Geochemistry of Aromatic Fractions in Es₄ Oil Extracts from the South Slope of Dongying Sag and Its Implications

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Abstract

In view of the characteristics of oils from different production areas in the South Slope of Dongying Sag, detailed geochemical analysis of aromatic hydrocarbon in Es₄ extracts were conducted. The results show that some typical high plants-sourced compounds are widely spread, such as pyrene, benzo[a]pyrene, fluoranthene, chryaene, benzo[a]fluoranthene, perylene and cadalene. The ratios of 1,2,5-/1,3,6-TMN are 0.39~1.04, 9-MP isomeride is in high content of 7.02-12.53%, and about 0.05%~14.50% of retene is detected, suggesting the Es₄ extracts are typical terrestrial origin. In F-DBF-DBT series, dibenzothiophene(DBT) is dominated with content of 33.07-73.17%, while dibenzofurane(DBF) is 9.56-33.20%, showing a reduction condition of brackish-saline lake. Furthermore three types of depositional environment can be distinguished according to the reduction intensities. The RICs are characterized by double peak with tricyclic aromatic compounds in predominance, ratios of 2,3,6-/2,3,6+1,2,5)-TMN are 0.37-0.64, MPI1 and MPI2 are 0.21-0.61 and 0.24-0.72 respectively, corresponding to the maturity of 0.53-0.77%Rc, indicating a mature stage.

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1. Introduction

The South Slope of Dongying Sag is the most typical and biggest ramp in Jiyang depression, covering an area of about 2500km² (Fig.1). The tectonics is simple and characterized by monocline and nose-shaped structure complicated by later rifting. Since the discovery of oils from Es₄ by well Tong4 in 1965, the exploration in The South Slope of Dongying Sag has been conducted for more than 30 years. Till now, Lean, Wangjiagang, Chunhua, Boxing, Xiaoying, Guangli, Jingjia, Bamianhe and Boxing oilfields are discovered in this ramp with proved reserves up to 5.5×10⁸t.

Several researches were conducted on the saturated hydrocarbons from oils in the South Slope of Dongying Sag[1-2], but aromatic hydrocarbons were less documented. The occurrences of aromatic fractions also suggest the influence of source inputs, sedimentary environments and thermal evolution[3],

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and is the essential supplements for saturated hydrocarbon study.

2. Samples and experiments

Eight Es4 oil-bearing sandstone samples were collected from the South Slope of Dongying Sag. Firstly, oils were extracted from these samples, then asphaltenes in crude oils were removed by ligarine. Subsequently those deasphaltened crude oil samples were fractionated into saturate, aromatic and polar fractions by SiO2:Al2O3 (2:3) column chromatography. The GC-MS analysis of aromatic fractions was performed on a HP5890-II gas chromatograph coupled with HP-5971 series mass selective detector, operating in full scan acquisition mode. The GC column is HP-5MS silicon capillary column (30 m×i.d.0.25mm×0.25μm). Temperature programmed for aromatic fraction: oven temperature was held at 60℃ for 2 min, ramped to 150℃ at 8 ℃·min⁻¹, then to 320℃ at 4℃·min⁻¹, and held for 10 min. The scan range was approximately 50–550 amu. Injector temperature was 280℃. Helium was used as carrier gas at 1.4 mL·min⁻¹.

3. Results and discussions

3.1 Source inputs

Abundant aromatic fractions are detected in Es4 extracts, including naphthalenes, phenanthrenes, biphenyl, fluorenes, dibenzothiophenes, dibenzofuranes and so on(Fig.2). Meanwhile, some compounds typically suggesting higher plant-source inputs are detected, such as pyrene, benzo(ghi)perylene, fluoranthene, chrysene, benzo(j)fluoranthene and perylene[4].

The naphthalenes amount to 1.04%~33.86% of the total aromatic fractions in Es4 extracts(Table 1), including naphthalene, methyl naphthalenes, dimethyl naphthalenes, trimethyl naphthalenes (TMN). The distribution of alkyl naphthalenes is related to the type of organic matter and depositional environment[5]. 1,2,5-trimethyl naphthalene is derived from pentacyclic triterpenoid amyrin from higher plants or dicyclic diterpenoid juniperic acid from resin and can be used as an indicator for higher plant-source input[6]. 1,2,5-/1,3,6-TMN ratios are low in marine oils in the Tarim Basin within the range of 0.15–0.29, while those in nonmarine oils are higher than 0.3 with the maximum of 1.48[7]. The ratios in Es4 extracts from the South Slope of Dongying Sag are within the range of 0.39–1.04, suggesting the characteristics of nonmarine oils.

Fig.1 The regional structure and the occurrences of oil fields in the South Slope of Dongying Sag
Table 1  The content of aromatic hydrocarbon of Es4 oils Es4 oils from the South Slope of Dongying Sag

| Oil field   | well  | F.M. | Phenanthrene series | Naphthalene series | Diphenyl series | F-DBT-DBF series | Dicyclic compounds | Tricyclic compounds | Tetracyclic compounds | Pentacyclic compounds |
|-------------|-------|------|---------------------|-------------------|-----------------|-----------------|------------------|-------------------|-------------------|----------------------|
| Chunhua     | Chun17| Es4  | 73.59               | 5.66              | 0.28            | 6.21            | 5.94             | 73.59             | 12.35             | 1.60                 |
|             | Chun 79| Es4  | 74.24               | 6.03              | 0.22            | 3.11            | 6.25             | 74.24             | 14.96             | 1.17                 |
| Liangjialou | Liang218| Es4 | 59.27               | 23.23             | 0.64            | 6.43            | 23.87            | 59.27             | 9.07              | 0.69                 |
| Zhenglizhuang| Fan134| Es4  | 62.81               | 20.70             | 0.71            | 6.62            | 21.41            | 62.81             | 7.77              | 0.60                 |
| Guangli     | Lai74  | Es4  | 40.80               | 33.86             | 1.19            | 11.88           | 35.05            | 41.17             | 9.04              | 0.97                 |
| Jingjia     | Jing29  | Es4  | 75.94               | 1.04              | 0.06            | 3.30            | 1.10             | 76.07             | 18.84             | 0.62                 |
| Gaoqing     | Gao421  | Es4  | 75.02               | 5.77              | 0.16            | 5.27            | 5.92             | 75.02             | 12.46             | 0.92                 |
|             | Gao 421| Es4  | 26.75               | 11.87             | 0.43            | 6.53            | 12.30            | 26.75             | 46.54             | 7.76                 |

Note: F-DBT-DBF series include fluorine, dibenzothiophene, dibenzofurane series and Benzo[a]fluorine, Benzo[a]dibenzothiophene series; dicyclic compounds: include naphthalene and biphenyl series; tricyclic compounds include Phenanthrene series and anthracene; tetracyclic compounds include aspyrene and chryseneseries, fluoranthene andbenzanthrene; and pentacyclic compounds include benzopyrene, benzofluoranthrene and perylene.

The phenanthrenes is the main component of aromatic fractions in Es4 extracts, amounting to 26.75%–75.94%, including phenanthrene (P), methyl phenanthrene (MP), dimethyl phenanthrene, trimethyl phenanthrene and so on. The occurrence of phenanthrene series is influenced by the type of organic matter and depositional environment in addition to thermal evolution\(^{[8]}\). Except for the influence of thermal evolution, content variations of 3-, 2- and 1-MP isomeride are unconspicuous among oils of different genuses, while 9-MP is variable. The contents of 9-MP isomeride are low in marine oils but abundant in nonmarine oils\(^{[9]}\). For oil Extracted from the South Slope of Dongying Sag the contents of 9-MP isomeride are so high as to be 7.02%–12.53%, suggesting a nonmarine genesis of oils.

About 0.05%–14.50% of retene was detected in Es4 samples. Retene is a compound of the phenanthrene series, 1-methyl-7-isopropyl phenanthrene, which nearly occurred in all nonmarine oils and is believed to be derived from the resin of terrestrial higher plants, especially the higher plants of conifers\(^{[9]}\).
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3.2 Sedimentary environment

Compositional characteristics of the F-DBT-DBF series are an effective indicator for distinguishing depositional environment. Oils from marine and saline lake environments have high contents of dibenzothiophene (DBT), while oils from fresh and brackish lakes are dominated by fluorine (F), oils of paludal facies and coal measure environment are abundant in dibenzofuranes (DBF)[10-11]. The F-DBT-DBF series may be sourced from the same precursor with similar basic skeletons and a five-membered ring. An α-C atom is linked on No.9 carbon, which is more active than other C atoms and easily substituted. Under weak oxidation or weak reduction conditions, α-C atom is oxidized to form abundant DBF, while in normal reduction conditions; α-C is saturated by H atom to improve the concentrations of F. Under strong reduction conditions like saline lake or marine environment, it can be reduced into S-bearing aromatic hydrocarbons and abundant with DBT [12]. DBF and DBT are thought to be related to the absolute oxidation and reduction environments respectively[13], simple triangle diagram of F-DBT-DBF series can only distinguish typical sedimentary environments and unfit for the transitional ones, thus plot of DBF/(DBF+F) vs. DBT/(DBT+F) is proposed to differentiate transitional environments[14].

From Fig. 3, it can be seen that DBT are dominated with 33.07-73.17% in content, while DBF is 6–60.59%, suggesting a reduction condition. Furthermore, three subtypes can be distinguished according to the reduction intensities, such as weak reduction in Liangjialou and Guangli oilfields, moderate reduction in Chunhua and Zhenglizhuang oilfields, and strong reduction with high salinity in Jinjia and Gaoqing oilfields.

3.3 Thermal maturity

Generally speaking, chromatograms of aromatic hydrocarbons from immature-low mature oils show back or double peaks with tetracyclic and pentacyclic compounds in predominance, while those from moderate-high mature oils show the front peaks with abundant dicyclic and tricyclic compounds[15]. Aromatic hydrocarbons from Eș4 oils are predominated by tricyclic compounds with double peak occurrence (Fig.2) and low aromatic steroids contents, indicating a low maturity.

In addition, 2,3,6-/(2,3,6+1,2,5)-TMN ratio is sensitive to the maturity without effect by migration fractionation, with the values in 0.4-0.6 in mature oils and source rocks[15]. The ratios in Eș4 extracts are 0.37-0.64, showing characteristics of mature oils(Table 2).
Fig. 3 the correlation among F-DBF-DBT of Es4 oils from the South Slope of Dongying Sag

Table 2 Geochemical parameters of aromatic hydrocarbon of Es4 oils from the South Slope of Dongying Sag

| Oil field | well | F.M. | 1,2,5,1,3,6-TMN | 2,3,6/(2,3,6+1,2,5)TMN | MPI | MPI1 | MPI2 | 4-/1-MDBT | DBT/DBF | Rc (%) | 9-MP (%) |
|-----------|------|------|-----------------|-----------------------|-----|------|------|------------|----------|--------|----------|
| Chunhua   | Chun79 | Es4  | 0.66           | 0.48                  | 2.54| 0.58 | 0.64 | 3.28       | 1.80     | 0.75   | 11.34    |
|           | Liangjialou | Es4  | 0.47           | 0.59                  | 1.81| 0.52 | 0.58 | 4.92       | 1.37     | 0.71   | 12.18    |
| Zhenglizhuang | Fan134 | Es4  | 0.80           | 0.43                  | 1.98| 0.52 | 0.62 | 1.87       | 1.63     | 0.71   | 12.27    |
| Guangli   | Lai74 | Es4  | 0.58           | 0.52                  | 0.81| 0.38 | 0.42 | 1.26       | 0.99     | 0.63   | 7.94     |
| Jingjia   | Jing29 | Es4  | 0.54           | 0.56                  | 1.08| 0.61 | 0.72 | 3.40       | 6.18     | 0.77   | 7.65     |
| Gaoqing   | Gao421 | Es4  | 0.99           | 0.53                  | 2.71| 0.59 | 0.69 | 4.43       | 3.46     | 0.75   | 12.53    |
|           | Gao421 | Es4  | 0.39           | 0.64                  | 0.38| 0.21 | 0.24 | 0.79       | 1.12     | 0.53   | 7.02     |

Note: TMN: Trimethyl-naphthalene; MPI1: 1.5(3-MP+2-MP)/(P+9-MP+1-MP); MPI2: 3×2-MP/(P+9-MP+1-MP); DBT/DBF: ∑Dibenzothiophenes/∑Dibenzofurans; 9-MP: 9-Methyl-PhenanthreneRadke (1988)[16] brought forward methyl phenanthrene indices to evaluate thermal maturity using the relative concentrations of phenanthrene and methyl phenanthrene in oils, and established an equation to convert $R_o$ through MPI1 ($R_o=0.6\text{ MPI}_1+0.40$). After that, the indices and equation are widely used by scholars both at home and abroad. The MPI1 and MPI2 in Es4 extracts from the South Slope of Dongying Sag are 0.21–0.61 and 0.24–0.72, respectively, corresponding to the Rc values of 0.53%–0.77%, indicating a mature stage.

4. Conclusions

(1) Abundant aromatic fractions occurred in Es4 oils extracted from the South Slope of Dongying Sag, including some typical higher plant-sourced compounds. Ratios of 1,2,5-/1,3,6-TMN are within the range of 0.39-1.04, showing the genetic characteristics of terrestrial oils, which has been further confirmed by the high contents of 9-MP.

(2) The F-DB-DBT series in Es4 oil extracts are dominated by DBF, suggesting a strong reduction condition of brackish-saline lake environment. However, three different intensities of weak, moderate and strong reduction can be distinguished.

(3) RIC of aromatic fractions demonstrates a dual peak with dominant tricyclic compounds and low contents of aromatic steroids. Maturity parameters like 2,3,6-/2,3,6+1,2,5-TMN MPI1, MPI2 and converted Rc are 0.37-0.64, 0.21–0.61, 0.24–0.72 and 0.53-0.77%, uniformly indicating Es4 oil extracts
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