

Experimental Study on Fractional Compositions of Residual Oil from Shale and Coal of China Using Grain-Based MSSV Pyrolysis

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ABSTRACT: For better understanding compositions and evolutions of residual oil of shale and coal, a grain-based microscale sealed vessel (MSSV) pyrolysis method to whole rock was used to investigate the residual oil contents and its fractional compositions from shale, coal, and coaly shale samples, as well as their variations at different temperatures and maturities. Quantities of extracted oil from residuals and yields of C1 to C5 gases were used to define oil, wet gas, and dry gas windows using equivalent Ro (%) calculated through EasyRo (%) method. Oil windows are defined as 0.6–1.3%Ro for shale and 0.5–1.2%Ro for coal; wet gas windows are 0.9–3.0%Ro for shale and 0.8–2.7%Ro for coal, and dry gas window are 1.3–4.0%Ro for shale and 1.2–4.0%Ro for coal, respectively. Coal shows relatively wider oil window than shale but similar gas window to shale. The maximum residual oil can reach 133.44 mg/g TOC, 69.84 mg/g TOC for marine and lacustrine shale, 10.03 mg/g TOC for coal, and 83.79 mg/g TOC for coaly shale, respectively. Comparing with natural residual oil, the laboratory residual oil of shale is much higher, while the residual oil in coal is mainly retained due to its unique structures. The results show that, in oil window, marine and lacustrine shale residual oil show mainly saturates, aromatics, resins but less asphaltenes, while coal residual oil are mainly asphaltenes, aromatics, resins but less saturates. In the wet and dry gas window, marine and lacustrine shale residual oil is mainly made up of saturates, aromatics, and resins, while coal residual oil is mainly made up of asphaltenes and resins. These results suggest that residual oil contents of marine shale, lacustrine shale, and coaly shale are higher with high proportions of saturated and aromatic hydrocarbons in low maturities which show high shale oil prospective than coal, while in high maturities the residual oil contents decrease quickly but still have higher potential for cracking gases which might become the source of shale gas. The residual oil in coal is low mainly in forms of aromatics, resins, and asphaltenes, which can only be the source of coal-bed methane as maturity increases.

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.¹ The residual oil in the shale and coal oil will crack into gases with further thermal maturation.² 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. Coals are both sources and reservoirs of large amounts of gas that has also received increasing attention in recent years as a largely untapped potential energy resource including coal-bed methane.³ Numerous studies have been conducted to determine how oil composition changes with thermal stress on the kinetics of kerogen and oil cracking,^{4–13} but the evolution of residual oil and its fractional compositions in the process of maturation for whole-rock has not been intensively studied.

In the current study we designed a grain-based MSVV (microscaled sealed vessel) pyrolysis method to explore how residual oil contents and its fractional compositions evolutions at different temperatures and maturities. Four low matured samples of marine, lacustrine shale, coal, and coaly shale from China were 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.

2. SAMPLES AND EXPERIMENTS

2.1. Samples. Four low matured whole-rock samples representing different lithologies were selected, including one marine shale (XHY) from Zhangjiakou, one lacustrine shale (YC) from Erdos basin, one coal (GY) from Sichuan basin, and one coaly shale (LS) from Sichuan basin. The sample locations are shown in Figure 1. The geochemical data listed in Table 1 show that four samples have higher TOC contents and lower maturities which are suitable for simulation. Unlike routine pyrolysis where one sample is used in different temperatures, we used different samples in different temperature in this study. To make sure that the samples in different temperatures are identical and the influence of sample heterogeneity is negligible, we tried to take samples from one rock using microdrilling method along vertical direction because the heterogeneity of shale rock is mainly along horizontal direction. Figure 2 shows our sample drilling method along vertical direction at the same horizontal bed. After crushing and sieving, samples were checked under microscope and X-ray diffraction (XRD) to make sure their mineral compositions are identical.

2.2. Experimental Methods. Figure 3 shows the whole process of experimental method including pyrolysis, isolation of residual, and

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Figure 1. Location map of samples used in this paper (1. XHY marine shale; 2. YC lacustrine shale; 3. GY coal and LS coaly shale).

expelled oil as well as separation of fractional compositions of residual oils.

2.2.1. Pyrolysis. For better simulating the process of hydrocarbons retention and expulsion, we designed a grain-based MSSV (Micro-scaled sealed vessel) pyrolysis method on whole rock. Different from routine MSSV pyrolysis, our method is conducted on whole rock grain rather than powder or extracted kerogen. Four samples with a grain size of 2–4 mm were putted 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 250–600 °C at 50 °C interval. After pyrolysis, the generated gases including C_1 to C_5 gases at each temperature point were analyzed using GC (gas chromatography). Then, the residual whole-rock grains and glass vessels were used to subsequently analyze residual and expelled oil, respectively. Considering high volatility of C_6 – C_{13} components, the residual oil in this study is mainly composed of C_{14+} hydrocarbons.

2.2.2. Isolation of Residual and Expelled Oil. 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 whole rock grain was used to extract the residual oil (C_{14+}) with dichloromethane. The cleaned and extracted solvents were collected separately with conical flask and were volatilized to 1–2 mL by a rotary evaporator and then were transferred to 5 mL bottles by dichloromethane. Finally, the transferred extracts were weighted after the dichloromethane solvents were completely evaporated, which were regarded as residual and expelled oil.

2.2.3. Separation of Fractional Compositions of Residual Oil. The residual oil (C_{14+}) was treated with excess *n*-hexane to precipitate asphaltenes. The *n*-hexane solvents were fractionated using a 10 mm i.d. column packed with a 4:1 mixture of preactivated silica gel (100–200) and alumina (100–200 mesh). Saturates, aromatics, and resins fractions were obtained by elution with *n*-hexane, benzene (*n*-hexane:dichloromethane = 7:3) and ethanol, respectively.^{14,15} The separated solvents of fractional compositions were collected separately

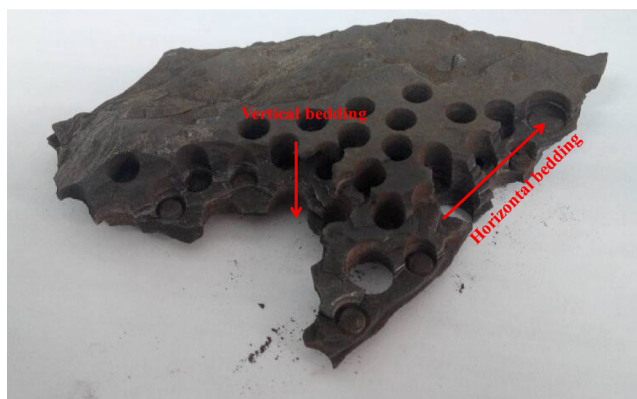


Figure 2. A picture showing our sample taking way by microdrilling along vertical direction from one rock sample.

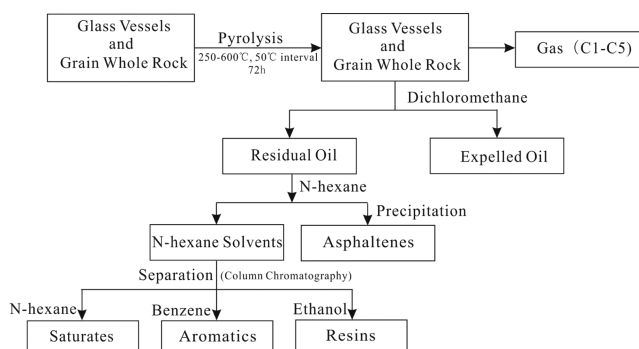


Figure 3. Flowchart of experimental method.

with conical flask and were volatilized to 1–2 mL by a rotary evaporator. Then they were transferred to 5 mL bottles by dichloromethane. Finally, the transferred separated solvents of fractional compositions were weighted after the dichloromethane solvents were completely evaporated.

3. RESULTS AND DISCUSSION

3.1. Oil/Gas Windows Determined by Whole-Rock Grain Pyrolysis. “Oil window” is a definite and specific temperature or maturity scale for oil generation,^{2,16,17} and “gas window” is similarly referred to the peak generation stages of gaseous hydrocarbons. Considering the gas compositions include C_1 – C_5 gases, the determination of “gas window” is relatively complicated. Here, we defined two types of gas windows: wet gas window and dry gas window. In this paper, oil window is defined according to the yields of C_{14+} hydrocarbons including expelled and residual ones; wet gas window is defined according to the yields of C_2 – C_5 gases, and dry gas window is defined according to the yields of C_1 gas.

Previous studies showed that the gases generated in gas window should account for 60–80% of the total gas

Table 1. Geochemical Data for Samples Used in the Study^a

sample	lithology	location	age	TOC (%)	S1 (mg/g)	S2 (mg/g)	T_{max} (°C)	HI (mg/g TOC)	Ro (%)
XHY	marine shale	Zhangjiakou	Pt ₂	9.15	1.25	36.49	432	399	0.63
YC	lacustrine shale	Erdos Basin	T ₃ y	23.41	8.10	79.01	435	338	0.64
GY	coal	Sichuan Basin	T ₃ x	73.34	0.34	90.34	443	123	0.67
LS	coaly shale	Sichuan Basin	P ₁ l	16.97	0.77	24.49	444	144	0.67

^aTOC, total organic carbon; S1, free (indigenous) hydrocarbons; S2, pyrolysis of HCs; HI, hydrocarbon index; T_{max} , pyrolysis temperature at maximum HC generation; Ro, vitrinite reflectance for coal and equivalent reflectance of solid bitumen for marine and lacustrine shale.

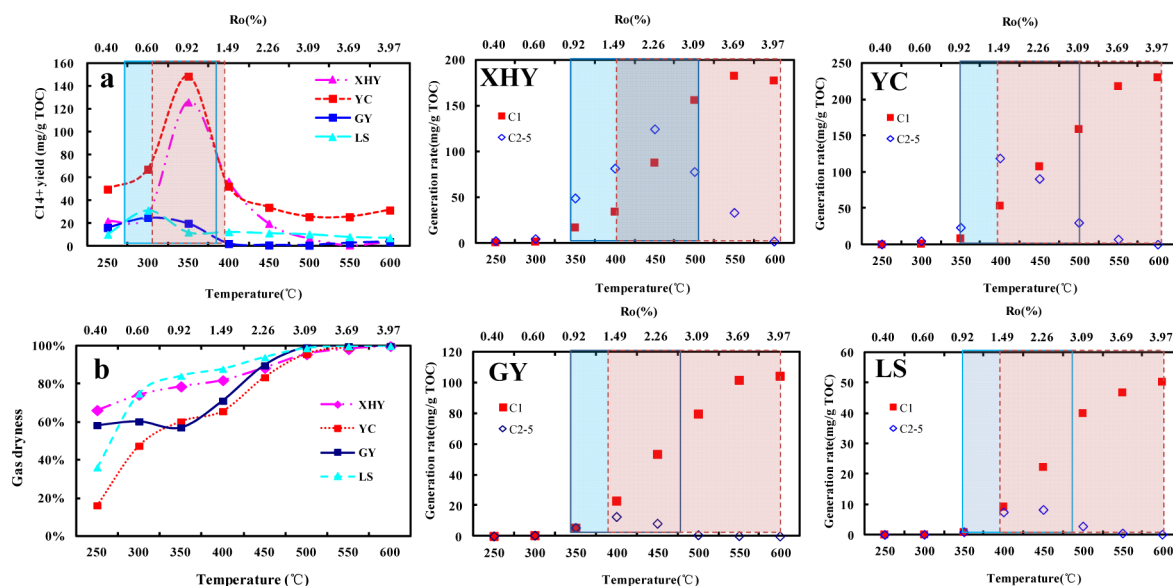


Figure 4. Comparisons of oil window, wet gas window, and dry gas window of shale and coal (solid square represents oil window of GY coal and LS coaly shale, while dashed square represents oil window of XHY, YC, and GY shale in part a. Solid squares in other four plots represent wet gas windows for XHY, YC, GY, and LS, respectively, while dashed squares represent dry gas windows for XHY, YC, GY, and LS, respectively. Part b shows the variations of gas dryness of four samples for comparison).

potential.^{18–21} In this paper, oil and gas window were defined according to the yields of oil/gas that account for at least 60% in the main gas-generation of the total oil and gas.¹⁸ Figure 4 shows the yield curve of C14+ oil, wet gases (C2–C5), and dry gas (C1) against pyrolysis temperature/maturity from XHY and YC shale, GY coal, and LS coaly shale. According to the methods above, the oil window, wet gas window, and dry gas window were determined and labeled. The oil windows are defined as 0.6–1.3%Ro for shale and 0.5–1.2%Ro for coal; wet gas window were defined as 0.9–3.0%Ro for shale and 0.8–2.7%Ro for coal; dry gas window were defined as 1.3–4.0%Ro for shale and 1.2–4.0%Ro for coal. Table 2 listed the maturity

Table 2. Maturity Ranges (in Ro%) of the Oil Window, Wet Gas Window, and Dry Gas Window for Shale and Coal

samples	initial Ro (%)	oil window (% Ro)	wet gas window (% Ro)	dry gas window (% Ro)
XHY shale	0.4	0.6–1.3	0.9–3.0	1.3–4.0
YC shale	0.4	0.6–1.3	0.9–3.0	1.3–4.0
GY coal	0.4	0.5–1.2	0.8–2.7	1.2–4.0
LS coaly shale	0.4	0.5–1.2	0.8–2.7	1.2–4.0

ranges (in Ro%) of the oil window, wet gas window, and dry gas window for shale and coal from the samples of this study. Comparing with the gas window of type II kerogen for marine shale in Zhangjiakou which is $Ro \% = 1.5–3.0\%$ in closed system,¹⁸ the results from whole-rock pyrolysis in this study show broader and later gas windows than pure kerogen. The main reason is that whole-rock pyrolysis reflects both hydrocarbon generation and expulsion while pure kerogen pyrolysis only reflects the hydrocarbon generation. In Figure 4a coal and coaly shale show broader oil window than marine and lacustrine shale which is caused by earlier oil generation onset temperature/maturity and later oil expulsion. Previous studies show that activation energy is relatively low for oil generation for type III kerogen from coal and coaly shale in contrast to marine and lacustrine shale which makes coal show lower oil

generation onset temperature/maturity.²² Coal enjoys higher porosity and higher adsorption capability to oils which makes oils difficult to be expelled out.^{23,24} This is the main reason for coal and coaly shale show later ending of oil window comparing with shale. Interestingly, shale and coal show very similar gas windows for both wet and dry ones, which suggests that source rock types and properties have great influence on oil expulsion but less influence on gas expulsion.

3.2. Residual Oil Contents and Evolutions. Table 3 listed the residual oil contents of four samples XHY, YC, GY, and LS 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 5 shows the evolution of residual oil of shale, coal, and coaly shale with increasing maturity. The residual oil of coal and coaly shale show typical episodic hydrocarbon expulsion pattern which is more obvious for coal. The first peak of residual oil occurs in oil window, and the second peak of residual oil occurs in dry gas window. The residual oil of marine shale and lacustrine shale show typical unimodal pattern where the only peak of residual oil occurs in oil window. The corresponding maturity to maximum residual oil of shale, coaly shale, and coal are 0.92%, 0.92%, and 0.6%, respectively. In initial Ro% ($Ro = 0.4\%$), the total residual oil contents of XHY and YC shale, GY coal, and LS coaly shale are 14.85 mg/g TOC, 34.54 mg/g TOC, 4.55 mg/g TOC, and 6.25 mg/g TOC, respectively. Lacustrine shale (YC) shows the highest residual oil content followed by marine shale (XHY) and coaly shale (GY). Coal (GY) shows the lowest content of residual oil.

In oil window, the residual oil yields of XHY and YC shale, GY coal, and LS coaly shale reach the maximum levels which are 133.44 mg/g TOC, 69.84 mg/g TOC, 10.03 mg/g TOC, and 83.79 mg/g TOC, respectively. These results indicate that the oil generation potential is the main control of residual oil in source rocks. The other important factor to control the residual oil contents is the physico-chemical properties of source rocks

Table 3. Residual Oil Contents of XHY, YC, GY, and LS and Their Fractional Compositions with Increasing Maturities

XHY						YC				
Ro(%)	residual oil (mg/g TOC)	saturates (mg/g TOC)	aromatics (mg/g TOC)	resin (mg/g TOC)	asphaltene (mg/g TOC)	residual oil (mg/g TOC)	saturates (mg/g TOC)	aromatics (mg/g TOC)	resin (mg/g TOC)	asphaltene (mg/g TOC)
0.40	14.85	3.64	5.98	5.13	0.11	34.54	15.41	5.21	13.19	0.73
0.60	18.67	4.23	6.84	7.15	0.45	37.30	18.17	8.45	9.85	0.83
0.92	133.44	38.93	34.32	31.56	28.64	69.84	23.02	15.24	24.82	6.75
1.49	60.41	13.69	19.68	20.68	6.35	34.70	11.04	10.70	10.33	2.63
2.26	13.40	9.24	1.76	2.01	0.39	17.09	8.17	0.63	8.15	0.14
3.09	8.61	1.71	2.63	3.48	0.79	14.39	9.46	0.88	3.47	0.58
3.69	4.61	0.86	2.49	1.12	0.15	12.28	6.34	2.04	3.43	0.48
3.97	4.71	2.25	1.05	1.20	0.21	21.40	8.36	2.13	9.63	1.28
GY						LS				
Ro(%)	residual oil (mg/g TOC)	saturates (mg/g TOC)	aromatics (mg/g TOC)	resin (mg/g TOC)	asphaltene (mg/g TOC)	residual oil (mg/g TOC)	saturates (mg/g TOC)	aromatics (mg/g TOC)	resin (mg/g TOC)	asphaltene (mg/g TOC)
0.40	4.55	0.42	1.65	1.73	0.75	6.25	1.48	1.01	3.50	0.25
0.60	10.03	0.49	2.20	2.69	4.65	8.18	1.49	2.53	3.18	0.99
0.92	7.88	0.45	1.92	3.73	1.79	83.79	9.90	18.38	40.83	14.67
1.49	4.56	0.67	1.04	2.07	0.79	5.32	0.80	1.70	2.23	0.60
2.26	1.02	0.07	0.06	0.69	0.20	3.50	0.91	0.54	1.97	0.09
3.09	3.85	0.17	0.21	2.34	1.12	13.01	6.01	0.35	6.04	0.61
3.69	1.62	0.11	0.07	1.44	0.00	39.61	3.07	3.98	19.35	13.20
3.97	3.18	0.00	0.11	2.91	0.16	14.98	1.55	4.00	5.22	4.22

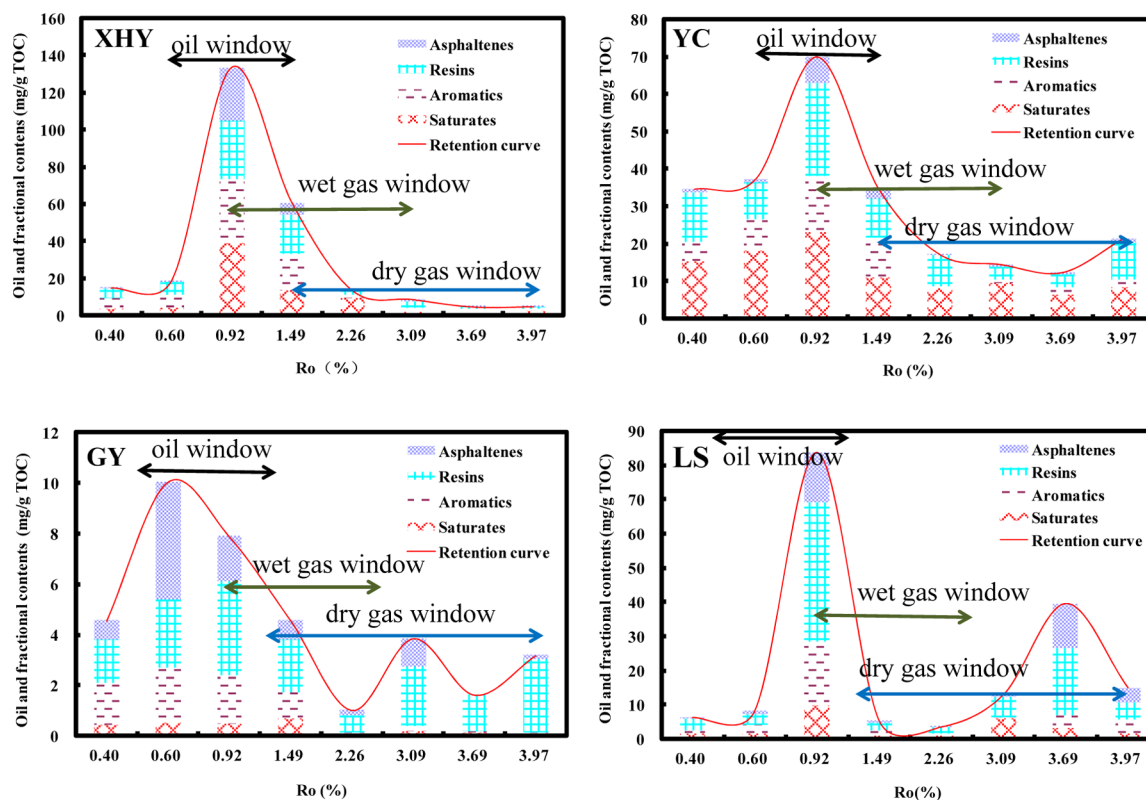


Figure 5. Evolution in residual oil and its fractions with increasing thermal maturity.

which influence the oil expulsion. Taking XHY and YC shale as examples, they show similar oil generation potentials (Figure 4a) but very different residual oil contents (Figure 5), which might be caused by the different physico-chemical properties of these two source rocks.

In wet gas window ($Ro = 1.49\%$), the maximum residual oil contents of XHY and YC shale, GY coal, and LS coaly shale

reach 60.41 mg/g TOC, 34.7 mg/g TOC, 4.56 mg/g TOC, and 5.32 mg/g TOC, respectively, while in dry gas window ($Ro = 3.69\%$), the contents of XHY and YC shale, GY coal, and LS coaly shale are still 4.61 mg/g TOC, 12.28 mg/g TOC, 1.62 mg/g TOC, and 39.61 mg/g TOC, respectively. The contents 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.^{25,26} Coal shows the lowest residual oil contents in whole process of thermal evolution which may be related to its poor hydrogen contents. Previous study has suggested that hydrogen-rich coals are few. Only a few commercial oil discoveries can be confidently correlated to coals. Therefore, most coals are hydrogen poor which are mainly source of gas in the process of thermal maturation.²⁷ The residual oil contents of shale are relatively higher even at high maturity stages ($R_o = 1.49\text{--}3.69\%$). LS coaly shale shows the highest residual oil content even in dry gas window which implies its very high gas potential at this stage.

Here, we also compared our residual oil results in laboratory with natural samples in geological conditions. Because Rock-Eval S1 is the dominant measurement of residual oil of natural samples, we used it as a proxy of residual oil at geological conditions. We selected the data of 2200 natural samples from USGS organic geochemical database (<http://energy.cr.usgs.gov/prov/og/>) and plotted the S1 against the maturities. It could be found from Figure 6 that the laboratory residual oil of

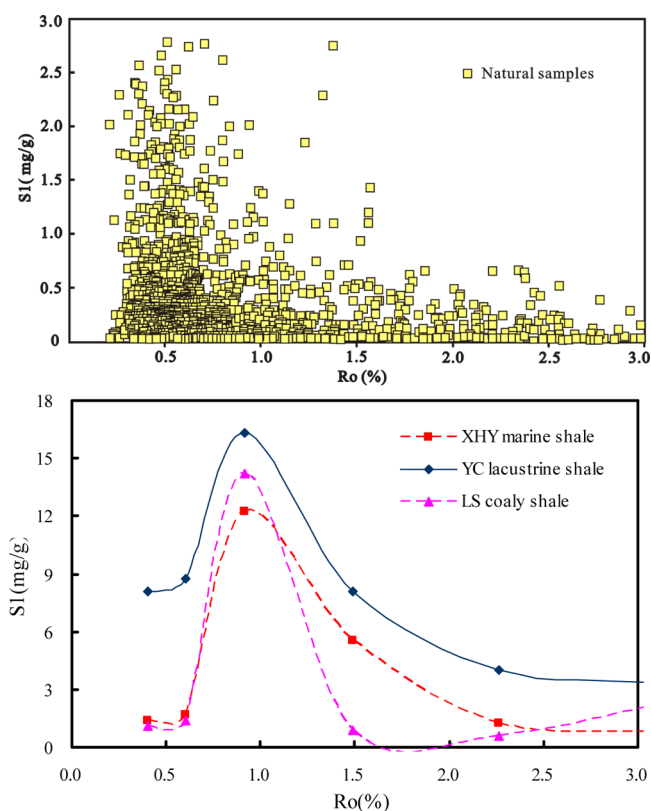


Figure 6. Comparison of the residual oil from XHY marine shale, YC lacustrine shale, and LS coaly shale in laboratory conditions with the S1 value of natural shale samples from Rock-Eval at geological conditions (data of natural samples are from organic geochemical database of USGS).

shale is much higher than that of natural samples. Considering the different sealing conditions of natural and laboratory conditions, our results suggest that residual oil content in nature is much higher than that we have measured. The residual-oil peaks of our results lag a little due to the difference of maturities calculated from EasyRo% method and those measured from natural samples. We also compared the residual oil of coal by our methods with the Rock-Eval S1 of natural

samples which are from Petersen (2002).²⁸ From Figure 7, it is clear that both amounts and peak maturity of coal at laboratory

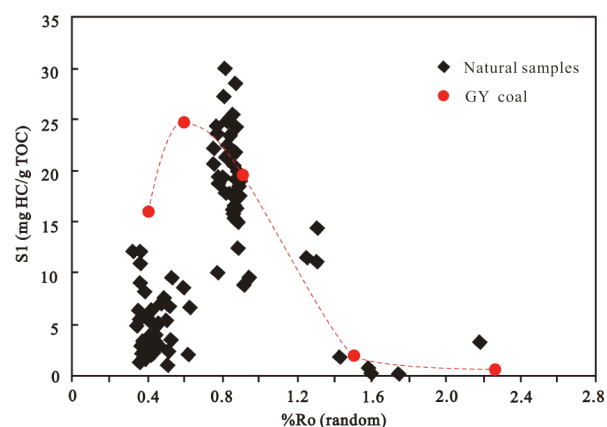


Figure 7. Comparison of the residual oil from GY coal in laboratory conditions with the S1 value of natural coal samples from Rock-Eval at geological conditions (data of natural samples are from a plot based on 85 Carboniferous Tertiary coals, see Figure 2 of Petersen (2002)).

conditions are identical to those at geological conditions, which are different from shale. It implies that the residual oil in coal is mainly retained due to its unique structures.

3.3. Fractional Compositional Evolution of Residual Oil. Following the experimental methods in Figure 3, 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 3 lists the fractional compositional content of XHY and YC shale, GY coal, and LS coaly shale at different thermal maturity stages. Figures 5 and 8 show the fractional composition variations and proportions of these four samples in the whole process of maturation. Oil window, wet gas window, and dry gas window are labeled in Figures 5 and 8.

In initial state ($R_o = 0.4\%$), the contents and proportions of saturates, aromatics, resins, and asphaltenes generated from XHY shale are 3.64 mg/g TOC (24.51%), 5.98 mg/g TOC (40.27%), 5.13 mg/g TOC (34.52%), and 0.11 mg/g TOC (0.71%), respectively. For YC shale, four fractional contents and proportions reach 15.41 mg/g TOC (44.62%), 5.21 mg/g TOC (15.07%), 13.19 mg/g TOC (38.19%), and 0.73 mg/g TOC (2.12%), respectively. For GY coal, four fractional contents and proportions are relatively lower, reaching 0.42 mg/g TOC (9.22%), 1.65 mg/g TOC (36.25%), 1.73 mg/g TOC (38.10%), and 0.75 mg/g TOC (16.44%), respectively. And for LS coaly shale, four fractional contents and proportions are 1.48 mg/g TOC (23.73%), 1.01 mg/g TOC (16.23%), 3.50 mg/g TOC (56.03%), and 0.25 mg/g TOC (4.02%), respectively. At initial state, source rocks have not yet begun to expel hydrocarbon. For the samples used in this study, the fractional components of residual oil from marine, lacustrine, and coaly shale are mainly saturates, aromatics, and resins, while the fractional components of residual oil from coal is mainly aromatics, resins, and asphaltenes at this stage. The fractional components of lacustrine shale (YC) and marine shale (XHY) show higher contents of saturates, aromatics, and resins than those from coal (GY) and coaly shale (LS).

In oil window ($R_o = 0.92\%$), the contents and proportions of four fractional compositional contents and proportions generated from XHY shale are 38.93 mg/g TOC (29.17%),

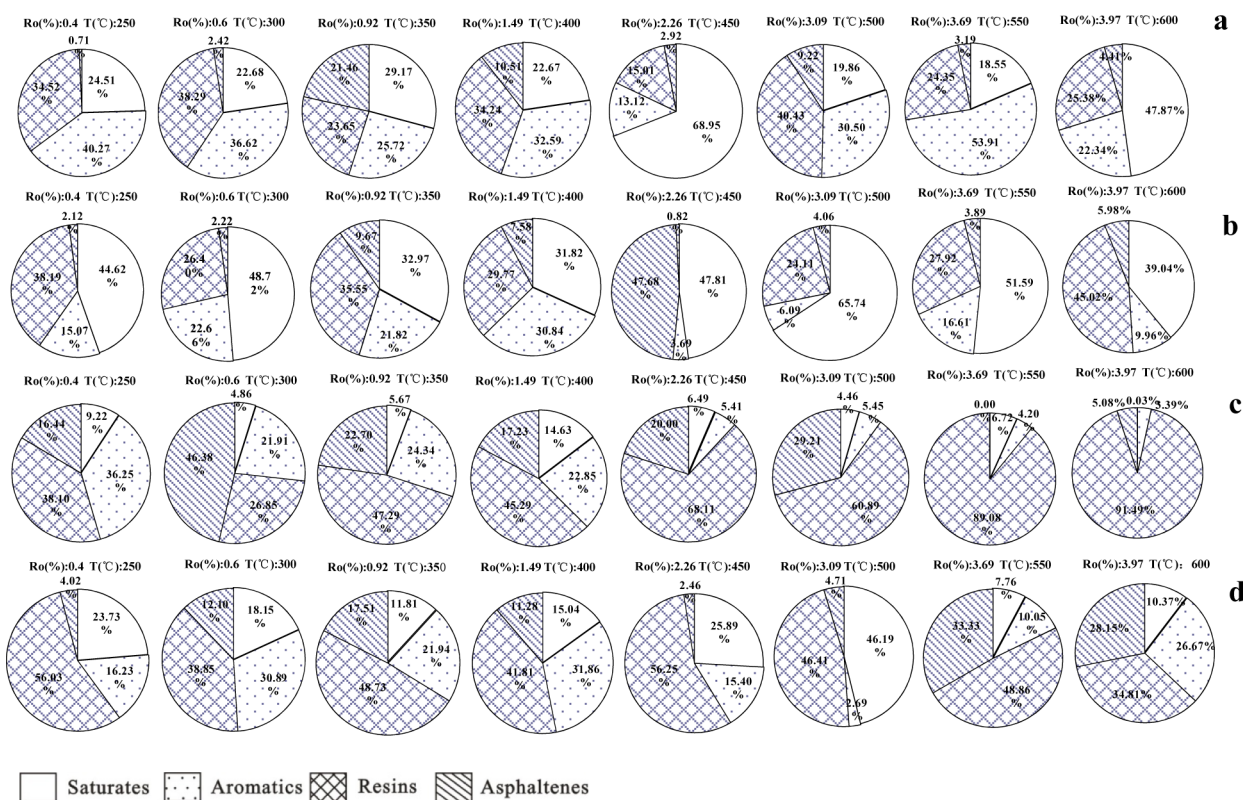


Figure 8. Proportions of saturates, aromatics, resins, and asphaltenes of XHY (a), YC (b), GY (c), and LS (d) with increasing thermal maturity.

34.32 mg/g TOC (25.72%), 31.56 mg/g TOC (23.65%), and 28.64 mg/g TOC (21.46%), respectively. The contents of those four fractional components are much closed. For YC shale, four fractional contents and proportions reach 23.02 mg/g TOC (32.97%), 15.24 mg/g TOC (21.82%), 24.82 mg/g TOC (35.55%), and 6.75 mg/g TOC (9.67%), respectively. The asphaltenes contents of lacustrine shale are the lowest and show great difference with saturates, aromatics, and resins. For GY coal, four fractional contents and proportions are still lower compared to marine shale (XHY) and lacustrine shale (YC) which are 0.45 mg/g TOC (5.67%), 1.92 mg/g TOC (24.34%), 3.73 mg/g TOC (47.29%), and 1.79 mg/g TOC (22.7%), respectively. For LS coaly shale, four fractional contents and proportions are 9.90 mg/g TOC (11.81%), 18.38 mg/g TOC (21.94%), 40.83 mg/g TOC (48.73%), and 14.67 mg/g TOC (17.51%), respectively. The contents of saturates, aromatics, resins, and asphaltenes from marine shale (XHY) and lacustrine shale (YC) and coaly shale (LS) reach the maximum levels in this stage. The fractional components of residual oil from marine shale (XHY) and lacustrine shale (YC) are mainly saturates, aromatics, and resins, while coal (GY) shows that asphaltenes are the dominant fraction, with higher aromatics, resins and rare saturates. The contents of four fractional components from marine shale (XHY) and lacustrine shale (YC), coaly shale (LS) are much higher than those from coal (GY). But for coal, the contents of saturates are the lowest among four fractional groups. The higher proportion of resins and asphaltenes from the residual oil of coal might be caused by its high porosity and high adsorption capability that makes it difficult to be expelled out.²⁹ Coaly shale shows a mixture feature of shale and coal at this stage.

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 asphaltenes generated from XHY shale are 13.69 mg/g TOC (22.67%), 19.68 mg/g TOC (32.59%), 20.68 mg/g TOC (34.24%), and 6.35 mg/g TOC (10.51%), respectively. For YC shale, four fractional contents and proportions reach 11.04 mg/g TOC (31.82%), 10.70 mg/g TOC (30.84%), 10.33 mg/g TOC (29.77%), and 2.63 mg/g TOC (7.58%), respectively. For GY coal, the four fractional contents and proportions are 0.67 mg/g TOC (14.63%), 1.04 mg/g TOC (22.85%), 2.07 mg/g TOC (45.29%), and 0.79 mg/g TOC (17.23%), respectively. For LS coaly shale, four fractional contents and proportions are 0.80 mg/g TOC (15.04%), 1.70 mg/g TOC (31.86%), 2.23 mg/g TOC (41.81%), and 0.6 mg/g TOC (11.28%), respectively. The fractional components of residual oil from marine shale (XHY) and lacustrine shale (YC) and coaly shale (LS) are mainly saturates, aromatics, and resins but less asphaltenes, while coal (GY) are mainly resins, aromatics, and asphaltenes but less saturates. The contents of saturates, aromatics, resins, and asphaltenes of coaly shale are decreasing rapidly, while the generation yields of wet gas is not increasing correspondingly (see Figure 4). The main reason may be the coal's property that makes the generated hydrocarbons expelled out episodically. Compared with oil window, four fractional components contents of shale decreased rapidly; the reason for this is that the heavy hydrocarbons and nonhydrocarbons retained in source rock mainly cracked into wet gases and condensate.²⁹

The dry gas window is the main generation period of methane. The total residual oil yields are very low, but there are still some saturates, aromatics, resins, and asphaltenes retained in source rock. In dry gas window ($Ro = 3.69\%$), the contents and proportions of saturates, aromatics, resins, and asphaltenes

of residual oil generated from XHY shale are 0.86 mg/g TOC (18.55%), 2.49 mg/g TOC (53.91%), 1.12 mg/g TOC (24.35%), 0.15 mg/g TOC (3.19%), respectively. For YC shale, four fractional contents and proportions reach 6.34 mg/g TOC (51.59%), 2.04 mg/g TOC (16.61%), 3.43 mg/g TOC (27.92%), 0.48 mg/g TOC (3.89%), respectively. The saturated contents of lacustrine shale are higher than that of marine shale (XHY) which suggests that lacustrine shale (YC) is slower in oil expulsion than marine shale (XHY). For GY coal, four fractional contents and proportions of residual oil are 0.11 mg/g TOC (6.72%), 0.07 mg/g TOC (4.2%), 1.44 mg/g TOC (89.08%), and 0.00 mg/g TOC (0.00%), respectively, which indicates that residual asphaltenes have been totally cracked into gases in high maturity. And for LS coaly shale, four fractional contents and proportions are 3.07 mg/g TOC (7.76%), 3.98 mg/g TOC (10.05%), 19.35 mg/g TOC (48.86%), and 13.20 mg/g TOC (33.33%), respectively. Similarly, the fractional components of residual oil from shale are mainly saturates, aromatics, and resins but less asphaltenes, while coal are mainly resins less saturates, aromatics, and asphaltenes. The second peak of typical episodic hydrocarbon expulsion pattern of coal (GY) and coaly shale (LS) occur in this stage, and the fractional components of coaly shale are mainly resins and asphaltenes. These results show that marine shale (XHY) and lacustrine shale (YC), coal (GY), and coaly shale (LS) are still having saturated hydrocarbons in high maturity that may be caused by higher stability of saturates. Figure 4 shows both shale and coal can generate amounts of dry gas, but the methane yields of shale are much higher than coal. Compared with the oil and wet gas yields, coal mainly generates dry gas that contributes great source to coal-bed methane.^{30,31} It is coincided with the maceral components of GY coal which is a vitrinite-dominant and gas-prone source rock in Sichuan Basin.^{32,33}

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 XHY and YC shale, GY coal, and LS coaly shale reach the maximum levels in oil window which are 133.44 mg/g TOC, 69.84 mg/g TOC, 10.03 mg/g TOC, and 83.79 mg/g TOC, respectively. The proportions of saturates and aromatics hydrocarbons of residual oil from shale are over 50%, while those from coal and coaly shale are less than 50% at this stage. The residual oil contents of shale and coaly shale are higher with high proportions of saturates and aromatics hydrocarbons than coal in low maturity which show higher shale oil prospective than coal. At higher maturation stages like 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 asphaltents of residual oil from shale are less than 50% while those fractions from coal and coaly shale are more than 50% at higher maturities, the contents of resins and asphaltenes from marine shale, lacustrine shale, and coaly shale are still much higher than those from coal. Considering that the fractional compositions have different expulsion efficiency and the ability to crack into gas, two shale samples are still showing much higher potential of methane generation than coal and coaly shale at high maturities. Our results show the wet gas yields of residual oil from XHY and YC shale, GY coal, and LS coaly shale are 81.40 mg/g TOC, 119.03 mg/g TOC, 12.68 mg/g TOC, and 7.42 mg/g TOC, respectively, and dry gas yields reach 182.46 mg/g

TOC, 218.07 mg/g TOC, 101.71 mg/g TOC, and 46.77 mg/g TOC, respectively, which indicates that shale show very good exploration potential of shale gas even at higher maturities. The contents and evolution of fractional compositions of residual oil from shale and coal provide 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 (MSSV) pyrolysis method to whole-rock. Oil windows are defined as 0.6–1.3%Ro for shale and 0.5–1.2%Ro for coal, wet gas window are 0.9–3.0%Ro for shale and 0.8–2.7%Ro for coal, and dry gas window are 1.3–4.0%Ro for shale and 1.2–4.0%Ro for coal, respectively by using residuals oil contents and yields of gases using equivalent Ro (%) calculated through EasyRo (%) method. Coal shows relatively wider oil window than shale due to its earlier oil generation onset temperature/maturity and later oil expulsion. Higher porosity and higher adsorption capability to oils of coal make coal difficult to expel out oil. However, both shale and coal show very similar wet and dry gas windows which suggest that source rock types and properties will influence oil expulsion greatly but gas expulsion less.

The residual oil of XHY and YC shale, GY coal, and LS coaly shale reach the maximum contents in oil window which are 133.44 mg/g TOC and 69.84 mg/g TOC, 10.03 mg/g TOC, and 83.79 mg/g TOC, respectively. Comparing with natural residual oil, the laboratory residual oil of shale is much higher while the residual oil in coal is mainly retained due to its unique structures. XHY and YC shale show mainly saturates, aromatics, and resins fractions but less asphaltenes fraction while GY coal shows mainly asphaltenes, aromatics, and resins but less saturates fraction at different thermal stages. LS coaly shale shows a mixture property of shale and coal at different thermal stages.

The residual oil contents of shale and coaly shale are higher with high proportions of saturates and aromatics hydrocarbons than coal in low maturity which show higher shale oil prospective than coal. At higher maturation stages, the contents of resins and asphaltenes from marine shale, lacustrine shale, and coaly shale are still much higher than those from coal. Two shale samples are still showing much higher potential of methane generation than coal and coaly shale at high maturities. The results of residual oil contents and their fractional compositions from shale and coal at different maturities provide a quantitative way for evaluating exploration prospective of shale oil and shale gas.

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Notes

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