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Research Article

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Biomarker characters and biodegradation of petroleum in Gangxi oil field, China

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ABSTRACT

Biomarker characters and biodegradation of petroleum were investigated in Gangxi oil field, China, using GC-MS analysis. TIC profiles suggested that the petroleum in oil reservoir was biodegraded seriously by indigenous microbiota, due to the secondary alteration processes (water flooding since 1972). The n-alkanes were missing in most of oil samples. The iso-alkanes were present in all of the samples but in low concentration. The polycyclic aromatic hydrocarbons were degraded at different degrees. The PAHs of 2 rings were almost missing, while that of 3 or 4 rings were present at low degraded rate. These suggested that the indigenous microorganism of oil well might have ability to degrade petroleum and it could be used for remedying oil spill. Through analysis of 28 kinds of biomarker, these oils showed similar characteristics: mid content of gammacerane, abundant hopane, and low content of oleanane. These meant that the source of oil might be prokaryotic organisms and algal, and the reservoirs was a not highly reducing and anoxic environment. The maturity parameters of 20S / (20S + 20R) and ββ / (ββ + αα) showed these oil was mature oil, and the maturity degree of oil samples increased as order: 2#, 5#, 3# or 1#, 4#, 6#.

Key words: Biodegradation, Petroleum, PAH, Biomarker

INTRODUCTION

Biodegradation of crude oil exists in many oil reservoirs over the world, and it affects the quality of recovered petroleum productions. Anaerobic degradation processes is proved as an important role to affect this biodegradation under methanogenic conditions, despite slow reaction kinetics and uncertainty as to the actual degradation pathways occurring in oil reservoirs [1, 2]. Methane is a downstream energy gas, which may be used directly, can reduce oil viscosity and enhance flow characteristics through the reservoir matrix. Dagang oil field is one of the important oil fields in China, where many wells have been in secondary alteration processes (secondary oil recovery) and the oil production was much degraded. So Gangxi zone in Dagang oil field was selected as the object of this study because of the heavy oil production and previously research [3], to know the degradation of oil in Dagang oil field.

Biomarkers are complex molecular fossils derived from biochemical, particularly lipids, in once-living organisms. They provide a method to relate the crude oils and extracts of petroleum source rocks (correlation) and be used by geologists to interpret the characteristics of petroleum source rocks when only oil samples are available. Biomarkers are commonly retained as indicators of petroleum contamination in the environment because of their general resistance to weathering, biodegradation, evaporation, and other processes [4]. The most common biomarkers include terpanes, steranes and mono – and triaromatic steroids[5-7]. The biomarker distributions in petroleums from Gangxi oil zone would be investigated in order to characterize possible source rocks, reconstruct depositional environments, determine the maturity levels of the oils, and provide the biomarker character parameter of Gangxi oil zone for sources apportionment, especially to assess the effects of biodegradation on the oil composition in the reservoir.That explores a better method of either reducing biodegradation, or stimulating methanogenic processes of oil for microbial enhanced oil recovery (MEOR).

EXPERIMENTAL SECTION

Gas-Chromatography Mass-Spectrometry of Oil

The oil samples taken from the reservoir in Gangxi zone of Dagang oil field, China, were extracted with dichloromethane and dehydrated through a 2-g anhydrous Na_2SO_4 column. Then the eluate was used to determine the oil content and prepare the samples of GC-MS. The eluate of 2.0ml was evaporated until dryness and the oil content was determined by gravimetry; the eluate of the same volume was cleaned through 2 g of Al_2O_3 (5% w/w deactivated) column with the solvent of dichloromethane-hexane (1:1 v/v) and then concentrated and exchanged to hexane (1.0 ml) by a gentle solvent evaporation under a stream of nitrogen gas for the inject-samples of GC-MS. GC-MS analysis was performed using a GCMS-QP2010 SE gas chromatograph - MS spectrometer equipped (SHIMADZU), fitted with a capillary column (RESTEK, USA) RXI-5 ms (30m × 0.25mm i.d., 0.25μm film).

Chemical character of biomarkers

The chemical type and relative content of biomarker compounds in a specific oil was considered as its unique fingerprint[7]. Terpane(m/z 191), Sterane(m/z 217 and 218) and Triaromatic steroid hydrocarbon (m/z 231) were identified and semi-quantitatively determined by selective ion monitoring (SIM) chromato-graphy.

RESULTS AND DISCUSSION

Degree of Crude Oil Degradation

Most samples of Gangxi zone were degraded, and the samples of 2#, 3#, 4#, 5# and 6# were completely depleted of n-alkanes, as shown in Fig.1. Compared to 1# sample, the lowest degraded sample in all samples, the degree of degradation of others was high (considering C_{10}-C_{35}). 1# samples still had *n*-alkanes, although it was low. The biodegradation characteristic of oil samples was showed in table 1. The *iso*-alkanes were present in all of the samples, but in low concentration (above 80 % of compound is degraded compared to non-degraded sample). The polycyclic aromatic hydrocarbons (PAHs) were degraded at different degrees.The PAHs of 2 rings were almost missing, while that of 3 or 4 rings were present at low degraded rate. The degradation degrees of all oil samples were similar. But that of 5# sample wasthe most in all, which might be caused by more mining time. All showed that the oil of Gangxi zone was degraded by the indigenous microorganism especially when interfered by mining.This also suggested that the indigenous microorganism of oil well might have ability to degrade petroleum and it could be used for remedying oil spill.

Table 1The biodegradation characteristic of oil samples compared with non-degraded oil

Compounds		Biodegradation characteristic[a]					
		Non-degraded sample	1#	2#	3#	4#	5#
Alkanes	*n*-alkanes	++	-	-	-	-	-
	iso-alkanes	++	*	*	*	*	*
PAHs	Benzo(b)thiphene	++	-	-	-	-	-
	Naphthalene	++	*	-	-	-	-
	Biphenyl	++	*	*	*	*	-
	Fluorene	++	*	*	*	*	*
	Phenanthrene	++	+	+	+	+	*
	Dibenzothiophene	++	+	+	+	+	+
	Fluoranthene	++	++	++	++	+	+
	Pyrene	++	++	++	++	++	++
	Benz(a)anthracene	++	++	++	++	++	++
	Chrysene	++	++	++	++	++	++

[a] *"++": above 80 % of compound is present; "+": above 50 % of compound is degraded; "*": above 80 % of compound is degraded; "-": the compound is not present.*

Biomarker character of oil in Gangxi oil filed

Some biomarkerswere analyzed and these oil samples have some similar characteristics: mid content of gammacerane, abundant hopane, and low content of oleanane. These biomarkers were clearly dominated by source input, and hopanes, C30 diahopane, tri-cyclic terpanes and regular steranes in oil respectively meant prokaryotic organisms (e.g., bacteria and blue-green algae), bacteria, algal, and eukaryotic organisms (e.g., diatoms, flagellates, zooplanktons) or higher organisms as source [8]. The analysis result, the content of regular steranes (m/z 217 and 218) was much lower (1 - 10%) than that of tri-cyclic terpanes and hopanes (m/z 191), and it showed that the source of these oil might be prokaryotic organisms and algal; the oil reserve of Gangxi zone came from sea in accordance with the filed site.

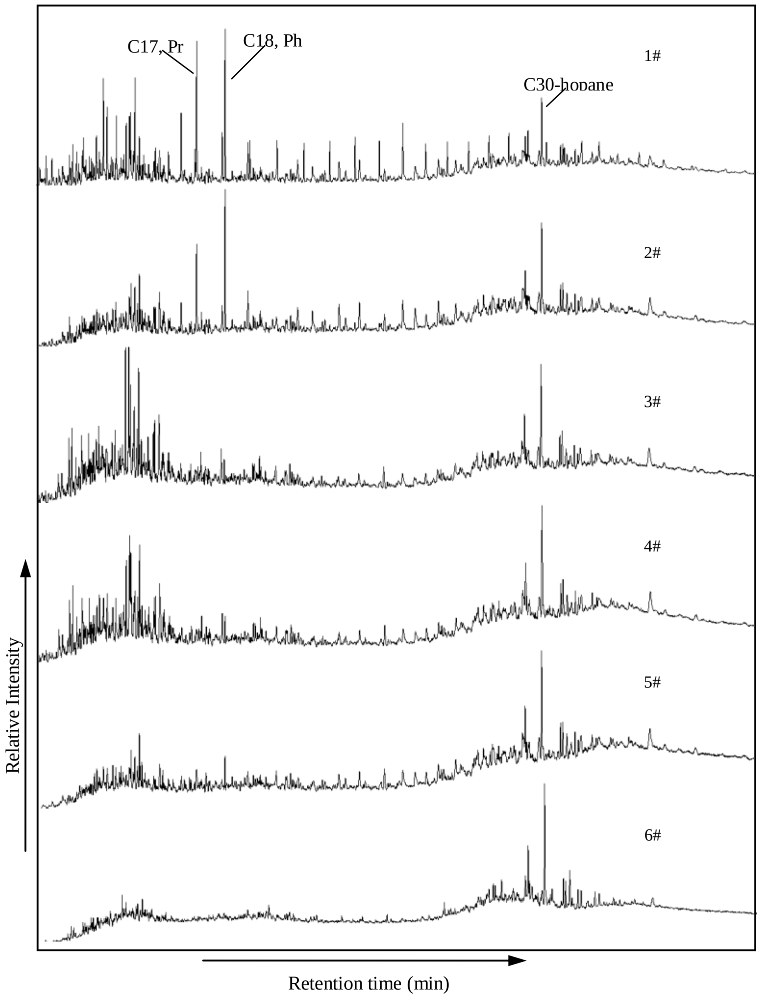

Fig. 1:GC–MS total ion current (TIC) profiles of oil samples

C35 was considered as an indicator for highly reducing and anoxic environments[4], but all samples were completely depleted of it, that meant a not highly reducing and anoxic environment of Gangxi oil reserve.

Oleanane was thought to be a Cretaceous or younger higher-plant (probably angiosperms) marker [9, 10]. Oleanane were detected in all samples, but its content was very low. The oleanane/(oleanane + hopane) ratios varied from 0.05 to 0.07[11]. This proof was consistent with the geologic time (from Oligocene to Pliocene) and the source (marine crude oil) of Gangxi oil reserve.

Oil maturity analysis

Maturity parameters of 20S / (20S + 20R) - C29 and ββ / (ββ + αα) - C29 described the degree of maturity effectually [4, 11-13] and they were present in range of 0.41-0.60 and 0.32-0.42 respectively, showing features of mature oil. The maturity degree increased as order: 2#, 5#, 3# or 1#, 4#, 6#. But these values could not show the thermal evolution extent of oil because of the degradation.

Diasterane relative concentration (diasteranes/regular steranes ratio, Dia/Reg) and Ts / (Ts + Tm) were also used to reflect the relative levels of maturity for the different samples. Fig. 2 showed that the Dia/Reg ratio increased as the value of 20S / (20S + 20R), that suggested the diasterane content of oil in Gangxioilfiled was controlled by matruration. But the Ts/(Ts+Tm) ratios did not correlate with 20S / (20S + 20R), because the degradation of oil occurred in Gangxi oilfield and the Ts/(Ts+Tm) ratios was sensitive to depositional environment or type organic matter [11].

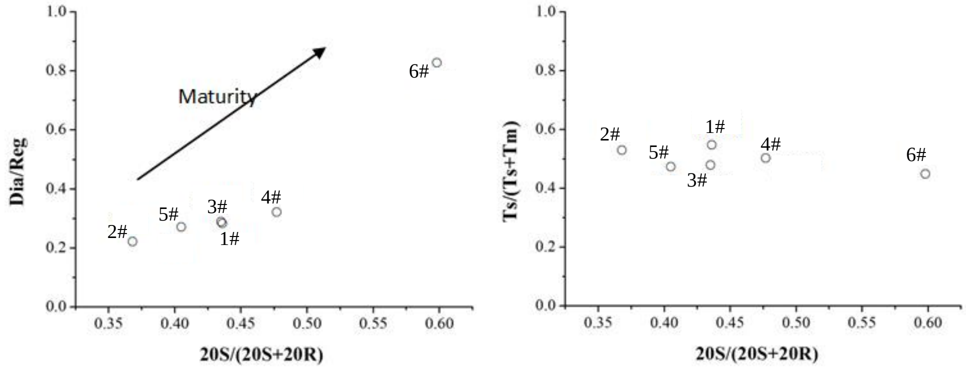

Fig. 2: The maturity analysis of oils applying two different parameters: (A) Dia./Reg vs. 20S/(20S+ 20R); (B) Ts/(Ts+Tm) vs. 20S/(20S+ 20R)

CONCLUSION

In this study, six representational samples of crude oil were taken from Gangxi zone of Dagang oil field, China. The degree of degradation, biomarker character, maturity analysis of crude oil was performed. All oil samples were degraded-oil, nearly depleted of n-alkanes. Branched alkanes and alkylcyclohexanes were few and aromatic compounds and PAHs were degraded at different degrees.

Some biomarkers suggested the source and maturity of oil. The low content of regular steranes and high content of tri-cyclic terpanes and hopanes showed the prokaryotic organisms and algal as the source; the lack of C35 and low content of oleanane showed a not highly reducing and anoxic environment, no-angiosperms source and the geologic time from Oligocene to Pliocene. Maturity parameters of 20S / (20S + 20R) - C29 (0.41-0.60) and $\beta\beta$ / ($\beta\beta$ + $\alpha\alpha$) - C29 (0.32-0.42) showed they were mature oil. The disaterane content of oil was controlled by matruration, but the Ts/(Ts+Tm) ratios was sensitive to depositional environment or type organic matter.

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