. Integrated three dimensional geological model of the Devonian Bakken Formation Elm Coulee Field, Williston Basin[D]. Richland county Montana: Colorado School of Mines, 2011.