Geochemistry of light petroleum from the North of Dongying Depression

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Abstract. With ever-increasing exploration for oils, exploration has inevitably extended into deep layers. Considerable quantity of light oil is discovered from deep Es4_lower layer in the northern steep slope zone of Dongying Depression, Bohai Bay Basin. The oils are characterized by high content of saturated hydrocarbon and low concentration of biomarker and sulphur content. Eleven oil samples and forty-five source rock samples are finely analysed. According to the results of monomer hydrocarbon isotope analysis, carbon and oxygen isotope composition analysis and light hydrocarbon analysis, it is confirmed that the oils in deep strata of northern steep slope zone reach high mature level. The light oils in the northern steep slope zone have a relationship with deep Es4_lower hydrocarbon source rocks by the results of monomer hydrocarbon isotope and light hydrocarbon analysis. Thermal evolution studies show the top Es4_lower hydrocarbon source rocks have a high thermal evolution level. The top Es4_lower hydrocarbon source rocks have relatively high organic abundance and are dominated by types I-II1 kerogen. This research is helpful for unravelling deep petroleum resources evaluation in this area. The viewpoint will be of great significance in future exploration. Moreover, the views in this paper can also be applied to other basins to explore for deep oil reservoirs.

1. Introduction
Previously petroleum exploration has shown that two Organic-rich strata in Dongying depression, including upper Es4 and lower Es3, and have been long regarded as the main sources of oils found in corresponding reservoirs. However, with ever-increasing exploration for oil and gas, exploration has inevitably extended into deep layers [1, 2]. Abundance of condensate oils and high wax oils are found in deep reservoirs, its biomarker is different from the two main hydrocarbon source rock mentioned above, the origin of oils, long the subject of scientific debate, remains uncertain. According to the seismic reflection researches, we can see obvious layered reflection, indicating the hydrocarbon resource rock in deep strata (lower Es4) may be the source of the oil found in deep Formation. Considering the high thermal maturity of deep hydrocarbon sources and some biomarkers reaching the equilibrium value, it is of great significance to finely evaluate these hydrocarbon source rocks. In this paper, the source of the condensate oils and the evaluation of the deep source rocks are finely discussed.

2. Geology
The Bohai Bay Basin consists of several sub-basins, namely the Liaohhe, Liaodong Bay, Bozhong, Jiyang, Huanghua, Jizhong and Linqing sub-basins. Dongying Depression, developed during the
Cenozoic rifting, lies in the southeast of Bohai Bay Basin with an area of 5850 km². It is considered as one of the most oil rich rift areas in the east of China [3].

Dongying Depression is an asymmetric “dustpan shaped” lacustrine basin, and it is subdivided into four sags (the Minfeng Sag, the Lijin Sag, the Niuzhuang Sag and the Boxin Sag) by several normal faults and one Uplift (the Central Anticlinal Belt). The Depression can be further subdivided into five secondary tectonic zones from the north to south, namely the Northern Steep Slope zone, Northern Sag zone, Central Anticline zone, Southern Sag zone and the Southern Gentle Slope zone.

The depression is filled with a thick Cenozoic sediment sequence, which comprises the Paleogene Kongdian (Ek), Shahejie (Es) and Dongying (Ed) formations, the Neogene Guantao (Ng) and Minghuazhen (Nm) formations, and the Quaternary Pingyuan (Qp) Formation.

The basin evolution can be divided into three stages: (1) the pre-rift stage, Lower Paleozoic marine platform sediments and Upper Paleozoic paralic facies of coal measures developed on the Precambrian crystalline basement; (2) the rift stage, abundant Mesozoic and Paleogene fluvial-lacustrine sediments deposited; and (3) depression stage, Neogene fluvial sediments developed.

3. Methodology
The samples are collected from drilling wells in Dongying Depression, Diamondoid hydrocarbons and light hydrocarbons are analyzed using GC-GC-TOFMS without any pre-treatment [4]. GC×GC/TOFMS analysis are performed on an Agilent 7890A gas chromatography coupled to a Pegasus 4D time-of-flight mass spectrometer. a DB-petro column (50 m, 0.2 mm i.d. and 0.5μm film thickness) is used for the 1D phase, and RESTEK-Rix column (2 m, 0.15 mm i.d. and 0.15μm) is selected for the 2D column.

A ground sample of about 0.5g are treated with HCl acid to remove carbonate minerals and then heated to 1700°C by Leco CS-844 to measure TOC.

The samples are ground into a fine powder in an agate mill, collected and analysed using an ISOpime100 mass spectrometer in accordance with standard phosphorylation techniques at Monash University, Melbourne, Australia. The results are presented as relative isotopic ratios for carbon (δ¹³C) and oxygen (δ¹⁸O), in permil units relative to the VPDB international standard. Saturated fractions isotope analyzed are dominated by n-alkanes with a carbon distribution ranging from n-C11 to n-C36 with a low level background.

4. Results and discussion

4.1. Bulk geochemical characteristics of the Ordovician Oils

![Figure 1. TIC of the oils from the Northern Steep Slope zone](image-url)
The \( \text{C}_{29}\text{alpha20R} \) and \( \text{C}_{29}\text{alpha20S} \) sterane ratios based on thermally driven isomerizations at asymmetric carbons and chain positions have been used as a common parameter to assess the thermal maturity of the oil. However, concentration of the biomarker in deep Es\(_3\) lower oils is quite low, indicating the thermal maturity information provided from the \( \text{C}_{29}\text{alpha} \) sterane biomarker is limited.

It is known that the bridgehead-methylated diamondoids thermodynamically more stable than other methylated diamondoid species, the diamondoid-related maturity indicators, e.g. \( 4\text{-MD}/(1+3+4\text{-MD}) \) (MDI) is regarded as a mularity parameters in high-mature crude oils and source rocks [5]. Our previously study indicate that the MDI parameter has a systematic change with vitrinite reflectance at high mature lever, and the oils in deep strata (lower Es\(_4\)) at maturity levels equivalent to \( R_0 > 1.0\% \). Moreover, the short-chain alkane is dominant in deep strata (lower Es\(_4\)) oils, combining the low density of these oils, it can be confirmed that the oils in deep strata of northern steep slope zone reach high mature lever.

Figure 2. Monomer hydrocarbon isotope values of oil from Es\(_4\) deep layer and hydrocarbon source rock from Es\(_4\) and Es\(_3\) layer

4.2. Oil-source correlation

Light hydrocarbon and isotope are demonstrated as effective parameters in oil-source correlation for high maturity lever. Galimov et.al documented the isotope is the effective parameter in the oil-source correlation [6]. The oils from the deep Es\(_4\) layer have a similar \( n \)-alkanes distribution and monomer hydrocarbon isotope value with lower Es\(_4\) hydrocarbon source rocks.

Oils sharing a common source rock are referred to as “homologous”. It is found \( K_1 \) and \( K_2 \) parameters are invariant in different thermal maturity level and it is used in oil-source correlation research.
Figure 3. Light hydrocarbon parameters of oil from Es$_4$ deep layer and hydrocarbon source rock from Es$_4$ and Es$_4$ layer

Figure 4. The relationship between the carbon and Oxygen isotope values of Es$_4$ lower hydrocarbon source rocks

4.3. Evaluation of hydrocarbon source rock

Carbon and oxygen isotope compositions of Es$_4$ lower formation are shown in Figure 4, the oxygen isotope composition varies between -15‰ and -7.0‰ PDB and carbon from -8.1‰ and -3.9‰ PDB.
Figure 5. organic geochemistry characterization of Es₄ lower hydrocarbon source rocks in Dongying Depression. (a) top of Es₄ lower hydrocarbon source rocks; (b) bottom of Es₄ lower hydrocarbon source rocks

For a closed-basin lake, the lake-water δ¹⁸O depends largely on the difference in volume and δ¹⁸O between the input and output waters, the lake volume is stabilized or changes slowly in the period of later Es₄ lower, the δ¹⁸O of lake water approaches a steady-state value, the magnitude of which is governed by vapor exchange across the lake surface and the δ¹⁸O of input water, as the lake δ¹⁸O value is much lighter than the steady-state δ¹⁸O value in the earlier of the Es₄ lower, vapor exchange will cause the lake δ¹⁸O to increase before it reaches the steady-state value.

Due to the enhanced productivity, the carbon pool in the water becomes depleted in ¹²C and consequently has a higher δ¹³C TDIC [7]. It has been proposed that photosynthesis by the calcareous algae Chara causes the remaining TDIC (total dissolved organic carbon) to be enriched in ¹³C (Colleta et al., 2001). Stratification in the water column in response to photosynthesis and organic production in the surface waters occurs in many lakes and leads to significant differences in the carbon isotopic composition of the total dissolved organic carbon which will be reflected in the carbon isotopic composition of carbonates precipitated at different depths in the water column. Thus, the heavier δ¹³C for the top of Es₄ lower can be attributed to the enhanced productivity.

In thin section of the top Es₄ lower, laminae could be identified. Truncated laminae occur may be attributed by the bioturbations, reflecting the fluctuation of oxygen level of the bottom water. The preserved character of amorphous alginate and the maceral compositions indicate the organic matter is mainly of type I-II1 and is deposited in reducing conditions. The abundance of organic matter determined by TOC measurement is shown in Figure 5. The top Es₄ lower have relatively high organic matter content though the rock has attained high thermal maturity(Ro > 1.0%). Thus, it can be speculated that the top Es₄ lower hydrocarbon source rock are the main source rocks for the light oil in deep Es₄.

5. Conclusions
The light oils from the deep $\text{Es}_4^{\text{lower}}$ layer in the Dongying Depression are finely characterized. These light oils bear a typical feature of deep $\text{Es}_4^{\text{lower}}$ source rocks and the top deep $\text{Es}_4^{\text{lower}}$ source rocks is mainly of type I-III and is deposited in reducing conditions. Relatively high organic matter content of deep $\text{Es}_4^{\text{lower}}$ source rocks indicate the deep layer has a good prospect for exploration in the Dongying Depression. This research is helpful for unravelling deep petroleum resources evaluation in this area. The viewpoint will be of great significance in future exploration. Moreover, the views in this paper can also be applied to other basins to explore for deep oil reservoirs.

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