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Evolutions of Oil Generation and Expulsion of Marine-Terrestrial Transitional Shales: Implications From a Pyrolysis Experiment on Water-Saturated Shale Plunger Samples

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Shale reservoirs are characterized by self-generation and self-accumulation, and the oil generation and expulsion evolution model of organic-rich shales is one of important factors that obviously influence the enrichment and accumulation of shale oil and gas resources. At present, however, relevant studies on marine-terrestrial transitional shales are inadequate. In this study, a pyrolysis experiment was performed on water-saturated marine-terrestrial transitional shale plunger samples with type II_b kerogen to simulate the evolutions of oil generation and expulsion. The results indicate that marine-terrestrial transitional shales have wider maturity ranges of oil generation and expulsion than marine and lacustrine shales, and the main stages of oil expulsion are later than those of oil generation, with corresponding R_o values of 0.85%–1.15% and 0.70%–0.95%, respectively. Although the oil generation and expulsion process induced a fractionation in compositions between the expelled and retained oils, both the expelled and retained oils of marine-terrestrial transitional shales are dominated by heavy compositions (resins and asphaltenes), which significantly differs from those of marine and lacustrine shales. The kerogen of marine-terrestrial transitional shales initially depolymerized to transitional asphaltenes, which further cracked into hydrocarbons, and the weak swelling effects of the kerogen promoted oil expulsions. The oil generation and expulsion evolutions of these shales are largely determined by their organic sources of terrigenous higher organisms. This study provides a preliminary theoretical basis to reveal the enrichment mechanism of marine-terrestrial transitional shale oil and gas resources.

Keywords: marine-terrestrial transitional shale, pyrolysis experiment, oil generation and expulsion, organic sources, maturity

INTRODUCTION

Organic-rich shales are widely developed in marine, lacustrine, and marine-terrestrial transitional strata in China, and the three types of shales significantly contributed to the oil and gas resources of both conventional and unconventional reservoirs (Zou et al., 2019; Zou et al., 2020). In the Sichuan Basin, for example, giant gas fields in the central Sichuan Basin, including the Anyue, Weiyuan, and Ziyang shale gas plays, were mainly sourced from the Lower Paleozoic marine shales (Zou et al., 2014); several tight sandstone gas reservoirs in the paleo-uplift of the central Sichuan Basin largely came from the Jurassic lacustrine shales (Huang et al., 2019); the Xinchang gas field in the western Sichuan Basin were basically derived from the Upper Triassic marine-terrestrial transitional shales (Chen et al., 2010; Wu et al., 2016). In the last 2 decades, developments of marine shale oil and gas resources in the North America have achieved a great success (Zhou et al., 2019). Marine shale gases and lacustrine shale oils in China also have been commercially developed in the past 10 years (Jin et al., 2019; Zhao et al., 2020). Although marine-terrestrial transitional shales were believed to have a large potential of shale oil and gas resources, few of them have achieved commercial developments until now (Guo et al., 2015; Guo et al., 2021).

Marine-terrestrial transitional source rocks generally have low yields of oil generation, and most of the generated oils remained in source rocks (Liu et al., 2005; Mao et al., 2012). Therefore, these source rocks are commonly believed to have few contributions to normal petroleum reservoirs. However, the oil and gas resources of marine-terrestrial transitional shale reservoirs are largely determined by their oil generation and expulsion model because shale strata generally acted as both source rocks and reservoirs. Although oil generation and expulsion models have been well documented for marine and lacustrine shales in many previous studies (Wei et al., 2012; Han et al., 2015; Tang et al., 2015; Han et al., 2017; Ziegs et al., 2017; Hakimi et al., 2018; Wu et al., 2018), relevant studies on marine-terrestrial transitional shales are still inadequate presently. Marine-terrestrial transitional shales generally have thin single layers and thick cumulative thickness. The sedimentary facies of marine-terrestrial transitional shales vary obviously with burial depth resulting in their organic and inorganic compositions exhibiting obvious heterogeneity, and these shales are obviously richer in terrestrial organic sources than the marine and lacustrine shales (Qin et al., 2016; Su et al., 2016). Because marine-terrestrial transitional shales are quite different from marine and lacustrine shales in both geological and geochemical characteristics, the oil generation and expulsion models deduced from the latter shales failed to be applied on the former shales. At present, oil generation and expulsion characteristics of marine-terrestrial transitional shales are still not fully understood, which limits the development of their oil and gas resources.

In previous studies, dried shale powder samples were commonly used for pyrolysis experiments (Inan and Schenk, 2001; Carr et al., 2009; Liang et al., 2015; Ko et al., 2018). However, this method has several disadvantages to simulate oil generation and expulsion of shale samples. Shale pore structures, especially the microfractures, may be obviously broken during crushing process, which affects the expulsion and storage of generated shale oils. In addition, connate pore waters in source rocks significantly influence oil generation process and the properties of generated oils (Sun et al., 2015). For example, artificially simulated oils generated under water-bearing conditions are more similar with natural oil samples than those generated under anhydrous conditions (Lewan et al., 1979). Differing from the methods in previous studies, in this study, small shale plunger samples that drilled from a lowly mature marine-terrestrial transitional shale core sample were first saturated with water, and then they were used for a pyrolysis experiment to simulate the oil generation and expulsion characteristics. This study intends to provide a preliminary theoretical model to further reveal the enrichment mechanism of marine-terrestrial transitional shale oil and gas resources.

EXPERIMENTS

Pyrolysis Experiments

In this study, water-saturated shale plunger samples were used for the pyrolysis experiment performed in gold tube reactors (Tang et al., 2005; Tian et al., 2012; Gai et al., 2015; Ko et al., 2018). The main experimental procedures are as follows: small shale plunger samples (30 mm in height × 8 mm in diameter) were drilled from the inner part of a big shale core sample in vertical stratification direction. After they were dried in an oven at 105°C for 24 h, the shale plunger samples were saturated with deionized water in a BH-1 pressurized instrument (Cheng et al., 2019). Then, the water-saturate shale plungers were loaded in gold tubes (70 mm length × 9 mm inside diameter), and both sides of the gold tube were filled with quartz sands to collect expelled oils. Next, the gold tubes were separately loaded into pressure vessels in a high-temperature high-pressure pyrolysis oven. The given temperatures of this experiment were 350°C, 375°C, 395°C, 415°C, 435°C, and 460°C, respectively. During the experiment, the pyrolysis instrument was heated at a rate of 20°C/h, and the experimental pressure was maintained approximately 50 MPa (±1 MPa).

TOC and Mineralogical Analysis

Shale samples were powdered to a grain size of less than 180 μm and were eluted by diluted hydrochloric acids to remove the carbonates. After the shale powders were dried in an oven, their TOC contents were analyzed by an Eario El Cube Elemental Analyzer. The analytical errors of the instrument is less than 0.1%. The mineralogical compositions of shales were analyzed by a Bruker D8 Advance x-ray diffractometer. The measurements were performed on shale grains less than 75 μm at 40 kV and 30 mA with Cu Kα radiation. The relative content of minerals was semi-quantitatively calculated based on their

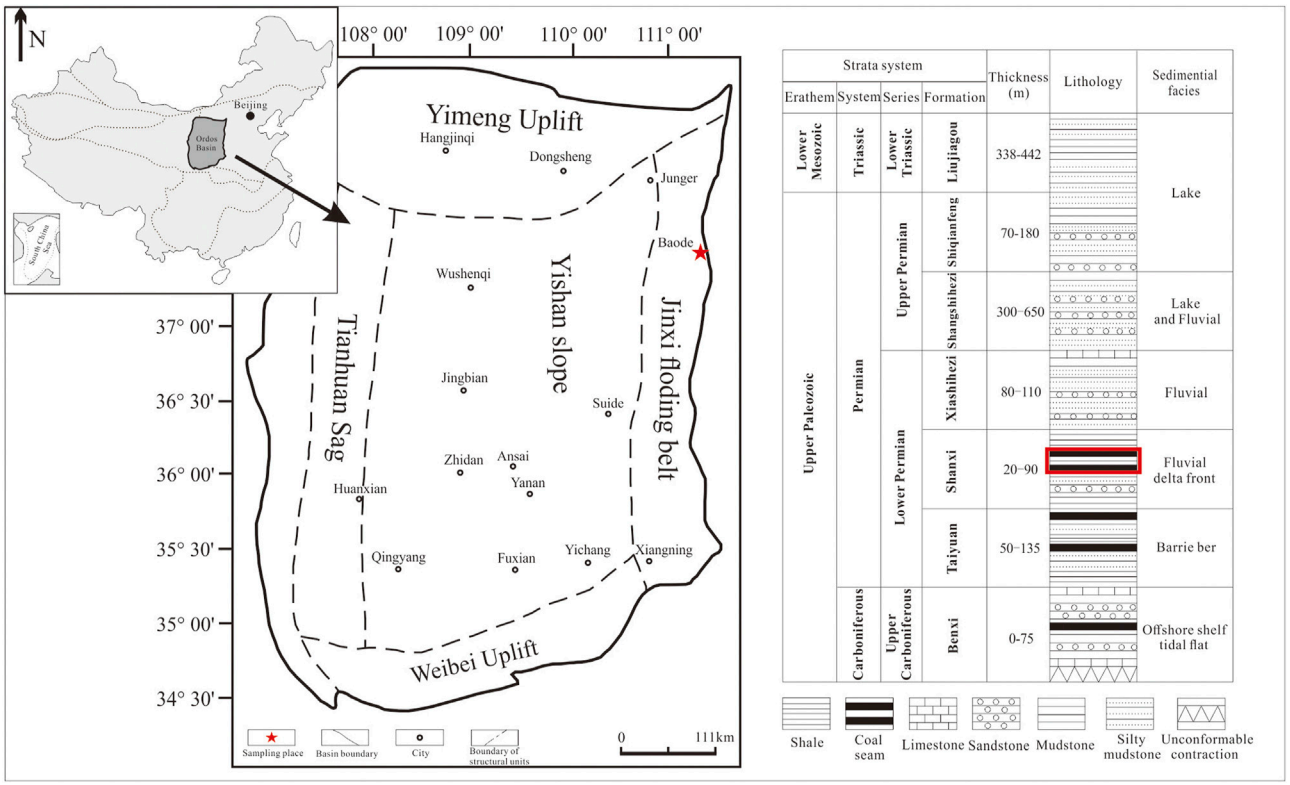

FIGURE 1 | Schematic maps showing the location and stratum of the studied shale sample (modified after Cao et al., 2019 and Su et al., 2005).

TABLE 1 | Geological and geochemical data of the shale sample used for pyrolysis experiment in this study.

Sample	Region	Stratum	Lithology	TOC (%)	R_o (%)	Rock-eval			Mineral compositions (%)						
						T_{max} (°C)	HI (mg/g TOC)	OI (mg/g TOC)	Quart	Clay	Pyrite	Siderite	Feldspar	Anatase	Dolomite
BLG14	Ordos Basin	Lower Permian Shanxi Formation	Black shale	15.65	0.68	434	292	2	33.6	47.5	13.6	1.5	1.3	1.6	0.9

peak areas and was corrected with Lorentz-Polarization method (Chalmers and Bustin, 2008).

Measurement of Vitrinite Reflectance (R_o)

The R_o values of shale samples were measured by a 3Y-DMR microphotometer equipped with a Leica microscope. The light source of this instrument is a high-pressure mercury vapor lamp with an excitation filter of 420–490 nm, and an oil immersion objective 50/1.0 is used for the measurement. Before the measurements, the instrument was calibrated by a standard yttrium aluminum garnet sample (YAG-08–57). A total of 50 individual vitrinite particles was measured for each shale sample, and the average value of these measured R_o values was used in this study.

Collection and Pretreatment of Liquid Hydrocarbons

After the pyrolysis experiment, shale plunger samples and quartz in the gold tube were separated. The shale plunger samples were crushed to powders less than 80 mesh, and then they were extracted with dichloromethane to obtain the retained oils. The collected quartz and gold tube were extracted together with dichloromethane to obtain the expelled oils. Both the retained and expelled oils were weighted by a Sartorius electronic balance with an analytical precision of 0.01 mg. The sum of the expelled and retained oils was the total generated oils. The gross compositions of these oil samples were further separated into four fractions, including saturates, aromatics,

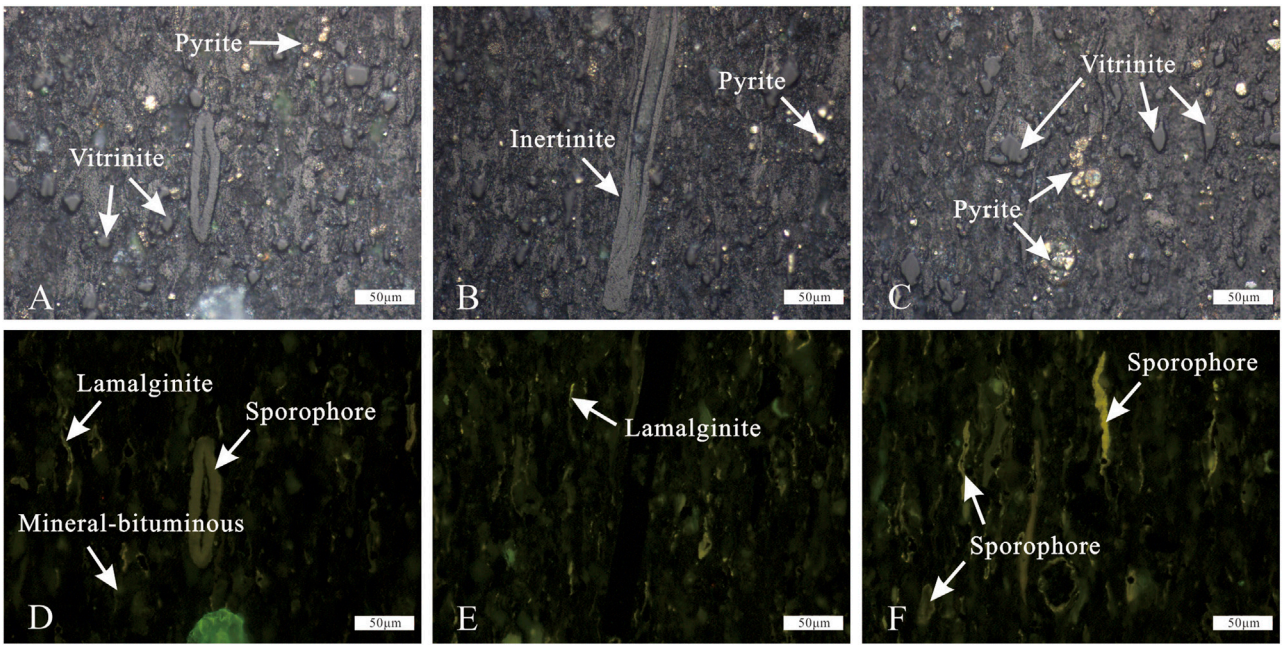

FIGURE 2 | Photomicrographs showing different macerals and organic sources of the studied marine-terrestrial transitional shale sample. **(A, D)** The exinite (sporophore), lamalginite, and mineral-bituminous under reflected light and fluorescence, respectively; **(B, E)** the inertinite, lamalginite, and its debris under reflected light and fluorescence, respectively; **(C, F)** the vitrinite and exinite (sporophore) under reflected light and fluorescence, respectively.

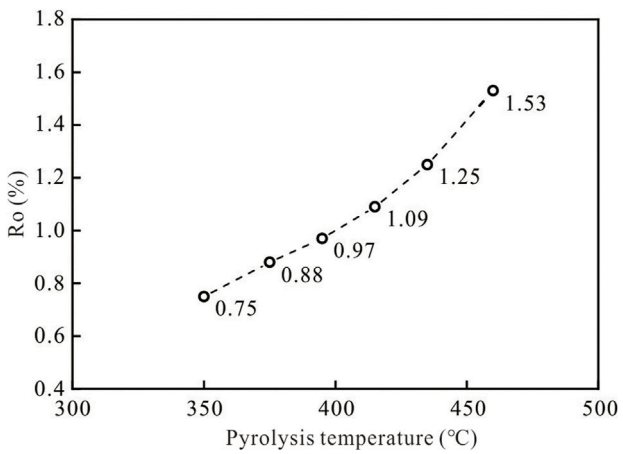

FIGURE 3 | Correlations of the R_o values with the experimental temperatures in this study.

resins, and asphaltenes, by a liquid chromatography on silica columns (Tang et al., 2005).

RESULTS AND DISCUSSION

Geological and Geochemical Characteristics of the Studied Shale

The shale sample used for the pyrolysis experiment was collected from the marine-terrestrial transitional strata of the Lower Permian Shanxi Formation in the northeast of the Ordos Basin (**Figure 1**). It has a low maturity with a R_o value of 0.68% and a high TOC content of 15.65%. The kerogen type of the shale belongs to type II_b based on the van Krevelen diagram (van Krevelen, 1961), and its HI and OI values are 292 mg/g TOC and 2 mg/g TOC, respectively. The minerals of this shale mainly include clays and quartz, with contents of 47.5% and 33.6%, respectively (**Table 1**).

Organic petrology analysis shows that this shale sample has various macerals. It contains plenty of vitrinite and inertinite that

TABLE 2 | Yields of the expelled oil, retained oil, and total oil for the studied marine-terrestrial transitional shale sample at different maturity stages.

Sample number	R_o (%)	Retained oil		Expelled oil		Total oil		Percentage of retained oil (%)[a]	Percentage of expelled oil (%)[b]
		(mg/g rock)	(mg/g TOC)	(mg/g rock)	(mg/g TOC)	(mg/g rock)	(mg/g TOC)		
BLG14–1	0.75	6.92	44.22	1.07	6.84	8.00	51.12	86.57	13.43
BLG14–2	0.88	11.30	72.20	2.84	18.15	14.14	90.35	79.89	20.11
BLG14–3	0.97	13.72	87.67	5.05	32.27	18.77	119.94	73.12	26.88
BLG14–4	1.09	13.67	87.35	6.86	43.83	20.53	131.18	66.60	33.40
BLG14–5	1.25	10.47	66.90	9.49	60.64	19.95	127.48	52.46	47.55
BLG14–6	1.53	5.36	34.25	7.79	49.78	13.15	84.03	40.78	59.22

[a]*Percentage of retained oil (P_{RO}): ratio of the retained oil yield to the total oil yield.*
[b]*Percentage of expelled oil (P_{EO}): ratio of the expelled oil yield to the total oil yield.*

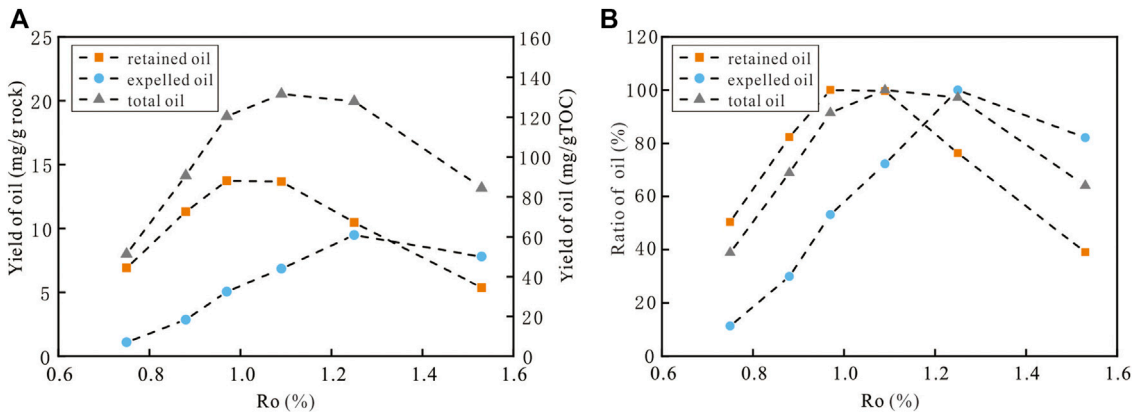

FIGURE 4 | Evolutions of total oil, expelled oil, and retained oil yield **(A)** and their relative yields **(B)** for the studied shale sample at different maturity stages.

exhibit gray color under reflected light (**Figure 2A–C**), and it also contains abundant exinite (sporophore) and lamalginite, which exhibit dark and bright yellow colors, respectively, under fluorescence excitation (**Figure 2D–F**). These characteristics indicate that the organic matter of this shale came from both terrigenous higher organisms and aquatic alga, and the contribution of the former sources was greater than that of latter sources.

Evolutions of Oil Generation and Expulsion

In this study, the R_o values of the artificially maturated shale samples correspond well with experimental temperatures, and they exhibit a significant positive relationship (**Figure 3**). With the experimental temperature increasing from 350°C to 460°C, the R_o value increases from 0.75% to 1.53% (**Table 2**). The maturity range of artificially maturated shales covers from the early oil generation stages to the wet gas stages.

The yields of the expelled oils (Y_{EO}), retained oils (Y_{RO}), and total generated oils (Y_{TO}) are listed in **Table 2**, and the Y_{EO}, Y_{RO}, and Y_{TO} exhibit different evolutions with the increasing maturity (**Figure 4A**). The Y_{EO} increases from 1.07 mg/g rock to the maximum yield of 9.49 mg/g rock with the R_o increasing from 0.75% to 1.25%. However, when the R_o > 1.25%, the Y_{EO} gradually decreases to 7.79 mg/g rock as the R_o increases to 1.53% (**Table 3** and **Figure 4A**). The Y_{RO} increases from 6.92 mg/g rock to the maximum yield of 13.72 mg/g rock with the R_o increasing from 0.75% to 0.97%. However, when the R_o > 0.97%, the Y_{RO} gradually decreases to 5.36 mg/g rock as the R_o increases to 1.53% (**Table 3** and **Figure 4A**). The Y_{TO} increases from 8.00 mg/g rock to the maximum yield of 20.53 mg/g rock with the R_o increasing from 0.75% to 1.09%, which indicates that the generation rates of oils are greater than their pyrolysis rates at this stage. However, when the R_o > 1.09%, the Y_{TO} gradually decreases to 13.15 mg/g rock as the R_o increases to 1.53%, which indicates that the generation rates of oils are smaller than their pyrolysis rates at this stage (**Table 2** and **Figure 4A**). The main oil generation and expulsion stages are generally defined in the range of 30%–80% of the maximum oil yield (Sun et al., 2019). According to this definition, the main stages of oil generation and expulsion are 0.85%–1.15% and 0.70%–0.95%, respectively, for the studied marine-terrestrial transitional shale sample. The main stages of oil expulsion are later than those of oil generation (**Figure 4B**).

Previous pyrolysis experiments performed on lacustrine shales with type I or type II kerogen indicate that these shales begin to generate oils when the R_o > 0.70%, and the oil generation windows are in the R_o range of 0.75%–0.90% (Sun et al., 2019). The differences in oil generation stages of various shales are largely determined by their organic sources. For example, the oil generation thresholds of terrestrial organic

TABLE 3 | Gross compositions of the expelled and retained oils at different maturity stages.

Sample number	R_o (%)	Expelled oil (%)				Retained oil (%)			
		Saturates	Aromatics	Resins	Asphaltenes	Saturates	Aromatics	Resins	Asphaltenes
BLG14-1	0.75	7.27	18.18	5.45	69.09	1.93	8.82	11.30	77.96
BLG14-2	0.88	6.33	25.32	13.90	54.43	2.45	7.34	20.00	70.17
BLG14-3	0.97	9.79	20.28	20.30	49.65	3.87	9.61	22.40	64.11
BLG14-4	1.09	15.85	16.67	30.10	37.40	7.17	11.03	22.00	59.85
BLG14-5	1.25	18.75	17.75	31.80	31.75	14.30	16.93	27.80	40.94
BLG14-6	1.53	19.59	26.32	32.20	21.93	20.17	17.85	35.50	26.50

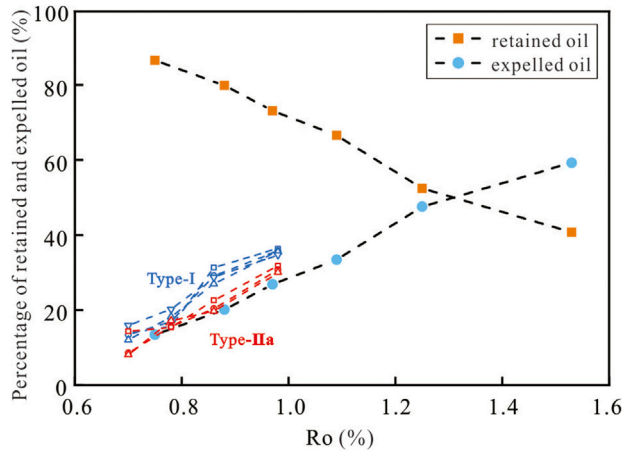

FIGURE 5 | Relative percentages of the expelled (P_{EO}) and retained oils (P_{RO}) in total generated oils at different maturity stages for the studied marine-terrestrial transitional shale. The data of type I and II_b lacustrine shales are cited from Sun et al. (2021).

matters, such as vitrinite and exinite, are generally at relative low maturity stages with R_o values of 0.50%–0.55%, and the main oil generation stages covered a wide maturity range with R_o values of 0.55%–1.00% (Li et al., 2002; Shuai et al., 2009). However, the oil generation threshold of aquatic alginates is generally at a higher maturity stage with the R_o value of 0.70%, and its main oil generation stage generally covers a shorter maturity range with R_o values of 0.70%–0.90%. In contrast to lacustrine shales, the studied marine-terrestrial transitional shale is richer in terrestrial organic matter, which results in an earlier oil generation threshold and a wider oil generation window.

The relative percentages of expelled (P_{EO}) and retained oils (P_{RO}) in total generated oils obviously vary at different maturity stages (**Figure 5**). With the R_o increasing from 0.75 to 0.97%, the P_{EO} successively increases from 14% to 34%, while the P_{RO} progressively decreases from 86% to 67%. When the R_o values <1.25%, the P_{RO} is higher than the P_{RO}; however, the P_{RO} is lower than the P_{RO} when the R_o values >1.25% (**Figure 5**). Heavy liquid hydrocarbons in the retained oils progressively cracked into light liquid hydrocarbons and promoted oil expulsions during the high maturity stages (Li et al., 2017). Shao et al. (2020) also reported that the peak P_{EO} value of Barnett lacustrine shales occurred in the late wet gas stage with the R_o value of 1.75%. For the Shahejie Formation lacustrine shales in the Bohaiwan Basin (Sun et al., 2021), the shales with type I and II_a kerogen generally have higher P_{EO} values than the shales with type II_b and III kerogen (**Figure 5**). Under similar maturity conditions, the studied marine-terrestrial transitional shale has lower P_{EO} values than the lacustrine shales; however, its P_{EO} values significantly increase at high maturity stages, which indicates that oil expulsions are enhanced at high maturity stages for the studied shale.

The evolution model of oil generation and expulsion of the studied marine-terrestrial transitional shale is different from that of lacustrine shales reported by previous studies. Compared with the lacustrine shales, the marine-terrestrial transitional shales have earlier oil generation thresholds and wider oil generation windows. In addition, the P_{EO} values are similar for the two types of shales, while the P_{EO} values of marine-terrestrial transitional shales are significantly enhanced at high maturity stages. However, it should be pointed out that further studies need to be performed on more marine-terrestrial transitional shale samples to verify the applications of this oil generation and expulsion model under geological conditions.

Changes in Gross Compositions of the Expelled and Retained Oils

The changes in gross compositions of the expelled and retained oils can be approximately divided into three stages. At the early stage with R_o < 0.97%, the gross compositions slightly changed with the maturity for both expelled and retained oils (**Figure 6**), which indicates that the fractionation effect caused by oil generation and expulsion is weak at this stage. At the middle stage with the R_o ranging from 0.97% to 1.25%, the light compositions (saturates and aromatics) obviously enriched while the heavy compositions (resins and asphaltenes) significantly decreased for both expelled and retained oils (**Figure 6**), because the kerogen generated more light compositions at this maturity stage. The percentages of the light compositions in expelled oils are significantly higher than those in retained oils (**Figure 6**), because the light compositions have low viscosity and tend to migrate (Pepper and Corvi, 1995). Therefore, a significant fractionation occurred between the expelled and retained oils at this maturity stage. At the late stage with R_o > 1.25%, only a small number of light compositions were generated from kerogen; meanwhile, part of the retained and expelled oils cracked into gaseous

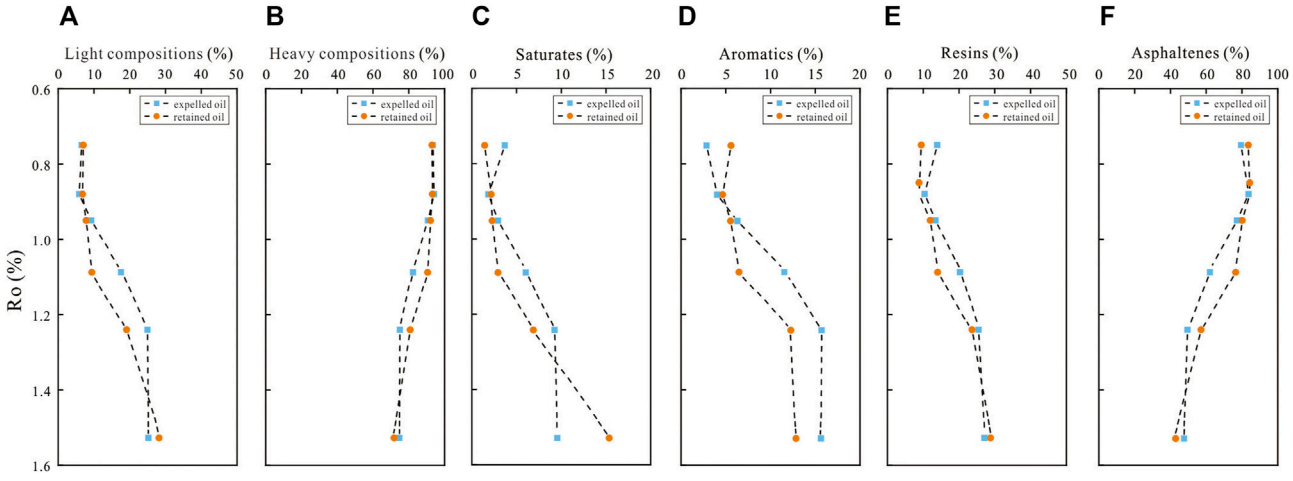

FIGURE 6 | Changes in the gross compositions of the expelled and retained oils with increasing maturity for the studied marine-terrestrial transitional shale sample.

hydrocarbons. Therefore, with the increasing maturity, the differences in gross compositions between the two types of oils gradually decrease.

It is noteworthy that heavy compositions, especially the asphaltenes, are dominated in both retained and expelled oils during the oil generation and expulsion processes. At the maturity stages with the R_o range from 0.75% to 0.97%, the percentages of asphaltene in the expelled and retained oils account for 50%–69% and 63%–77%, respectively. At the high maturity stage with R_o of 1.53%, the percentages of asphaltene in the two types of oils account for 54% and 62%, respectively (**Table 3**). The gross compositions of expelled and retained oils significantly differ from those of lacustrine shales. At the stages with R_o values of 0.71%–1.41%, the light compositions account for 50%–69% and 63%–77% for the Eocene Shahejie lacustrine shales in the Bohaiwan Basin, respectively; moreover, with the increasing maturity, the resin content decreases while the asphaltene content increases for the lacustrine shales (Sun et al., 2021). Asphaltenes are dominated in the retained and expelled oils of marine-terrestrial transitional shales because of their abundant terrestrial organic sources.

Mechanisms of Oil Generation and Expulsion

Ungerer et al. (1990) proposed that hydrocarbon generations from kerogen pyrolysis were mainly through two approaches, i.e., the depolymerization and functional group desorption. The former refers to the idea that kerogen initially cracks to intermediate products (resin and asphaltene), and then these intermediate products are further decomposed to oils and gases. The latter refers to the notion that functional groups initially bonded in kerogen skeletons can be directly liberated from the kerogen and form hydrocarbons. In this study, the Y_{TO} exhibits obvious positive correlations with the resin yield (Y_R) and its percentage during the main oil generation and expulsion stages (**Figures 7A,B**). The Y_{TO} is positively correlated with the asphaltenes yield (Y_A) and its percentage when the R_o < 1.09%, while it shows no obvious correlations with the Y_A and its percentage when R_o > 1.09% (**Figures 7C,D**). Combined with the gross compositions and their evolutions of the expelled and retained oils (**Figure 6**), this study indicates that the organic matter of this studied marine-terrestrial transitional shale first depolymerized to asphaltenes at the early stages of oil generation, and then the transitional asphaltenes were further cracked into hydrocarbons at the late stages of oil generation, while the organic matter of lacustrine shales generates hydrocarbons mainly *via* transitional resins (Sun et al., 2021). Therefore, shales with different sedimentary facies are diverse in oil generation mechanism.

The oil generation and expulsion of shales are mainly controlled by their geochemical properties, including TOC content, kerogen type, maturity, and mineral compositions (Pepper and Corvi, 1995; Chen et al., 2014; Liang et al., 2015), and by their geological conditions, including geological temperature and pressure, water-bearing characteristic, strata thickness, and its boundary condition (Lewan 1997; Chen and Cha, 2005). Previous studies indicated that the pore systems of shales were fully adsorbed and filled by generated oils before oil expulsions, and kerogen swelling effects were the controlling factor on the oil retention in shale reservoirs (Li et al., 2016; Han et al., 2017; Ziegs et al., 2017; Shao et al., 2018). This study further shows that the marine-terrestrial transitional shale exhibits obvious oil expulsion under experimental conditions. Under similar maturity and kerogen-type conditions, marine-terrestrial transitional shales have similar P_{EO} values with lacustrine shales. The high P_{EO} values of the studied marine-terrestrial transitional shale can be illustrated by the following factors.

The kerogen swelling effect is closely related to kerogen types, and it decreases in the order of type I, type II_a, and type II_b kerogen. For example, the swelling amounts of type I, II_a, and II_b

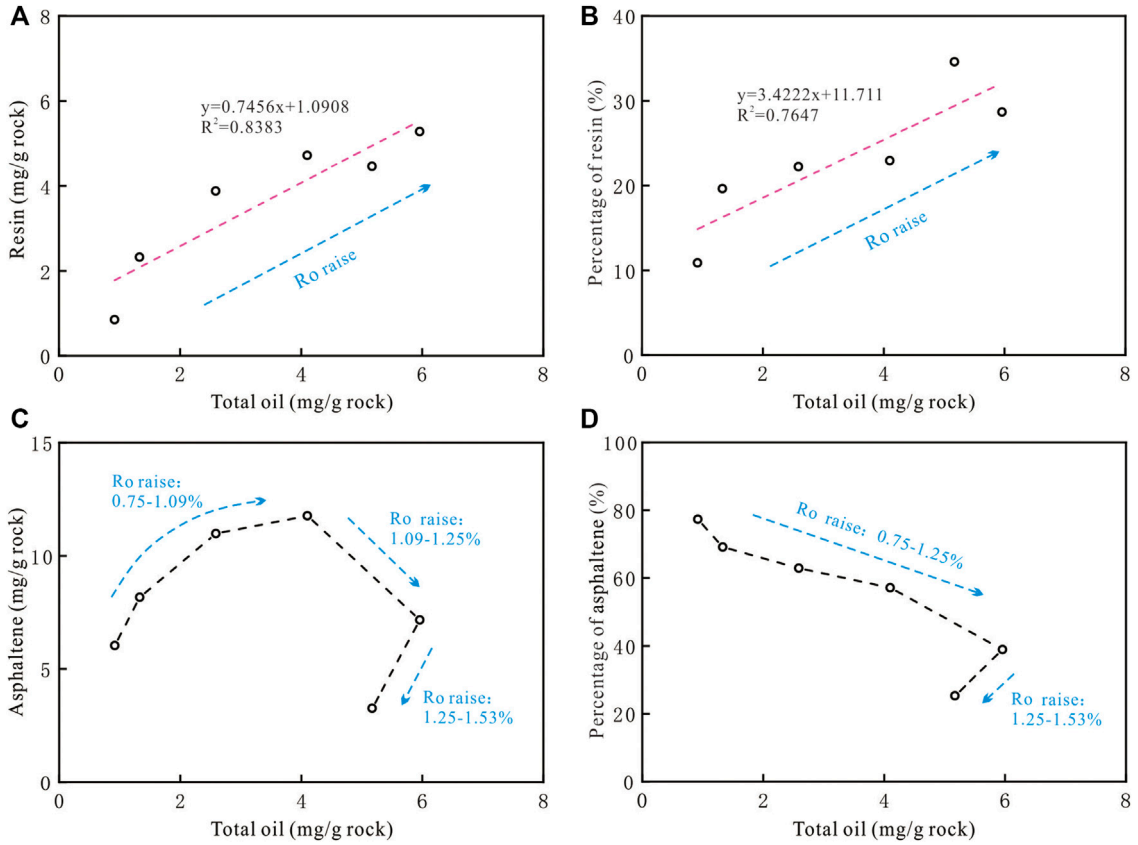

FIGURE 7 | Correlations of the total oil yield (Y_{TO}) with the resin (Y_R) and asphaltene yields (Y_A) as well as their percentages in total oils at different maturity stages.

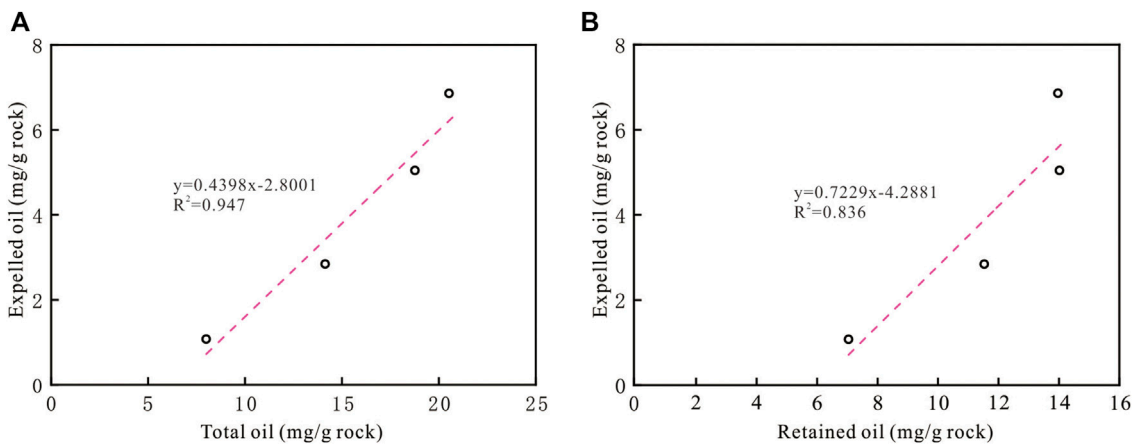

FIGURE 8 | Correlations of the expelled oil contents with the total generated oil contents **(A)** and the retained oil contents **(B)** for the studied shale sample during the main oil generation and expulsion stages with the R_o value of 0.75%–1.09%.

kerogen, with a low maturity of 0.5%, are 142 mg/g TOC, 119 mg/g TOC, and 95 mg/g TOC, respectively (Tian et al., 2014). According to the intercept of the linear correlation equations in **Figure 8**, this study further estimated that the oil expulsion threshold of the studied marine-terrestrial transitional shale corresponded to the Y_{TO} value of 6.4 mg/g rock and the Y_{RO} value of 5.9 mg/g rock. The maximum Y_{RO} value of this shale is 88 mg/g TOC (**Figure 4**) and is much lower than the maximum Y_{RO} values of the type I and type II_a lacustrine shales, with values of 300–350 mg/g TOC and 150–200 mg/g TOC, respectively (Sun

et al., 2021). Although some retained oils are stored in inorganic-hosted nanopores of minerals, most of the retained oils are associated with the kerogen swelling effect (Li et al., 2016; Zhao et al., 2019). The studied marine-terrestrial transitional shale with type II_b kerogen has a low capacity of retaining oils resulting from its weak kerogen swelling effect, which may be the main mechanism for its high oil expulsion efficiency.

Under geological conditions, shale reservoirs generally contain some pore waters that significantly influence the accumulation and enrichment of shale oil and gas resources (Lewan 1997; Burnham 1998; Carr et al., 2009; Lewan and Roy, 2011; Cheng et al., 2018). The pore waters not only take up the pore spaces available for oil storage, but also occupy pore surfaces and change the interfaces between hydrocarbons and pore walls, which significantly prompts oil migrations and expulsions (Korb et al., 2014; Ma et al., 2015; Cheng et al., 2017; Zolfaghari et al., 2017). Moreover, pore waters may also cause an overpressure in shale pore systems, and thus enhance the oil expulsion efficiency (Zhang et al., 2011; Huang et al., 2017). In addition, since the oil expulsion efficiency is positively correlated with the TOC content (Zhang et al., 2006; Sun et al., 2021), the high TOC content of the studied shale sample may also raise its oil expulsion efficiency.

At present, the oil generation and expulsion model of marine-terrestrial transitional shale remains unclear. The results of this study show that oil expulsions of marine-terrestrial transitional shales with high TOC contents may occur under geological conditions, and the oil expulsion efficiency and the geochemical properties of expelled and retained oils are largely determined by the organic sources and maturities of shales. The new understanding on the oil generation and expulsion model in this study may have a certain theoretical significance for the exploration and development of marine-terrestrial transitional shale resources. However, the oil generation and expulsion model of marine-terrestrial transitional shales with type III kerogen needs to be investigated in further studies.

CONCLUSION

In this study, a pyrolysis experiment was performed on water-saturated marine-terrestrial transitional shale plunger samples, to simulate the evolutions of oil generation and expulsion. The main conclusions are as follows:

1) In contrast to marine and lacustrine shales, marine-terrestrial transitional shales have wider maturity ranges of oil generation and expulsion, and the main stages of oil expulsion are later than those of oil generation, with corresponding R_o values of 0.85%–1.15% and 0.70%–0.95%, respectively.
2) The expelled and retained oils of marine-terrestrial transitional shales exhibit obvious fractionations in compositions during the oil generation and expulsion process. However, the two types of oils are dominated by heavy compositions, which significantly differs from the generated oils from marine and lacustrine shales.
3) The oil generation and expulsion evolutions of marine-terrestrial transitional shales are largely determined by their organic sources of terrigenous higher organisms. The kerogen of these shales initially depolymerized to transitional asphaltenes, which further cracked into hydrocarbons, and the weak swelling effects of the kerogen promoted oil expulsions.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, Further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

QF: Conceptualization, Methodology, Data curation, Writing - Original Draft. PC: Conceptualization, Methodology, Review and Editing. XX: Supervision, Review and Editing. HG: Methodology and Review. QZ: Investigation and Editing. TL: Review and Editing. PG: Review and Editing. All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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