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Evaluation of residual oil content, composition, and evolution of marine shale from the Middle Ordovician Pingliang Formation, Erdos Basin, China

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ABSTRACT
A grain-based microscale sealed vessel pyrolysis method to a whole rock sample from Pingliang (PL) marine shale was used to investigate the residual oil contents, fractional compositions and evolutions at different temperatures and maturities. The maximum residual oil of PL marine shale can reach 116.86 mg/g TOC. In oil window, PL marine shale residual oil is mainly composed of saturates, aromatics, and resins, but less asphaltenes showing higher shale oil prospective. In wet and dry gas windows, its residual oil is mainly made up of saturates, resins, and asphaltenes, showing higher gas generation potential at high maturities.

KEYWORDS
Grain-based MSSV pyrolysis; marine shale; fractional compositions; residual oil; evolution; Erdos basin

1. Introduction

During thermal maturation, portions of oil generated from source rock are expelled and the oil retained in shale is regarded as residual oil (Gai et al., 2015). The residual oil in the shale oil will crack into gases with further thermal maturation (Tissot and Welte, 1984). Recent studies and explorations have shown great potentials of unconventional oil gas resources such as shale gas and shale oil, which shows important roles of retained hydrocarbons in source rocks. Numerous studies have been conducted to determine how oil composition changes with thermal stress on the kinetics of kerogen and oil cracking (Bjorøy et al., 1988; Ungerer et al., 1988; Behar et al., 1991; Behar et al., 1992; Horsfield et al., 1992; Kuo and Michael, 1994; Pepper and Dodd, 1995; Schenk et al., 1997; Tsuzuki et al., 1999; Hill et al., 2003), but the evolution of residual oil and its fractional compositions in the process of maturation for whole rock has not been intensively studied.

In this study, a grain-based MSVV (microscale sealed vessel) pyrolysis method was designed to explore how residual oil contents and its fractional compositions evolutions at different temperatures and maturities. A marine shale from Pingliang Formation of Erdos basin was used for pyrolysis to simulate the process of maturation. Different from the routine pyrolysis, our method simulated both hydrocarbon generation and expulsion processes, and the residual rock grains were used to analyze the residual oil contents and fractional compositions.

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Table 1. Geochemical data for marine shale from Pingliang Formation, Erdos Basin, China.

Sample	Lithology	Location	Stratum	TOC,%	S1, mg/g	S2, mg/g	Tmax,°C	HI, (mg/g TOC)	Ro,%
PL	Marine shale	Erdos basin	O2p	25.95	5.47	98.38	429	379	0.60

TOC, total organic carbon; S1, the amount of free (indigenous) hydrocarbons; S2, Pyrolysis of hydrocarbons; HI, hydrocarbon index; *T*max, pyrolysis temperature at maximum HC generation; Ro, vitrinite reflectance.

2. Samples and experiments

2.1. Samples

The marine shale sample was selected from Pingliang Formation in Erdos Basin, China. The geochemical data for the marine shale presented in Table 1 show that sample has higher TOC contents and lower maturities, which are suitable for simulation.

2.2. Pyrolysis

The sample with a grain size of 2–4 mm were put into glass tubes or vessels (when T >500°C, we used quartz vessels) and sealed under vacuum condition. These glass vessels were heated in the muffle furnace from room temperature to a preset temperature for 72 h. Pyrolysis temperature was set within a range of 250°C to 600°C at 50°C interval. After pyrolysis, the generated gases including C_1 to C_5 gases at each temperature point were analyzed using gas chromatography (GC).

The surface of the whole rock grain and the glass vessels were cleaned with dichloromethane and the solvated oil were regarded as the expelled oil. The rest of the whole rock grain was used to extract the residual oil (C_{14}+) with dichloromethane. The extracts were weighted after the dichloromethane solvents were completely evaporated, which were regarded as residual and expelled oil. And then, the residual oil (C_{14}+) was treated with excess n-hexane to precipitate asphaltenes. Saturates, aromatics, and resins fractions were obtained by elution with n-hexane, benzene (n-hexane:dichloromethane = 7:3) and ethanol, respectively (Li et al., 2001; Pan et al., 2015). Finally, the separated solvents of fractional compositions were evaporated from the extracts and the extracts weighed. The experimental procedures and products analysis were in detail described by Liao et al. (2016).

3. Results and discussion

3.1. Oil/gas windows of PL marine shale

According to the method presented in Liao et al (2015), oil and gas windows were determined using the yield of C_{14}+ oil, C_2–C_5 wet gases, and dry gas (C_1; Liao et al., 2016; Wang et al., 2008). Figure 1 shows

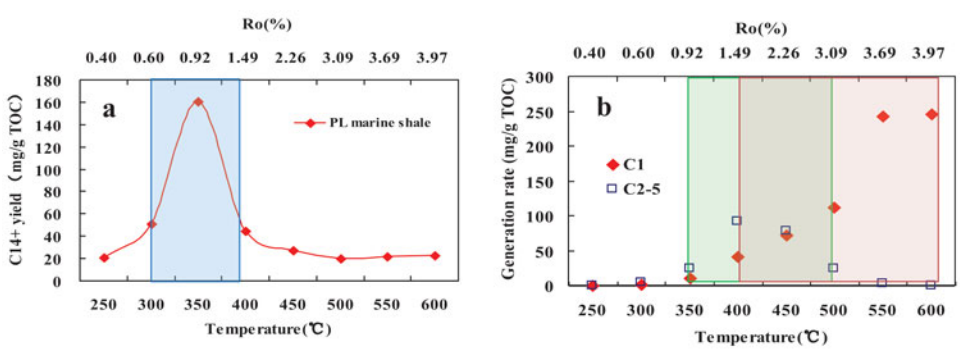

Figure 1. Division of oil window, wet gas window, and dry gas window for PL marine shale. (a) Oil window variation. (b) Solid square represents wet gas window while dashed square represents dry gas window for PL marine shale.

Table 2. Residual oil contents of PL marine shale and their fractional compositions, wet gas yield, and dry gas yield with increasing maturities.

T,°C	Ro,%	Residual oil, mg/g TOC	Saturates, mg/g TOC	Aromatics, mg/g TOC	Resin, mg/g TOC	Asphaltene, mg/g TOC	Wet gas yield, mg/g TOC	Dry gas yield, mg/g TOC
250	0.40	16.44	6.74	2.27	7.15	0.28	0.31	0.10
300	0.60	31.60	11.56	11.36	8.22	0.46	4.19	1.95
350	0.92	116.86	30.04	38.12	30.91	17.78	25.21	10.76
400	1.49	39.73	13.20	13.23	8.12	5.18	92.98	42.12
450	2.26	23.90	11.19	5.80	5.93	0.98	77.88	71.88
500	3.09	14.00	5.85	2.04	2.16	3.95	25.27	112.06
550	3.69	14.39	4.28	2.36	3.53	4.21	2.86	243.69
600	3.97	17.37	7.78	1.12	4.37	4.10	0.00	245.49

the yield curve of $C_{14}+$ oil, wet gases (C_2–C_5), and dry gas (C_1) against pyrolysis temperature/maturity from PL marine shale. The oil window, wet gas window, and dry gas window of PL marine shale were determined as 0.6–1.3% Ro, 0.9–3.0% Ro, and 1.3–4.0% Ro, respectively.

3.2. Residual oil contents and evolution

Table 2 lists the residual oil contents of PL marine shale and their fractional compositions with increasing maturities. For better discussing the evolution of the residual oil, the evolution process was divided into four stages: initial maturity (Ro = 0.4%), oil window, wet gas window, and dry gas window.

Figure 2 shows the evolution of residual oil of PL marine shale with increasing maturity. The residual oil of PL marine shale shows typical unimodal pattern where the only peak of residual oil occurs in oil window. The corresponding maturity to maximum residual oil of PL marine shale is 0.92%. In initial Ro% (Ro = 0.4%), the total residual oil contents of PL marine shale is 16.44 mg/g TOC.

In the oil window, the residual oil yields of PL marine shale reach the maximum level around 116.86 mg/g TOC. The result indicates that the oil generation potential is the main control of residual oil in source rocks. In wet gas window (Ro = 1.49%), the maximum residual oil contents of PL marine shale reach 39.73 mg/g TOC while in dry gas window (Ro = 3.69%), the residual oil contents of PL marine shale are still as higher as 14.39 mg/g TOC. The content of residual oil decreases after the maximum is reached which may be caused by faster cracking into wet gas or lighter components of residual oil with increasing thermal maturity in the closed system (Cao et al., 2014). The residual oil contents of PL marine shale are relatively higher even at high maturity stages (Ro = 1.49–3.69%), which implies its very high gas potential at this stage.

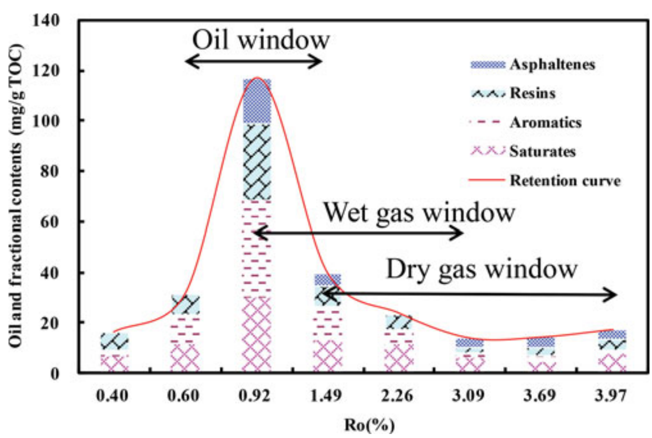

Figure 2. Evolution in residual oil and its fractions with increasing thermal maturity of PL marine shale.

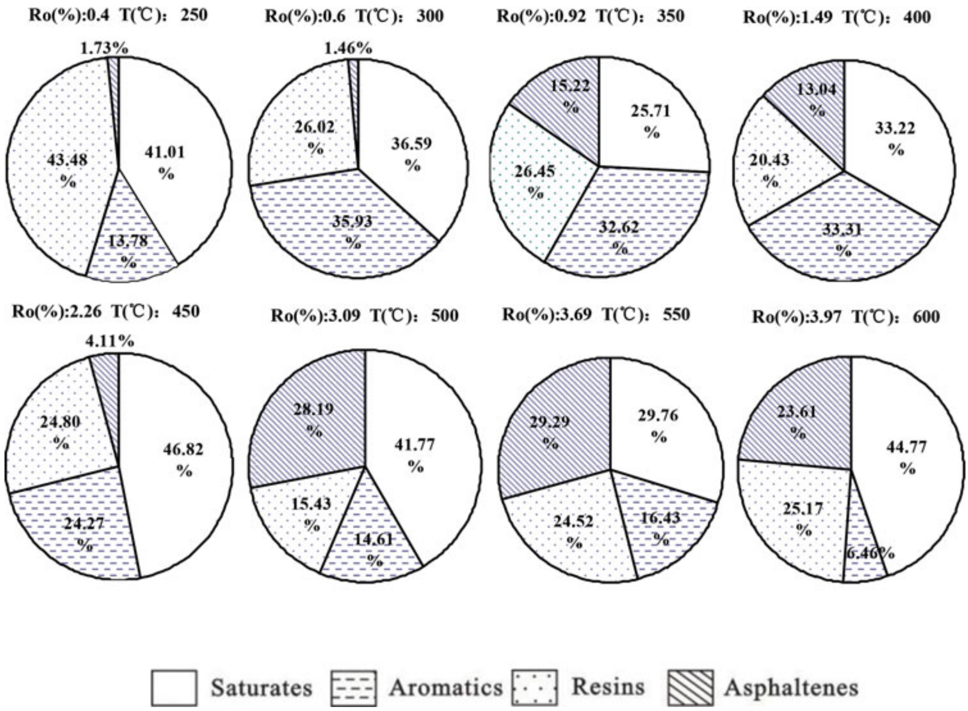

Figure 3. Proportions of saturates, aromatics, resins. and asphaltenes of PL marine shale with increasing thermal maturity.

3.3. Fractional composition and evolution of residual oil

Residual oil was separated into four fractional groups, which are saturates, aromatics, resins, and asphaltenes in this study. The contents and proportions may change accordingly with increasing thermal maturity. Table 2 also lists the fractional compositional content of PL marine shale at different thermal maturity stages. Figures 2 and 3 show the fractional composition variations and proportions of PL marine shale in the whole process of maturation.

In initial state (Ro = 0.4%), the contents and proportions of saturates, aromatics, resins and alphaltenes generated from PL marine shale are 6.74 mg/g TOC (41.01%), 2.27 mg/g TOC (13.78%), 7.15 mg/g TOC (43.48%), and 0.28 mg/g TOC (1.73%). At this stage, source rock has not yet begun to expel hydrocarbon. The fractional components of residual oil from PL marine shale are mainly saturates, aromatics and resins at this stage.

In oil window (Ro = 0.92%), the contents and proportions of the fractional compositional contents and proportions generated from PL marine shale are 30.04 mg/g TOC (25.71%), 38.12 mg/g TOC (32.62%), 30.91 mg/g TOC (26.45%), and 17.78 mg/g TOC (15.22%). At this stage, the fractional components of residual oil from PL marine shale are mainly saturates, aromatics, and resins.

Wet gas window is the transition between oil and dry gas generation. Parts of heavy hydrocarbon will be cracked into wet gas and condensate in this stage. In wet gas window (Ro = 1.49%), the contents and proportions of saturates, aromatics, resins, and alphaltenes of the residual oil from PL marine shale are 13.20 mg/g TOC (33.22%), 13.23 mg/g TOC (33.11%), 8.12 mg/g TOC (20.43%), and 5.18 mg/g TOC (13.04%), respectively. The fractional components of residual oil from PL marine shale are mainly saturates, aromatics, and resins but less asphaltenes. Compared with oil window, four fractional components contents of PL marine shale decreased rapidly, the reason for this is that the heavy hydrocarbons and nonhydrocarbons retained in source rock cracked into wet gases and condensate (Petersen et al., 2002).

The dry gas window is the main generation period of methane. The total residual oil yield is very low, but there are still some saturates, aromatics, resins, and alphaltenes retained in source rock. In dry gas window (Ro = 3.69%), the contents and proportions of saturates, aromatics, resins and alphaltenes of residual oil generated from PL marine shale are 4.28 mg/g TOC (29.76%), 2.36 mg/g TOC (16.43%), 3.53 mg/g TOC (24.52%), and 4.21 mg/g TOC (29.29%), respectively. The result show that PL marine shale is still having saturated hydrocarbons in high maturity that may be caused by higher stability of saturates. Figure 1b shows PL marine shale can generate amounts of dry gas and the methane yield is much higher than wet gas.

3.4. Residual oil and potentials for unconventional oil and gas

Residual oil and its fractional components contents from source rock determine the potential of shale oil and shale gas exploration. In this study, the residual oil yields of PL marine shale reach the maximum levels in oil window, which are 116.86 mg/g TOC. The proportions of saturate and aromatic hydrocarbons of residual oil from PL marine shale are over 50% at this stage. The residual oil content of PL marine shale is higher with high proportion of saturates and aromatics hydrocarbons in low maturity which shows higher shale oil prospective. At higher maturation stages such as wet gas window and dry gas window, the residual oil contents decrease quickly due to expulsion and cracking into gases. Although the proportions of resins and asphaltenes of residual oil from PL marine shale are more than 50% at higher maturities, the contents of saturates and aromatics hydrocarbons are still very higher. Considering that the fractional compositions have different expulsion efficiency and the ability to crack into gas, PL marine shale shows very higher potential of methane generation at high maturities. Our results show the wet gas yield of residual oil from PL marine shale is 92.98 mg/g TOC and dry gas yield reaches 243.69 mg/g TOC, which indicates that marine shale still has good exploration potential of shale gas even at higher maturities. The content and evolution of fractional compositions of residual oil from PL marine shale provides possibilities for evaluating exploration prospective quantitatively of shale oil and shale gas.

4. Conclusions

The contents and evolution of residual oil and its fractional compositions were studied by a grain-based microscale sealed vessel pyrolysis method to whole rock. The oil window, wet gas window and dry gas window of PL marine shale were determined as 0.6–1.3% Ro, 0.9–3.0% Ro, and 1.3–4.0% Ro, respectively. The residual oil of PL marine shale reaches the maximum contents in oil window, which are 116.86 mg/g TOC. PL marine shale shows mainly saturates, aromatics and resins fractions but less asphaltenes fraction at low maturity and mainly asphaltenes, resins, and saturates but less aromatics fraction at high thermal stages. The residual oil content of PL marine shale is higher with high proportion of saturates and aromatics hydrocarbons in low maturity which show higher shale oil prospective. At higher maturation stages, the contents of resins and asphaltenes from PL marine shale are still much higher, which indicates that shale is still showing very higher potential of methane generation at high maturities. The results of residual oil contents and their fractional compositions from marine shale at different maturities provide a quantitative way for evaluating exploration prospective of shale oil and shale gas.

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