

Pool-formation and secondary change of biodegraded viscous oils: Case study of reservoir section in the Zhengjia-Wangzhuang Oilfield, Jiyang Depression

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Abstract It is demonstrated by various geochemical indexes that the Zhengjia-Wangzhuang Oilfield with viscous crude oil in the Jiyang Depression has been sourced from the contribution of matured source rocks in the upper Es₄. The principal cause leading to the densification of crude oils would be biodegradation, with the degradation level of crude oils being ranked as 2—8; vertically, the biodegradation level increases from the top to bottom of the oil column, with a distinctive biodegradation gradient occurring. Calculated parameters of sterane, terpane and methyl-phenanthrene have indicated that the source-rock's maturity of crude oils and asphaltic sands ranges from 0.7 to 0.9, and based on the calculation of Easy Ro model, the temperature of hydrocarbon generation in the source rock would be within 120—140°C, which coincides with the measurements of reservoir inclusions. The measured homogenization temperature would represent the generation temperature of the source rock, and be fairly different from that of reservoir while being charged with hydrocarbons, which reflects the hydrocarbon-charging to be a fast process, and the period of pool-formation to be consistent with that of peaked generation. According to the evaluation of generation history, the pool-formation could have been occurring in 7—15 Ma. And the biodegradation of crude oils in the study area would be considered to take place in 4—15 Ma based on the examination of biodegradation order and dynamic calculations.

Keywords: viscous oil, biodegradation, time of pool-formation, time of degradation, Jiyang Depression.

DOI: 10.1360/04wd0334

Alongside the increasing demand of modern society for energy resources and the continuous advancement of

techniques in exploration and development for petroleum, the viscous oil, a huge sum of resources, has progressively been thought highly by petroleum geologists, and thus becoming a frontier and one of “heat spots” of research in petroleum geology.

Biodegradation would be considered as an important secondary modification experienced by petroleum in reservoirs. It is one of main mechanisms leading to densification of crude oils^[1]. Most of crude oils in the world have been subjected to biodegradation in varying degrees^[2]. Predecessors have conducted a great deal of highly effective investigation concerning the influence of biodegradation on the molecular composition and physical properties of crude oils^[3—8]. With the occurrence of biodegradation, firstly alkanes, including acyclic isoprenoid pristane and phytane, are consumed to produce large molecular and unidentified complex mixture (UCM or “swell”)^[9,10], which would result in a significant alteration to the physical and chemical properties of crude oils^[4,11,12]; the abilities of saturated and aromatic biomarkers to resist biodegradation and their isotopic features have been inquired^[4,13—17]; the order of resisting biodegradation of biomarkers has been established^[16,18]. The scales to assess levels of biodegradation experienced by crude oils have been erected on the basis of relative abundances of different hydrocarbons^[4—6]. Based on these results, mechanism inducing biodegradation has been probed^[3,4,19]; in the light of geological setting where the crude oils actually experienced biodegradation in subsurface reservoirs, it is considered that biodegradation in most of oil-gas pools would be an anaerobic degradation process^[1,20—24]. At the same time, the occurrence of biodegradation of crude oils in oil-pools often has close relation to activities in deep biosphere, and is strictly limited by the maximum paleotemperature in strata (<80—90°C)^[25].

Biodegradation has seriously modified physical and chemical properties of crude oil, leading to the oil-source correlation always puzzling petroleum geologists, and thus becoming one of scientific problems we have wanted to resolve but not to achieve a real progress. Because of a good deal of uncertainty in the discrimination, of parent sources of biodegraded crude oils, and these oil-pools' shallow burials, as well as the less developmental diagenesis of reservoirs, petroleum geologists would often be of ability not equal to their ambitions. Whether the biodegradation of crude oils is occurring contemporaneously with charging of hydrocarbon into reservoirs or occurs in some one period after charging and forming hydrocarbon pools, will relate to one's recognition of biodegradation mechanism, pool-forming information, and secondary changing in pools, etc., which is also one of scientific issues not to be solved effectively so far.

Distributed in the periphery of the Jiyang Depression are pools with viscous oil and varying in size. For them

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predecessors have conducted a great deal of research work, probing into the origin of viscous oil and the formation mechanism of viscous oil pools^[26-31]; however, as for the newly discovered and huge in reserves Zhengjia-Wangzhuang viscous oilfield, the research work appears to be very poor.

1 Geological setting and distribution of samples

The Zhengjia-Wangzhuang oilfield is located in Lijin County, Shandong Province, structurally in the western part of the northern steep slope belt of Dongying sag, Jiyang Depression. Its north part leans closely against the Chenjiazhuang Projection, being limited by the big Chen-nan Fault, the boundary fault of the sag; its east part is adjacent to the Shengtuo Oilfield; in the south it is contiguous to Lijin Oilfield, and controlled by the Bin-li-Sheng-yong faulted structure belt (Figs. 1 and 2). A set of continental sedimentary strata of Cenozoic has developed on the background of basement rocks. These strata are successively (from bottom to top) as follows: the Archean Group (Anz); the Shahejie Formation of the Palaeogene (Es), the Dongying Formation (Ed), the Guantao Formation of the Neogene (Ng), the Minghuazhen Formation (Nm), and the Pingyuan Formation of the Quaternary

(Qp). The Shahejie Formation can be subdivided as the Sha-1st Member (Es₁), the Sha-2nd Member (Es₂), the Sha-3rd Member (Es₃) and the Sha-4th Member (Es₄). The Sha-4th Member immediately is onlap the Archean basement rocks. The Kongdian Formation of the Palaeogene (Ek) and the Sha-2nd Member are commonly absent in the region; and near the Chenjiazhuang Projection the Sha-4th Member and the Dongying Formation are not present. Vertically, the strata would show a distinction of layer-by-layer lapping from south to north, and laterally pinch out towards the projection. The structurally repeated elevating-subsiding movements would result in many larger sedimentary gaps and stratigraphic unconformities, such as the angled unconformity contacts between AnZ and Es₄ (i.e. AnZ/Es₄), Es₄/Es₃, Es₃/Es₁, as well as Es₁ (or Ed)/Ng.

Because of the inheritance in the structural development of the study area, its location in the margin of the sag, and being controlled compositively by the stratigraphic onlap and erosion as well as the structural conditions, the composite oil-pools controlled by the stratigraphic screen combined with the lithologic and structural screen factors are bound to be formed in this area. Their major oil-producing horizons would be occurring in the

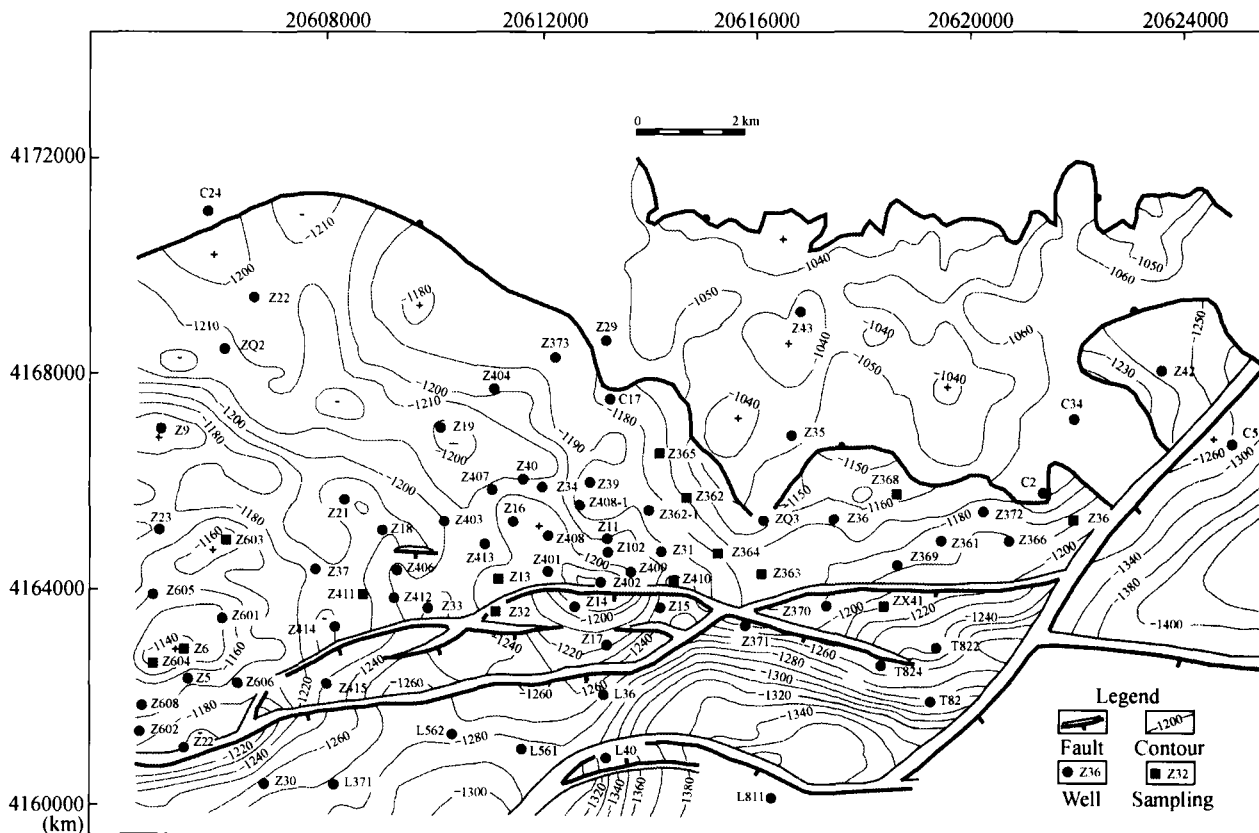


Fig. 1. Structural contour map of Zhengjia-Wangzhuang Oilfield in Dongying Depression¹⁾.

1) Internal information of Shengli Oilfield, 2002.

Guantao Formation and the Sha-1st Member.

From the available analytical data of the formation waters, the waters are of CaCl₂ type, with the total mineralization being 9990—15927 mg/L, and the content of Cl⁻ in the formation water being 5427—8164 mg/L, which would reflect a relatively closed environment of ground water.

In the study area, the formation pressure ranges usually between 9.86 and 13.07 MPa, with a pressure coefficient being 0.84—1.09; the formation temperature is within 46—61 °C, with the gradient of geotemperature being 3.55—3.63 °C/100 m; which indicates a normal temperature and pressure system of oil-pools in the

Zhengjia-Wangzhuang area.

Totally 14 crude oil samples and 20 core samples have been taken from 15 wells and in some horizons of Ng-Es₄-AnZ. This time in the study area, and the systematic sampling has been conducted for the continuously coring interval in the well Zhengxie41, with the distribution of samples as being shown in Fig. 1 and Table 1.

The GC-MS analyses of saturated and aromatic hydrocarbons and the C, N isotopic measurements of asphaltene have been carried into practice for all samples; the Py-GC-MS analyses and carbon isotopic measurements for partial samples; the homogenization temperature measurements of inclusions for 20 core samples.

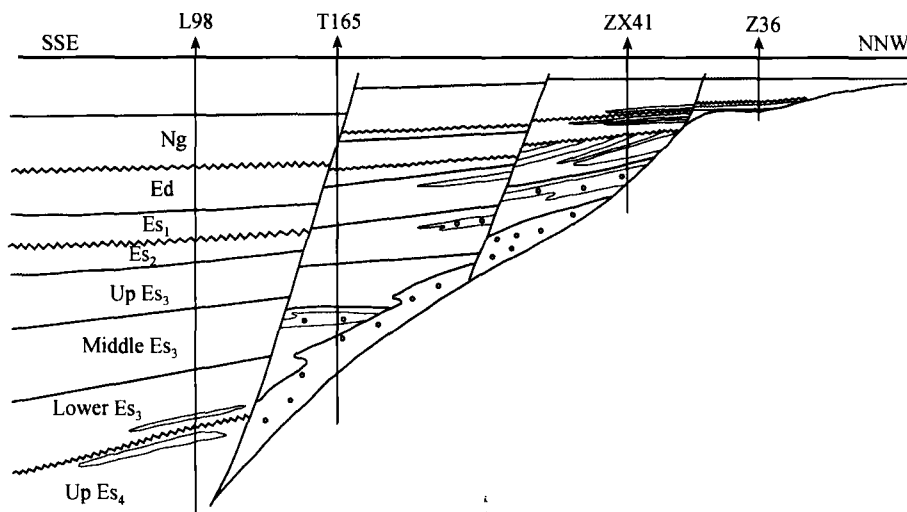


Fig. 2. Profile of oil-pool across Zhengjia-Wangzhuang area¹⁾.

Table 1 Group composition of extracts of crude oils and oil sands in the Zhengjia-Wangzhuang area

Well	Depth/m	Strata	Sat/Aro/Res+Asp	Type	Well	Depth/m	Strata	Sat/Aro/Res+Asp	Type
Z4-3	1332.4—1339.0	Es ₃	0.36/0.27/0.37	O	Z365	1198.4	Es ₁	0.33/0.23/0.44	S
Z6-3	2003ul—30.00	Es ₃	0.25/0.23/0.52	O	Z603	1149.8	AnZ	0.28/0.19/0.53	S
Z32	1327.2—1333.2	Es ₃	0.28/0.25/0.47	O	Z603	1174.2	AnZ	0.27/0.20/0.53	S
ZX41	1219.3—1229.5	Ng	0.33/0.26/0.41	O	Z604	1105.25	Ng	0.25/0.19/0.56	S
Z104	2954—2962	Es ₄	0.18/0.15/0.67	O	Z604	1087.6	Ng	0.25/0.17/0.58	S
Z362	1196.3—1210.0	Es ₁	0.33/0.26/0.41	O	Z411	1327.5	Es ₃	0.20/0.16/0.64	S
Z363	1149.4—1154.0	Ng	0.34/0.27/0.40	O	Z411	1339	Es ₃	0.22/0.16/0.62	S
Z363	1222.9—1230.0	Es ₁	0.31/0.28/0.42	O	ZX41	1247.35	Es ₁	0.45/0.25/0.30	S
Z364	1198.8—1218.5	Es ₁	0.31/0.26/0.43	O	ZX41	1260	Es ₁	0.41/0.25/0.34	S
Z365	1195.10—1200.0	Es ₁	0.31/0.28/0.41	O	ZX41	1261	Es ₁	0.40/0.25/0.35	S
Z366	1198.0—1214.0	Es ₁	0.37/0.26/0.38	O	ZX41	1262.5	Es ₁	0.39/0.25/0.36	S
Z367	1204.4—1220.0	Es ₁	0.26/0.26/0.48	O	ZX41	1275.5	Es ₁	0.38/0.26/0.36	S
Z368	1210.6—1221.5	Es ₁	0.31/0.25/0.44	O	ZX41	1277.3	Es ₁	0.39/0.25/0.36	S
Z410	1241.8—1248.4	Ed	0.30/0.30/0.40	O	ZX41	1328	Es ₁	0.29/0.23/0.48	S
Z363	1191	Es ₁	0.37/0.19/0.44	S	ZX41	1482	Es ₃	0.23/0.20/0.57	S
Z363	1197.7	Es ₁	0.38/0.21/0.41	S	ZX41	1499.95	Es ₃	0.22/0.19/0.59	S
Z365	1191.4	Es ₁	0.39/0.21/0.39	S	ZX41	1561.8	Es ₃	0.18/0.18/0.64	S

Sat, Aro, Res and Asp: content of saturated hydrocarbons, aromatic hydrocarbons, resin and asphaltene in the oil or oil sand; O and S: heavy oil and oil sand.

1) Internal information of Shengli Oilfield, 2002.

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2 Experimental methods and circuit

Firstly contaminants should be removed from the surface of core samples. Crush the samples after having been dried. Put them into Soxhlet's extractor, and extract continuously for 72 h in order to obtain the soluble organic material, the chloroform asphaltene A, which is used with column chromatography to separate into group composition and precipitated asphalt. The extractant is a mixture of dichloromethane and methanol (93 : 7, volume ratio).

(i) Separation of group components. *n*-hexane (dichloromethane : *n*-hexane = 1 : 40) is used to precipitate the asphaltene from crude oils or chloroform asphaltene A, and make the precipitated asphaltene be in constant weight with the gravimetric method. The component soluble in the *n*-hexane is through column chromatography eluted respectively with eluants *n*-hexane, dichloromethane and methanol to separate into alkanes, aromatics and non-hydrocarbons; the filler used in dry column chromatography is silica gel and neutral alumina of 1 : 1 (volume ratio).

The separated fractions (alkanes, aromatics and resin) would be constantly weighted and added with internal standard samples (with the deuterated tetracosane standard sample adding to saturated hydrocarbon solution, and the hexamethylbenzene standard sample adding to aromatic hydrocarbon solution), in order to conduct GC-MS analysis.

(ii) Instrumental analysis. GC analysis is conducted on the HP-6890 (II), with split stream sampling, type DB5-MS capillary column (50 m × 0.32 mm × 0.25 μm), nitrogen (N₂) as carrier gas; initial temperature 35 °C; retention time 10 min; with temperature programming to 290—3 °C/min, and keep it being constant for 30 min.

GC-MS analysis was carried out on the Finnigan-MAT Voyager; with the cold on-column sample injector, DB5-MS capillary column (30 m × 0.32 mm × 0.25 μm), helium gas as carrier gas.

The initial temperature for saturated hydrocarbons is 35 °C, with temperature programming to 120 °C at 10 °C/min, and then to 300 °C at 3 °C/min, being constant for 30 min. EI source, with the energy of ionic current being 70 eV, the temperature of ionic source 200 °C, and the temperature at jointer as 250 °C. The initial temperature for aromatics is 50 °C, with the temperature programming to 300 °C at 3 °C/min, then keep it being constant for 30 min, with others as above.

The observation of inclusions would be put into effect with Leitz LABORLUX 12 POL S type and LEICA DMRX polarizing and fluorescent microscope; and the measurement of homogenization temperatures is conducted using the USGS FLUID INC gas-flowing hot-and-cold stage and the LINKAM THMS-G 600

hot-and-cold stage.

3 Results and discussion

(i) Discrimination of biodegradation levels.

Along with the increase in level of biodegradation, the gross expression of group composition of crude oil is that the content of saturated and aromatic hydrocarbons becomes decreasing, while those of non-hydrocarbon and asphaltene increasing, as well as the oil thickening (Fig. 3, Table 1).

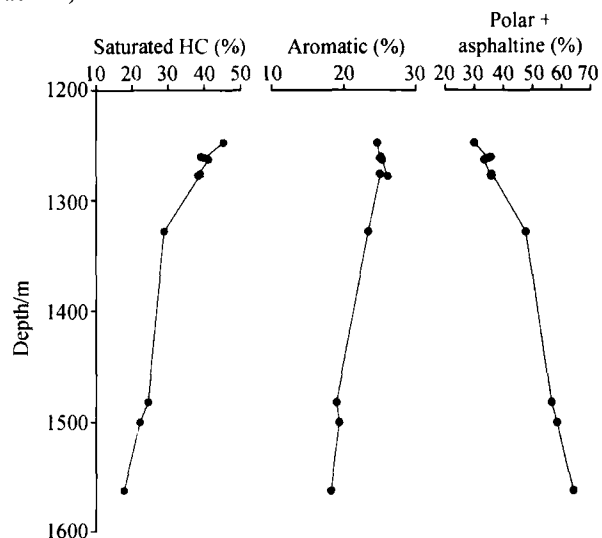


Fig. 3. Relationship of variation in group composition of oil sands versus depth in the well Zhengxie-41.

Connan et al.^[4], according to the variation features of saturated and aromatic hydrocarbons in crude oil, have qualitatively described the level of biodegradation. Volkman et al.^[5] have divided the level of biodegradation into 9 ranks. On the basis of predecessors' investigations, Peters and Moldowan^[6], fully considering the juxtaposition relationship of different series of compounds, and in the light of abundances of various compounds in crude oil, have established a quantitative scale evaluating the level of biodegradation experienced by oil to divide the degradation into 5 levels with 10 ranks. Based mainly on the distribution features of biomarkers in the saturated hydrocarbon, the authors of this paper, using the discrimination criteria of Peters and Moldowan, have made a differentiation of the biodegradation levels of crude oil in the study area.

Figure 4 shows the total ionic current (TIC) of saturated hydrocarbons and the mass chromatograms of relevant steroids and terpenoids of representative samples at different depths of continuously coring interval in the well Zhengxie41. From the figure, it can be seen that for sample A, its *n*-alkanes have been lost by the biodegradation, while a small part being remnant; the isoprenoid pristane and phytane etc. have basically not experienced biodegradation; from these, its level of biodegradation would be

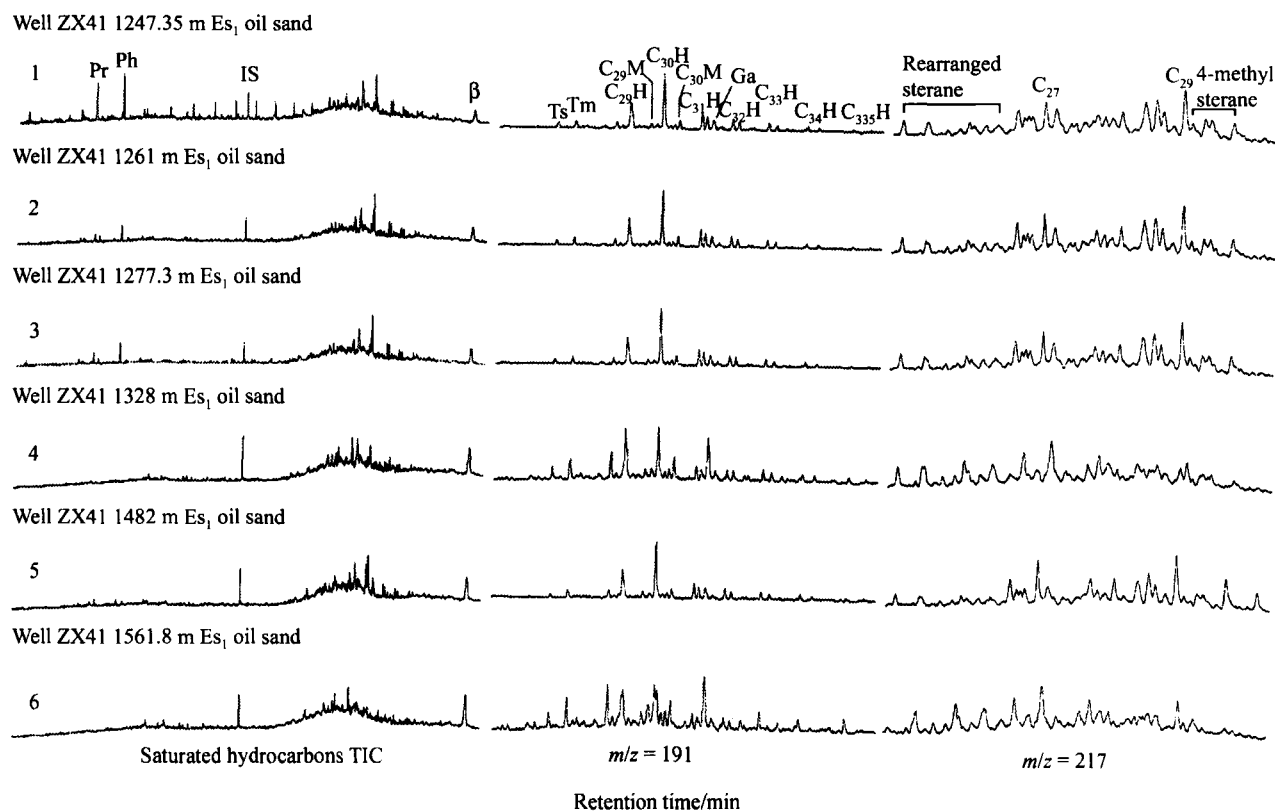


Fig. 4. Map showing the total ionic current (TIC) of saturated hydrocarbons in representative samples with different levels of biodegradation, and the m/z 191, m/z 217 mass chromatograms of saturated hydrocarbons. Notes: Pr, pristane; Ph, phytane; IS, internal standard; β , β -carotane; Ts, $18\alpha(\text{H})$ -22,29,30-trisnorhopane; Tm, $17\alpha(\text{H})$ -22,29,30-trisnorhopane; C_{29}H , $17\alpha(\text{H})$, $21\beta(\text{H})$ -30-norhopane; C_{29}M , $17\beta(\text{H})$, $21\alpha(\text{H})$ -25-normoretane; C_{30}H , $17\alpha(\text{H})$, $21\beta(\text{H})$ -hopane; C_{30}M , $17\beta(\text{H})$, $21\alpha(\text{H})$ -moretane; C_{31}H , $22\text{S}(22\text{R})$ - $17\alpha(\text{H})$, $21\beta(\text{H})$ -homohopane; Ga, gammacerane; C_{32}H , $22\text{S}(22\text{R})$ - $17\alpha(\text{H})$, $21\beta(\text{H})$ -bishomohopane; C_{33}H , $22\text{S}(22\text{R})$ - $17\alpha(\text{H})$, $21\beta(\text{H})$ -trishomohopane; C_{34}H , $22\text{S}(22\text{R})$ - $17\alpha(\text{H})$, $21\beta(\text{H})$ -tetrahomohopane; C_{35}H , $22\text{S}(22\text{R})$ - $17\alpha(\text{H})$, $21\beta(\text{H})$ -pentahomohopane; C_{27} , C_{27} -sterane; C_{29} , C_{29} -sterane.

determined being slight, i.e. the rank 2. For samples B and C, their n -alkanes have nearly been lost out by the biodegradation; moreover, the isoprenoid pristane and phytane etc. would be remaining only in small amount due to the effect of biodegradation. Their level of biodegradation would thus be determined being moderate, i.e. the rank 4. For samples D and E, the biodegradation leads to the complete loss of their alkane and isoprenoid pristane and phytane, the partial loss of regular C_{27} — C_{29} steranes, especially obvious on the C_{27} — C_{29} $\alpha\alpha\alpha 20\text{R}$ and $\alpha\alpha\alpha 20\text{S}$; and the relatively increasing in concentration of rearranged steranes, while the hopanoids nearly not being affected, only the Ts, Tm and the concentrations of 25-norhopane, 30-norhopane, moretane and gammacerane etc. relatively raising with the biodegradation strengthening; from these indications their biodegradation levels would be determined as the serious, i.e. the rank 7. Similarly, for sample F, the biodegradation has resulted in the complete loss of its n -alkane, pristane and phytane isoprenoids, with the steroids being like samples D and E, more significantly affected by the biodegradation; the hopanoids also being influenced to a certain extent, with the

expressions of the decrease in the concentrations of C_{30} -hopane and C_{29} -hopane, and the obvious increase in the concentrations of C_{25} -norhopane and gammacerane even obviously higher than the former; thus its level of biodegradation can be defined as the very serious, i.e. the rank 8.

In a word, vertically the law of variation in the biodegradation level is slight to heavy from top to bottom.

(ii) Parent source of biodegraded Viscous oils and analysis of maturity

(1) Parent source of viscous oil. Zhang et al.^[30] have through research thought the upper Es_4 Submember, Lower Es_3 Submember and Es_1 Member to be the major high-quality source rocks for hydrocarbon in the Palaeogene of the Jiyang Depression. The principal reason for the Dongying sag to become petroleum-prolific sag lies in fact that there are two sets of high-grade source rocks, i.e. the upper Es_4 and lower Es_3 Submembers in it. Predecessors have carried out a thoroughgoing and painstaking organic geochemical research on the source rocks of upper Es_4 and lower Es_3 Submembers in the Jiyang Depression

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and Lijin sag^{[27,30,31],1)}. They have thought that the source rocks in the upper Es₄ Submember possess an obvious phytane predominance and a lower pristane/phytane ratio (generally <0.75) which reflects a fairly strong reduction sedimentary environment; in this set of source rocks, the high content of gammacerane in saturated hydrocarbons and the ratio of gammacerane/C₃₀-hopane being over 0.2 (even over 1.0 in individual samples) have suggested a saline deposition feature. For source rocks in the lower Es₃ Submember, its high ratio of pristane/phytane, averagely 1.05, would reflect a weak reduction sedimentary environment; the lower content of gammacerane, the less ratio of gammacerane/C₃₀-hopane than 0.2, as well as the predominance of three high values of rearranged sterane, C₂₉-sterane ββ configuration and 4-methylsterane, has been indicated a deposition environment with fresh water lake being dominant. Moreover, the oils of study area are mainly sourced from the adjacent Lijin sag.

This research primarily based on the organic geochemical properties of crude oil combined with the previous study results has probed into the parent source of viscous oils in the Zhengjia-Wangzhuang area, and thought that crude oils in the area have been mainly coming from the matured source rocks of the upper Es₄ Submember. The principal bases are as follows: i) The C-isotopic values of asphaltenes of crude oils in the Zhengjia-Wangzhuang area are largely between -26.57‰ and -28.72‰ (15 samples), with the average value being -27.19‰. The C-isotopic values of the alkanes of crude oils in the lower Es₃ Submember range in -23‰—29‰, with the major frequency peak being between -26.5‰ and -28.5‰^[30]. Commonly, the distribution regularity of C-isotopic values of crude oil fraction is $\delta^{13}\text{C}_{\text{alkane}} < \delta^{13}\text{C}_{\text{crude}} < \delta^{13}\text{C}_{\text{aromatic}} < \delta^{13}\text{C}_{\text{resin}} < \delta^{13}\text{C}_{\text{asphaltene}}$, from this we may speculate that the C-isotopic values of asphaltene of crude in the lower Es₃ Submember are heavier than -26.5‰—28.5‰, which indicates that the fair significant difference would exist between the C-isotopic of asphaltene of the crude in the study area and that of the crude from the lower Es₃ Submember. ii) In the distribution curve of C-isotopic of individual *n*-alkane in the crude oil (Fig. 5), the C-isotopic composition of low carbon numeric *n*-alkanes, the *n*C₁₄—*n*C₂₅, would be relatively heavy, mainly ranging in -28.1‰—24.8‰; the *n*C₂₅—*n*C₂₈ alkane monomers are of relatively light C-isotopic composition, concentrating in a range of -29.8‰—27.8‰; the C-isotopic composition of *n*C₂₈—*n*C₃₄ alkane monomers would assume a tendency of slightly weighing, distributing mainly in range of -29.5‰—28.0‰. They wholly assume a marked “three-segment-style” distribution, being fairly coincided with that in the upper Es₄ Submember^[27]. iii) In the viscous oils,

Pr/Ph ratio is fairly low (0.41—0.68), assuming an obvious phytane predominance, reflecting a quietly reducing deposition environment with higher salinity; the higher contents of gammacerane (Ga/C₃₀H=0.17—0.71) and β-carotane evidently indicates a comparatively reducing deposition environment of brackish lake. The crude oils have experienced biodegradation to various extents, but for crude oils being of slighter biodegradation, their pr/ph features would still be expressed markedly; while the contents of gammacerane and β-carotane are higher regardless of the biodegradation level. These are relatively consistent with the geochemical distribution characteristic of source rocks in the upper Es₄ Submember. iv) The steranoids display a distribution pattern of aquatic life source with the C₂₇ regular sterane being more than the C₂₉ regular sterane; the contents of short-chain pregnane and homopregnane are relatively high, while that of rearranged sterane being relatively low; the content of C₃₀ methyl-sterane is not high, which is not consistent with that of the source rocks with higher content of rearranged sterane in the Es₃ Member; the steranoids in the cracked products of asphaltene of crude oil also possess the features of source rocks in the Es₄ Member, such as the distribution pattern of the relatively low contents of 4-methyl-sterane and rearranged sterane, as well as the C₂₇-regular sterane being more than C₂₉-regular sterane. v) Among the pentacyclic terpanes, there is distinct distribution of long-chain (C₃₄, C₃₅) heptanes, indicating its parent source (or source rock) belonging to the carbonate-evaporate deposition environment.

(2) Maturity analysis of viscous oils. In the saturated hydrocarbon fraction of the viscous oil, Ts/Tm ratio is less than 1, with the range of 0.58—0.94; Ts/(Ts+Tm)<0.5, between 0.36 and 0.48; the 22S/(22S+22R) in the range of 0.57—0.61; the 20S/(20S+20R) of sterane distributed between 0.41 and 0.53; and the ratio of the αββ/(ααα+αββ) of C₂₉ sterane between 0.34 and 0.51. All of these would reflect the viscous oil in the Zhengjia-Wangzhuang area in maturing phase.

For the aromatic fraction of the crude oil, the calculations of measured methyl-phenanthrene indexes have suggested the reflectance *R_c* of equivalent vitrinite of the viscous oil mainly distributed in the range of 0.71—0.91, averagely 0.78, and shown it in the maturing phase, and not yet into hyper-maturation phase.

(iii) Studying of pool-formation time. In this research, the measurement of fluid inclusions has been adopted in combination with the previous results to study the time of pool-formation of pools, with viscous oil in the Zhengjia-Wangzhuang area. The samples have been collected from the coring intervals in the wells Zhengxie 41, Zheng 411, 604, and 365 etc. in the Zhengjia-Wangzhuang

1) Lu Hui, Chen Zhilin, Wang Guangli et al., Oil source and oil migration and accumulation research of northern steep slope belt in Lijin sag, in Symposium of Organic Geochemistry (ed. Geology Research Institute of Shenli Oilfield), 2002.

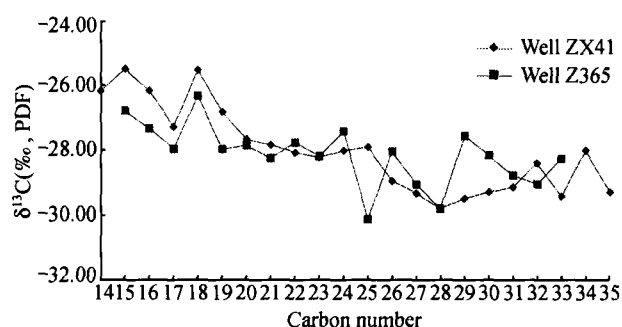


Fig. 5. C-isotopic distribution curves of individual *n*-alkane of viscous oil in Zhengjia-Wangzhuang area.

area, with the sampling stratigraphic horizons intervals concentrated in the Tertiary system, and the relevant information of samples shown in Table 2. From the observation of thin sections, these inclusions are all occurring in the micro-fractures of quartz grains, regardless of the saline inclusions or hydrocarbon inclusions. Because of the shallow burial, the cementation is less developmental, with the overgrowth of quartz being less evident; it is thus difficult to find out the inclusions in the cement and the rim of overgrowth of quartz.

(1) Type and characteristic of inclusions. From the composition of inclusion, the inclusions in the studied intervals can be classified into the type of saline solution inclusion, the type of hydrocarbonaceous inclusion and the type of organic inclusion.

The liquid phase saline inclusions are quite small in size, about 3 μm , mostly assuming ellipse, and colourless in plainlight microscope; the gas-liquid bi-phase saline solution inclusions are somewhat larger than the liquid phase saline inclusions, about 3–5 μm , mostly assuming the quadrilateral, ellipse, and colourless under plainlight microscope. Its gas/liquid ratio is commonly lower, generally less than 20%, with some one even smaller to be a black point jumping within the inclusion. The hydrocarbonaceous inclusion consists mainly of liquid phase saline and gas-liquid phase hydrocarbons, largely being quadri-

lateral, oval and bar in shapes. At room temperature and under microscope, two phases of gas and liquid can be seen, with its gas/liquid ratio being lower, generally less than 20%, while the liquid phase hydrocarbons assuming a thin circular ring surrounding the gas bubble, thus forming a liquid phase hydrocarbon ring. Under plainlight microscope, the inclusion would be colourless or slightly yellow-brown, while the liquid phase hydrocarbon ring assuming black, and the high or low content of liquid hydrocarbons would determine the ring to be thick or thin; under fluorescence, the saline solution and gaseous hydrocarbon (gas bubble) are not luminescent, while the liquid phase hydrocarbon ring would give out a fairly clear yellow fluorescence. This type of inclusions is commonly smaller, generally about 3–5 μm .

(2) Measurement of homogenization temperature of inclusions. In the study area, the homogenization temperature of inclusions can roughly be classified into IV groups, with their distribution respectively ranging in 75–100°C, 100–125°C, 125–150°C and over 150°C (Table 2). If the measured temperatures are over 150°C, they would be generally thought to be primary inclusions or those captured nonhomogenizedly, which cannot really reflect the paleotemperature when hydrocarbon-charging and pool-forming. Moreover, we have observed under microscope that the distribution strings of inclusions with about 120°C temperature have offset those of inclusions with temperatures over 150°C, which reflects inclusion with higher homogenization temperatures to be formed prior to those with relatively low homogenization temperatures; therefore in this study, the data of homogenization temperatures over 150° have not been considered.

There are not obvious correlation between the homogenization temperatures of inclusions and the burial depth of samples. The samples, regardless of in the Neogene or the Paleogene, are all of two temperature-distributing ranges, namely the range of 100–125°C and the range of 125–150°C.

Table 2 Measurements of homogenization temperatures of inclusions in the Tertiary System of the Zhengjia-Wangzhuang area

Sample #	Well	Depth/m	Strata	Homogenization temperature/°C		
				Group I	Group II	Group III
SS-3	ZX41	1260.00	Es ₁		105.6–124.7	126.5–132.6
SS-5	ZX41	1277.30	Es ₁		118.7–119.6	134.7–147.6
SS-7	ZX41	1328.00	Es ₁		102.3–124.2	131.3–151.4
SS-9	ZX41	1497.45	Es ₃		101.3–125.3	135.7–153.8
SS-10	ZX41	1561.65	Es ₃		115–124.9	135.6–143
SS-11	Z363	1191.00	Es ₁	81.6–84.8	114.6–124.8	131.2–151
SS-16	Z411	1327.50	Es ₃	77.2–94.7	104.1–116.3	134.6–152.2
SS-18	Z604	1087.60	Ng	79.5–93.6	107.5–124.8	127.7–151
SS-19	Z604	1105.25	Ng	70.2–95.2	104.2–107.5	131.1–142
SS-25	L98	3141.30	Es ₃	83.2–98.3	108.4–120.7	135.4–148.9

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The measured temperatures of hydrocarbonaceous inclusions range mainly in group II and group III temperature sections. In comparison with the associated gas-liquid biphasic saline solution inclusions, their measured temperatures are basically consistent. Judging from this, these two can all reflect the paleotemperature when the pools initially had been charged with hydrocarbons in the study area.

Figure 6 shows the distribution histogram plot of homogenization temperatures of fluid inclusions in the Tertiary of the Zhengjia-Wangzhuang area. We can, from the figure, find that the homogenization temperatures of fluid inclusions are distributed in a wide range of 70–150 °C. The peak values would mainly be in three ranges, i.e. respectively 80–90, 100–110 and 130–150 °C, with the major peak temperatures of 130–140 °C, which would represent the preferential temperature range when the inclusions being formed; while the range of 110–130 °C appears to be a median platform, reflecting a long continuously constant charging process. Because of the distribution of measured inclusions mainly in the microfractures between the quartz grains, thus these different homogenization temperature sections may represent the temperature ranges of the fluids activating and the fractures' opening or closing.

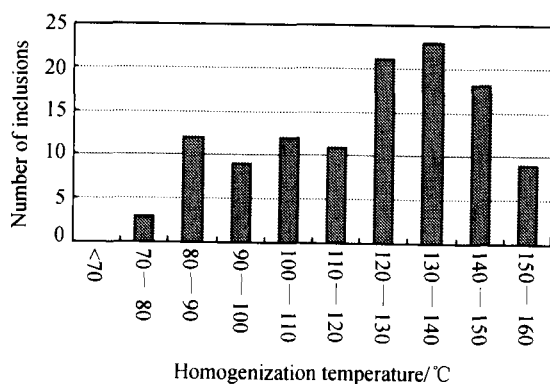


Fig. 6. Distribution histogram plot of homogenization temperatures of fluid inclusions in the Zhengjia-Wangzhuang area.

(3) Approach to the time of pool-formation. From the resultant data, we find the measured temperatures of inclusions to be far different from the present reservoir temperatures (46–61 °C). It is thought from the study of diagenesis for reservoirs that the reservoir with viscous oil has yet been in the early diagenetic stage, with the sandstones yet assuming a hemi-consolidating state, which would reflect the maximal paleotemperature experienced by the reservoir not being over 85 °C^[32]; vertically viewing the structural developmental history, the reservoir temperature can absolutely not reach so high as that, then, what has been reflected by the measured homogenization temperatures of inclusions? What geological information

do they implicate?

We think that what the homogenization temperatures of inclusions reflect would be the reservoir temperatures when the fluid had been captured. If the hydrocarbon charging was a slow process, the fluid temperature would progressively balance the temperature of reservoir; if it was high-speed, the fluid temperature would rather be approximate to the temperature of source rock; in even more situations, the fluid temperature would be between the reservoir temperature and that of source rock, and in a particular condition, especially in the case of intense deep hydrothermal activity, the fluid temperature would still be over that of source rock.

Figure 7 shows curves of burial history of Li-98 well in the Lijin Sag. In this sag, the present geothermal gradient is 3.6 °C/100 m, while the paleogeothermal gradient would be higher, averagely 4.0 °C/100 m, with the palaeo-surface temperature being 14 °C^[33]; the know calculated crude maturity R_c is 0.7–0.9, namely the R_o when the crude oil having been generated in the source rock of the upper Es₄, the calculation, using Easy R_o model, has given out the temperature when crude oils generating would be 120–140 °C (Fig. 8), and then from this the time of pool-formation can be inferred to be 7–15 Ma.

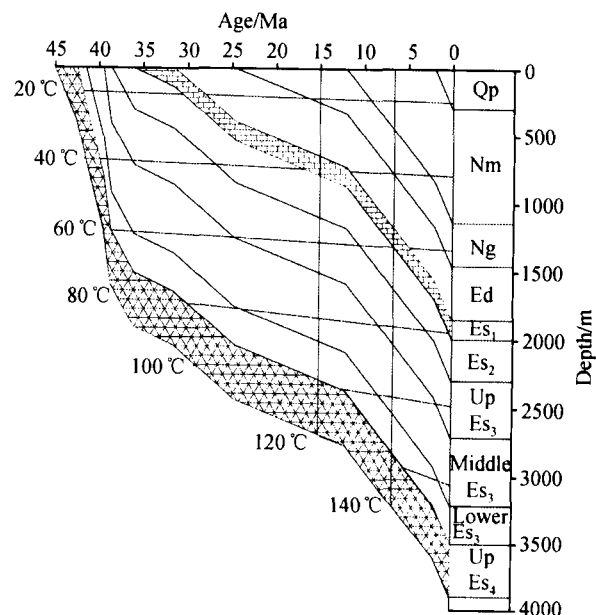


Fig. 7. Curves of burial history of Li-98 well in the Lijin Sag (the stratigraphic erosion not being considered).

The reason for selection of Li-98 well lies in the fact that the oil-source correlation indicated the crude oil in the study area to be from the source rock of the upper Es₄ Submember in the Lijin Sag; this well is mediated between the hydrocarbon-generating center of Lijin Sag and the study area, and adjacent to the Bin-li-Sheng-yong fault zone; its thickness and burial depth of source rock in the upper Es₄ Submember can represent the average condition

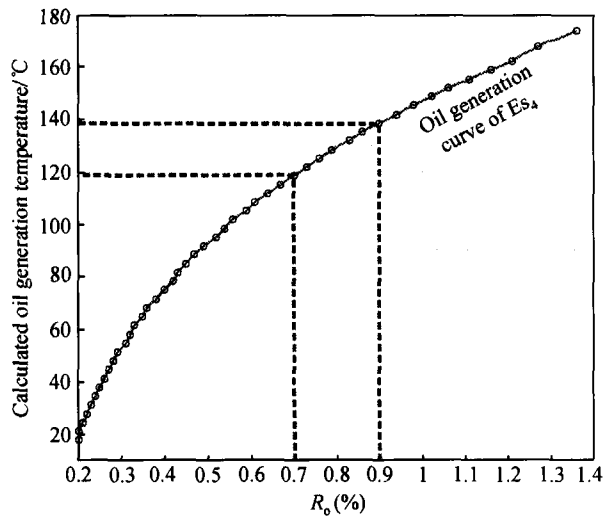


Fig. 8. Results of Easy- R_o calculation.

in the Lijin Sag, and its level of thermal evolution and hydrocarbon-generating history can also reflect the average level of evolution in the Lijin Sag. From the major frequent temperature of reservoir inclusions in the Zhengjia-Wangzhuang area, it is more approximate to the temperature while the hydrocarbon generation occurred in the source rock of the upper Es_4 Submember, which would reflect a "high-speed" geological process of the fast hydrocarbon-generation, -expulsion, -migration, -accumulation, as well as the fast pool-formation.

Through the analysis of fluid inclusions in the Lijin Oilfield, Guo¹⁾ held that the homogenization temperatures of saline inclusions in the Lijin Oilfield can be divided into two ranges, one in 96—110°C and another in 115—130°C, corresponding to its two phases of hydrocarbon migration and accumulation histories, with hydrocarbon generating time as 8—12 Ma, which is very consistent with the research results of this study.

(iv) Approach to the time of biodegradation. The time of biodegradation of crude oil has been a key problem concerned but not yet been completely resolved by petroleum geologists. Generally thinking, with the oil-charging into a reservoir, the biodegradation of hydrocarbons would immediately be occurring; however, the biodegradation of hydrocarbons has often been controlled by many geological factors. Therefore, the relatively precise estimation on the time of hydrocarbon biodegradation will be useful to the quietly exact prediction on the time of hydrocarbon-charging or pool-forming, and to the accurate analysis on the features of secondary alteration after the pool-formation.

Larter et al.^[1] have probed into the biodegradation rate of crude oil through the analysis on the detailed geological information of many biodegraded petroleum fields,

and using a lot of methods, such as the estimation on minimum biodegradation rate of field-wide entire oil column, the diffusion controlled model on the vertical change in gradient of hydrocarbon composition, and the crude-mixing dynamic model etc. The present paper attempts to do some useful approach in this respect.

Regardless of the type of biodegradation, its degradation rate and level are not dependent on the supply of hydrocarbons, but are compositely controlled by the abilities of the groundwater in supplying nutrients and electron acceptors and of the diffusion^[1]. The relatively large or small volume of groundwater and oil column will directly control the biodegradation rate and level^[5,20]. It is commonly thought that the mechanism of biodegradation would be the saturated and aromatic hydrocarbons being mineralized into CO_2 and H_2O , or transforming into some unknown compounds in the biodegradation process^[1].

Generally thinking, in the biodegradation zone of crude oils, the biodegradation of crude oils would follow the diffusion-adsorption principle and the first-order dynamic equation of chemical reaction. Therefore, in the light of the biodegradation-induced vertical gradient change in the concentration of saturated hydrocarbons, we can probe into the time of biodegradation of crude oils. Assuming the reaction $A \rightarrow P$, the initial concentration of the reactant A being a , the initial concentration of the product P being zero, at time t , the concentration of A being $a-x$, and the concentration of P being X , the rate equation can be written as

$$\ln\left(\frac{a}{a-x}\right) = K_1 t,$$

where K_1 is the rate constant (kg hydrocarbon/kg oil/a).

The analysis of group compositions of abstracts from the source rock in the upper Es_4 Submember indicated the saturated hydrocarbons of about 55%. In the present study, we have carried out a relatively continuous sampling for the oil sands of coring intervals in the well Zhengxie-41, and its oil column is about 360 m in height. Because of the effect of biodegradation, a vertical gradient change in the content of saturated hydrocarbons appears in the oil column (Fig. 3), and this gradient change can be approximately considered as a kind of linear relationship.

The crude oil in the top part of the oil column has been influenced by a slight biodegradation, with the content of saturated hydrocarbons being about 45%; in the lower part of the oil column, the more it is towards the boundary of oil/water, the more serious the biodegradation is, with its content of saturated hydrocarbons being about 18%. The vertically changing gradient of the content of saturated hydrocarbons is about 0.00075 kg saturated hydrocarbons/kg oil/m. At the time of oil-charging (the biodegradation did not yet occur), the percentage content of

1) Guo Rutai, Complex oil and gas bearing system research of North Dongying Depression, PhD Thesis, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 2002.

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saturated hydrocarbons is about 55%. Through the computer-modeling research on the biodegraded crude oils of several oilfields in the world, Larter et al. thought the biodegradation rate constant to be about 10^{-6} — 10^{-7} . If only the changes in the biodegradation level and the hydrocarbon content of crude oils near the boundary of oil/water are considered, and these parameters are introduced into the abovementioned equation, then it can be found the t of about 0.40—4.0 Ma, i.e. assuming in the condition of lacking mass-diffusional exchange, the required time for the crude oil near the boundary of oil/water from the beginning of accumulating into the reservoir to the present biodegradation level would be 0.4—4.0 Ma. In this study we would like to take the conservative value of 4.0 Ma.

In fact, there is fairly distinct difference of vertical biodegradation levels in the continuous oil column, namely the biodegradation level of crude oils near the boundary of oil/water would be higher, while that far from the boundary of oil/water is relatively low. It is due to the vertical difference in the biodegradation level, i.e. the saturated hydrocarbon concentration, that the vertical diffusion and mixing of saturated hydrocarbons will not be avoided.

Assuming that the diffusion coefficient is homogeneous, for a fluid column with length, the time volume range (t) of response to the change in concentrations of fluid composition induced by diffusion, can be shown as follows:

$$t = (\text{height of column})^2 / \text{diffusion coefficient.} \quad (1)$$

For a thick, continuous viscous oil column, its diffusion effect tends to be seriously influenced due to the high viscosity of viscous oil; therefore, because of the change in crude oil's component concentration induced by diffusion, the time volume range (t) of response is about 70% of the value found by the above equation. We would like to consider the time " t " as the "inducing time" of oil column's response to biodegradation. After this "inducing time", even if a slight level biodegradation (alkanes' loss only several percentages), the vertical gradient change in the concentration of saturated hydrocarbons will be approximate to a constant.

The vertical changing gradient of saturated hydrocarbons' contents in the well Zhengxie-41 is about 0.00075 kg saturated hydrocarbon/kg oil/m, the percentage content of saturated hydrocarbons when oil-charging (i.e. the biodegradation did not yet occur) is about 55%, from this, the length of the continuous oil column can be developed to be about 490 m; the diffusion coefficient of alkanes in viscous oil is $0.5 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, introducing it into formula (1), we can find the " t " to be about 4.8×10^{14} s, namely 15.23 Ma.

Analyzing from the view of geology, the biodegradation time of crude oils near the boundary of oil/water would be the lower limit time for the biodegrada-

tion-occurring of crude oils, while the "inducing time" of response to the biodegradation would be the upper limit time for the biodegradation-occurring of crude oils. Through this composite research, we can think the most conservative time for the biodegradation of crude oils in the Zhengjia-Wangzhuang area to be about 4—15 Ma.

4 Conclusion

The biodegraded viscous oil in the Zhengjia-Wangzhuang area would come from the contribution of matured source rocks in the upper Es₄ Submember.

The maturity of parent sources of crude oils and asphaltene sands would range in 0.7—0.9, with the temperature for hydrocarbon generation of parent source being 120—140°C. The oil-charging is a fast process, the homogenization temperature is approximate to the temperature when hydrocarbon-generating from source rocks, the pool-formation phase is consistent with the peak phase of hydrocarbon generation, and the major phase of hydrocarbon generation and pool-formation would be in about 7—15 Ma. The pool-formation would occur in two phases, with the major phase occurring in the peak phase of hydrocarbon generation.

The biodegradation levels of crude oils in the study area are ranks 2—8. The biodegradation levels are dependent upon the distance from the crude oil to the boundary of oil/water. The biodegradation level would be progressively increasing from the top to bottom of the oil column, and vertically, an obvious gradient of biodegradation appears. Through studying the order of biodegradation and the dynamic calculation, it can be found that the time for biodegradation of crude oils in the Zhengjia-Wangzhuang area is about 4—15 Ma.

Acknowledgements The authors are grateful to the Research Institute of Geology of Shengli Oilfield for supplying samples and information. The thanks are extending to Dr. Jia Wanglu, Dr. Qin Yan and Dr. Gong Se for their help to complete the analysis of relevant samples. This work was supported by the Chinese Academy of Sciences (KZCX1-SW-18) and the Natural Science Foundation of Guangdong Province (04300762).

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(Received August 5, 2004; accepted October 22, 2004)