Acta Geochim (2016) 35(2):203–214
DOI 10.1007/s11631-015-0090-2

ORIGINAL ARTICLE

The effect of slight to minor biodegradation on C_6 to C_7 light hydrocarbons in crude oils: a case study from Dawanqi Oilfield in the Tarim Basin, NW China

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Received: 26 October 2015 / Revised: 11 November 2015 / Accepted: 29 December 2015 / Published online: 27 January 2016

Abstract Light hydrocarbons (LHs) are one of the main petroleum fractions in crude oils, and carry much information regarding the genetic origin and alteration of crude oils. But secondary alterations—especially biodegradation—have a significant effect on the composition of LHs in crude oils. Because most of the LHs affected in oils underwent only slight biodegradation (rank 1 on the biodegradation scale), the variation of LHs can be used to describe more the refined features of biodegradation. Here, 23 crude oils from the Dawanqi Oilfield in the Tarim Basin, NW China, eleven of which have been biodegraded to different extents, were analyzed in order to investigate the effect of slight to minor biodegradation on C_6–C_7 LHs. The study results showed that biodegradation resulted in the prior depletion of straight-chained alkanes, followed by branched alkanes. In slight and minor biodegraded oils, such biodegradation scale could not sufficiently affect C_6–C_7 cycloalkanes. For branched C_6–C_7 alkanes, generally, monomethylalkanes are biodegraded earlier than dimethylalkanes and trimethylalkanes, which indicates that branched alkanes are more resistant to biodegradation, with the increase of substituted methyl groups on parent rings. The degree of alkylation is one of the primary controlling factors on the biodegradation of C_6–C_7 LHs. There is a particular case: although 2,2,3-trimethylbutane has a relative higher alkylation degree, 2,2-dimethylpentane is more resistant to biodegradation than 2,2,3-trimethylbutane. 2,2-Dimethylpentane is the most resistant to biodegradation in branched C_6–C_7 alkanes. Furthermore, the 2-methylpentane/3-methylpentane and 2-methylhexane/3-methylhexane ratios decreased steadily with increasing biodegradation, which implies that isomers of bilateral methyl groups are more prone to bacterial attack relative to mid-chain isomers. The position of the alkyls on the carbon skeleton is also one of the critical factors controlling the rate of biodegradation. With increasing biodegradation, Mango's LH parameters K1 values decrease and K2 values increase, the values of *n*-heptane and isoheptane decrease, and the indices of methylcyclohexane and cyclohexane increase. LH parameters should be applied cautiously for the biodegraded oils. Because biodegraded samples belong to slight or minor biodegraded oils, the values of *n*-heptane and isoheptane from Dawanqi Oilfield can better reflect and determine the "Biodegraded" zone. When the heptane value is 0–21 and the isoheptane value is 0–2.6, the crude oil in Dawanqi Oilfield is defined as the "Biodegraded" zone.

Keywords Crude oils · Light hydrocarbons · Biodegradation · Dawanqi Oilfield · Tarim Basin

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This contribution has been accepted as a poster presentation in the 27th International Meeting on Organic Geochemistry.

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1 Introduction

Light hydrocarbons (LHs) are one of the main petroleum fractions in crude oils, especially for light oils in which commonly used biomarkers are usually present in extremely low concentrations or even under the detection limit of routine gas chromatography–mass spectrometry analyses (Peters et al. 2005).

Benchmark research has suggested that LHs carry much information regarding the genetic associations and alteration of crude oils. It has been documented that LHs can be applied to oil–oil correlation studies, distinguishing genetic types of crude oils, and determining their thermal maturation levels (Williams 1974; Philippi 1975; Thompson 1983; Halpern 1995; Haven 1996; Chung et al. 1998; Zhang et al. 2005). However, secondary alteration—especially biodegradation—has a significant effect on the composition of LHs in crude oils. Based on the differing resistance of compound classes to biodegradation, Peters et al. (2005) developed a scale of 1–10 to assess the degree of biodegradation. Much work has been done on the effect of biodegradation on the molecular composition of crude oils (Volkman et al. 1983; Connan 1984; Palmer 1993; Fisher et al. 1998), whilst relatively little work has been done on the effect of biodegradation on the behavior of LHs.

Welte et al. (1982) demonstrated the preferential depletion of straight-chain alkanes relative to branched and cyclic alkanes during biodegradation and proposed two parameters (*iso*-pentane/*n*-pentane, 3-methylpentane/*n*-hexane) that could be used to indicate biodegradation. BeMent et al. (1994) suggested that 2,3-dimethylpentane is more subject to bacterial attack than 2,4-dimethylpentane. Masterson et al. (2001) showed that *n*-heptane, 3-methylhexane, cyclohexanel and methylcyclohexane were more easily removed by biodegradation than benzene or toluene. George et al. (2002) suggested three main controls on the susceptibility to biodegradation (carbon skeleton, degree of alkylation, and position of alkylation).

Up to the present, details have been limited on the relative susceptibility of LHs to biodegradation. Because most of the LHs in oils underwent only slight biodegradation (rank 1 of the biodegradation scale), the variation of LHs can be used to describe more the refined features of biodegradation. Here, a total of 23 light oils from the Dawanqi Oilfield in the Tarim Basin (NW China) were analyzed to investigate the effect of slight to minor biodegradation on the distribution of C_6–C_7 LHs. The results can broaden the current understanding of biodegradation effects on these low molecular weight hydrocarbons in crude oils.

2 Geologic setting

The Dawanqi Oilfield is located in the western margin of the Kuqa Depression, north of the Tarim Basin, NW China (Fig. 1). The oil field covers an area of 5.4 km^2 with a proved oil reserve of 48.35×10^6 bbl, with 13.64×10^9 scf of dissolved gas (Zhao et al. 2003). The Kuqa Depression is situated in the southern foot of the Tianshan orogenic Belt and is dominated by Mesozoic and Cenozoic deposits. This east–west trending depression, 450 km long and 50–80 km wide and covering an area of about 2.8×10^4 km^2, is one of the most productive gas depressions in China. It contains the North and South Slopes, Baicheng and Yangxia Sags, and Yiqikelike, Kelasu and Qiulitage structural Belts (Graham et al. 1993; Jiang et al. 2010). The Dawanqi Anticline, situated in the western part of the Baicheng Sag, is composed of several normal fault blocks or broken anticlines separated by a number of normal faults (Zhang et al. 2011). These faults, as pathways for oil migration, lead to the accumulation of oil and gas in traps under the gypsum salt (Tang et al. 2014).

Based on seismic, drilling and logging data, the sequence stratigraphic framework of Dawanqi Oilfield is: Paleogene Suweiyi Formation, Neogene Jidike, Kangcun and Kuqa Formations, and the Quaternary (Liu et al. 2005). The Neogene Kuqa Formation is the most important prolific payzone in Dawanqi Oilfield. The Upper Triassic lacustrine shales/mudstones, thin coal seams formed in fluvial–deltaic and lacustrine environments, and the Lower–Middle Jurassic coal beds deposited in a swamp–lacustrine system were considered to be the main potential source rocks in the Kuqa Depression (Liang et al. 2003; Zou et al. 2006).

3 Samples and experimental procedures

Twenty-three light oil samples were carefully selected at wellheads from the Dawanqi Oilfield in the Tarim Basin. These samples were collected at temperatures between 25 and 30°, but were quickly refrigerated at below −6° (Canipa-Morales et al. 2003). The production zones of these samples are 69.5–662.5 m deep.

Gas chromatography (GC) of the whole oil samples was performed on an Agilent 6890 gas chromatograph, equipped with two sets of electronic pressure controllers and a flame ionization detector (300°). A 50 m PONY capillary column was used with Helium as the carrier gas and a split ratio of approximately 50:1. The oven was programmed to an initial temperature of 35° for 5 min, followed by a heating ramp at 4°/min to 300° for 20 min. LHs were identified based on the GC analysis technique and by

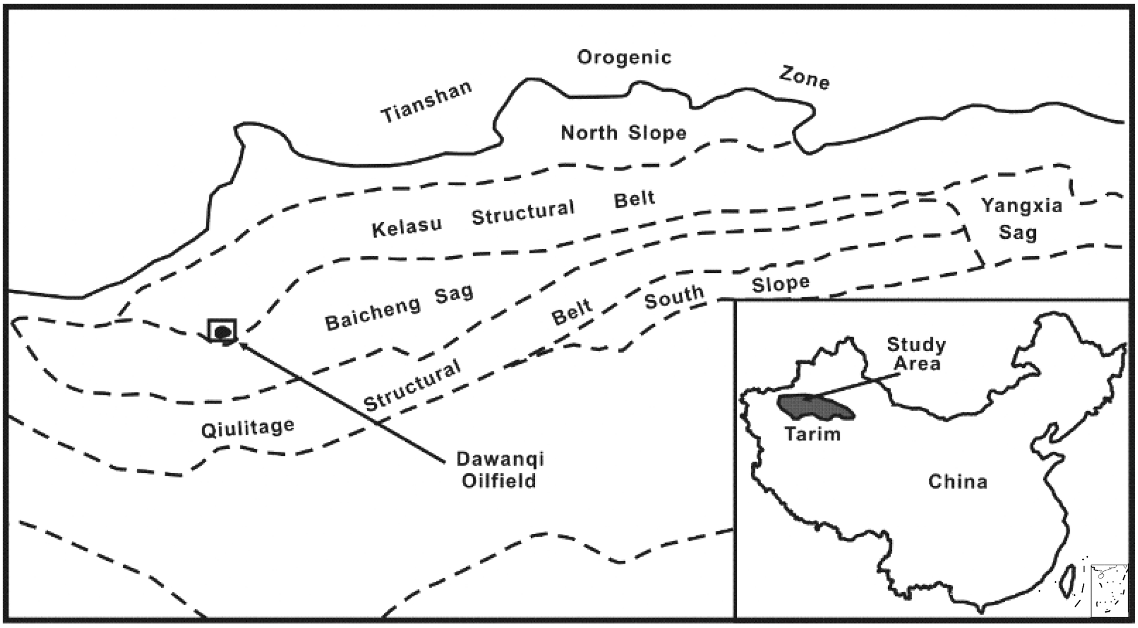


Fig. 1 Location map of the Dawanqi Oilfield in the Tarim Basin

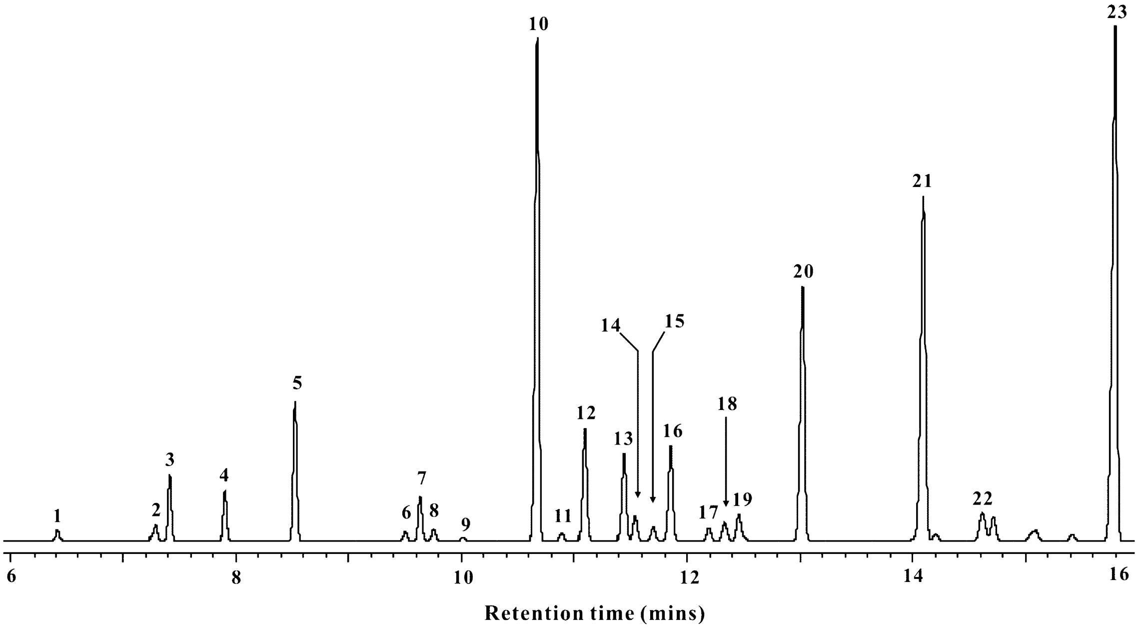


Fig. 2 Partial whole oil gas chromatograms of well DW126-8, showing the C_6–C_7 region. Peak numbers are listed in Table 1

relative retention times. The whole oil GC of C_6–C_7 LHs in well DW126-8 and their qualitative analyses are shown in Fig. 2 and Table 1, respectively.

These crude oil samples have MPR values ranging from 0.96 to 1.17 ($R_O \approx 0.88\ \%$–$0.92\ \%$) (Table 2). They have similar thermal maturity. Their densities are commonly lower than 0.8000 g cm^{-3}, with a minimum of 0.7801 g cm^{-3}. The variations in the relative amounts of fluorenes, dibenzothiophenes, and dibenzofurans from the oil samples are plotted on a ternary diagram from Li et al. (2013). As shown in Fig. 3, all the data points are distributed in Zone 4, which shows that Dawanqi oils may originate from brackish/saline lacustrine shales. All Dawanqi oil samples belong to the same oil family.

Table 1 List of C_6–C_7 light hydrocarbon in Dawanqi oils

Peak	Identification	Abbreviation
1	2,2-Dimethylbutane	$2,2DMC_4$
2	2,3-Dimethylbutane	$2,3DMC_4$
3	2-Methylpentane	$2MC_5$
4	3-Methylpentane	$3MC_5$
5	*n*-Hexane	nC_6
6	2,2-Dimethylpentane	$2,2DMC_5$
7	Methylcyclopentane	$MCYC_5$
8	2,4-Dimethylpentane	$2,4DMC_5$
9	2,2,3-Trimethylbutane	$2,2,3TMC_4$
10	Benzene	Benz
11	3,3-Dimethylpentane	$3,3DMC_5$
12	Cyclohexane	CYC_6
13	2-Methylhexane	$2MC_6$
14	2,3-Dimethylpentane	$2,3DMC_5$
15	1,1-Dimethylcyclopentane	$1,1DMCYC_5$
16	3-Methylhexane	$3MC_6$
17	1,*cis*-3-Dimethylcyclopentane	$1,c3DMCYC_5$
18	1,*trans*-3-Dimethylcyclopentane	$1,t3DMCYC_5$
19	1,*trans*-2-Dimethylcyclopentane	$1,t2DMCYC_5$
20	*n*-Heptane	nC_7
21	Methylcyclohexane	$MCYC_6$
22	Ethylcyclopentane	$ECYC_5$
23	Toluene	Tol

4 Results and discussion

4.1 Gas chromatography of whole oils

Whole oil gas chromatograms show that Dawanqi oils are characterized by the distribution of light oil, with a predominance of low molecular-weight normal alkanes. In general, the crude oils in the Dawanqi Oilfield have the following distribution types (Fig. 4; Table 2).

Type I The normal alkanes have a common range of carbon numbers from nC_4 to nC_{30}, with a unimodal pattern maximizing at nC_9 or nC_{10}, are observed. The values of nC_{21-}/nC_{22+} and nC_{13-}/nC_{14+} have a higher relative abundance (9.43–11.68 and 1.33–1.79). They are dominated by low molecular-weight normal alkanes. Most of crude oils in Dawanqi Oilfield belong to this type (Fig. 4a).

Type II The normal alkane series of this type exhibit a common carbon number range of nC_4 to nC_{30} and a bimodal distribution pattern, predominated by nC_9 and nC_{17}. The value of nC_{21-}/nC_{22+} ranges from 3.32 to 6.40 and the value of nC_{13-}/nC_{14+} ranges from 0.29 to 0.95 (Fig. 4b).

Type III The carbon numbers of normal alkanes range from nC_4 to nC_{30} maximizing at nC_{14}. The samples have a nC_{21-}/nC_{22+} value ranging from 4.35 to 5.27 and a nC_{13-}/nC_{14+} value between 0.40 and 0.56 (Fig. 4c).

Type IV There is no obvious n-alkane distribution in this type. Pristine and phytane have been depleted (Fig. 4d).

Except Type IV, the values of pristane/phytane (Pr/Ph) values range from 1.90 to 3.06. Twenty-two crude oil samples have Pr/nC_{17} values ranging from 0.10 to 0.18 and Ph/nC_{18} values between 0.05 and 0.08. These two ratios show slight changes (Table 2).

Welte et al. (1982) proposed two LH ratios, $3MC_5/nC_6$ and *iso*-pentane/*n*-pentane (iC_5/nC_5), to identify biodegradation. In the major crude oils (Type I), there are lower relative ratios of $3MC_5/nC_6$ and iC_5/nC_5 (0.35–0.37 and 0.79–0.93). In contrast, from type II to type III, these two ratios increase gradually (0.48–2.86 and 0.95–2.51), which shows that crude oils from the Dawanqi Oilfield are characterized by obvious biodegradation. In type IV oils, nC_5 was totally depleted (Fig. 5; Table 2).

Based on the above analyses, as reported by Yang et al. (2015), the Dawanqi oils from shallower depth usually show biodegraded characteristics. Type I oils are non-degraded oils. Type II oils and Type III oils belong to slight biodegraded oils (rank 1 on the degree of biodegradation scale), and Type IV oils belong to minor biodegraded oils (rank 3 on the degree of biodegradation scale) (Peters et al. 2005). From Type I to Type IV, the extent of biodegradation exhibits a marked tendency to increase.

4.2 Effect of biodegradation on C_6–C_7 light hydrocarbons

A total of 23 homologues and isomers of C_6–C_7 LHs, including straight-chained alkanes, branched alkanes, 5-membered cycloalkanes, 6-membered cycloalkanes, and aromatic hydrocarbons, were detected with the GC analysis technique (Fig. 2; Table 1). Here, no significant systematic susceptibility to biodegradation was found within Benz and Tol, so we will not discuss these two compounds. Except aromatic hydrocarbons, C_6–C_7 LHs are mainly controlled by biodegradation.

4.2.1 Relative abundance of C_6–C_7 homologues and isomers

The relative abundance of C_6–C_7 homologues and isomers in Dawanqi oils show regular distribution during biodegradation.

In Type I oils, six-membered cycloalkanes have a relatively higher abundance (33.69 %–36.70 %), followed by straight-chained alkanes (27.00 %–28.41 %) and branched alkanes (24.90 %–27.70 %). The proportions of five-membered cycloalkanes range from 10.39 % to 11.26 %, with relatively lower values. With increasing biodegradation

Table 2 General information for oils from Dawanqi Oilfield

Well no.	Depth (m)	Formation	Pr/Ph	Pr/C$_{17}$	Ph/C$_{18}$	C$_{21-}$/C$_{22+}$	C$_{13-}$/C$_{14+}$	3MC$_5$/nC$_6$	iC$_5$/nC$_5$	MPR	Oil type
DW105-192	290.5–468.5	K1–K2	2.73	0.13	0.05	9.98	1.53	0.36	0.84	1.14	I
DW105-182	363.8–605–5	K2–K3	2.77	0.12	0.05	9.69	1.43	0.36	0.90	1.11	I
DW105-197	129.5–422.5	K1–K2	2.46	0.11	0.05	11.68	1.79	0.37	0.93	1.12	I
DW1-10-1	417–418	K2	3.06	0.13	0.05	10.27	1.54	0.37	0.89	1.16	I
DW105-179	366–449.5	K2	2.70	0.13	0.05	10.45	1.47	0.37	0.89	1.11	I
DW107-1	140.5–458	K1–K2	2.09	0.11	0.06	10.58	1.68	0.36	0.89	1.17	I
DW1-30	241–489.5	K1–K2	2.76	0.12	0.05	10.72	1.51	0.37	0.86	1.14	I
DW126-8	201.5–263	K1	2.63	0.12	0.05	9.43	1.33	0.35	0.79	1.15	I
DW1-3-2	146–580	K1–K3	2.38	0.11	0.05	10.06	1.55	0.37	0.88	0.96	I
DW109-5-3	264–270.5	K1	2.83	0.12	0.05	9.91	1.38	0.37	0.90	1.08	I
DW126-7	113–287.5	K1	2.31	0.11	0.05	10.61	1.56	0.35	0.81	1.11	I
DW109-5-1	199.5–269	K1	2.36	0.10	0.05	11.04	1.50	0.37	0.92	1.09	I
DW126-9	127.5–362.5	K1–K2	1.90	0.13	0.07	5.62	0.82	0.48	1.00	1.10	II
DW126-6	113–287.5	K1	2.83	0.13	0.05	6.40	0.95	0.51	0.95	1.09	II
DW117-6	265.5–440	K1–K2	1.92	0.14	0.08	4.30	0.53	0.75	1.40	1.12	II
DW117-7	204–397	K1–K2	2.80	0.14	0.05	5.14	0.64	0.75	1.41	1.12	II
DW105-34	69.5–250	K1	2.36	0.18	0.08	3.32	0.29	0.73	1.30	1.08	II
DW105-145	107–545	K1–K3	1.92	0.14	0.08	5.27	0.56	0.93	1.17	1.15	III
DW105-108	129.5–221	K1	1.92	0.14	0.08	4.61	0.49	0.93	1.18	1.11	III
DW105-79	127–555	K1–K3	2.42	0.11	0.05	5.26	0.55	1.44	2.00	1.08	III
DW105-20-2	146.5–662.5	K1–K4	2.92	0.13	0.05	4.36	0.42	2.75	2.46	1.06	III
DW105-20-1	137.5–549.5	K1–K3	2.79	0.12	0.05	4.35	0.40	2.86	2.51	1.06	III
DW105-208	107.5–156	K1	–	–	–	–	–	–	–	1.08	IV

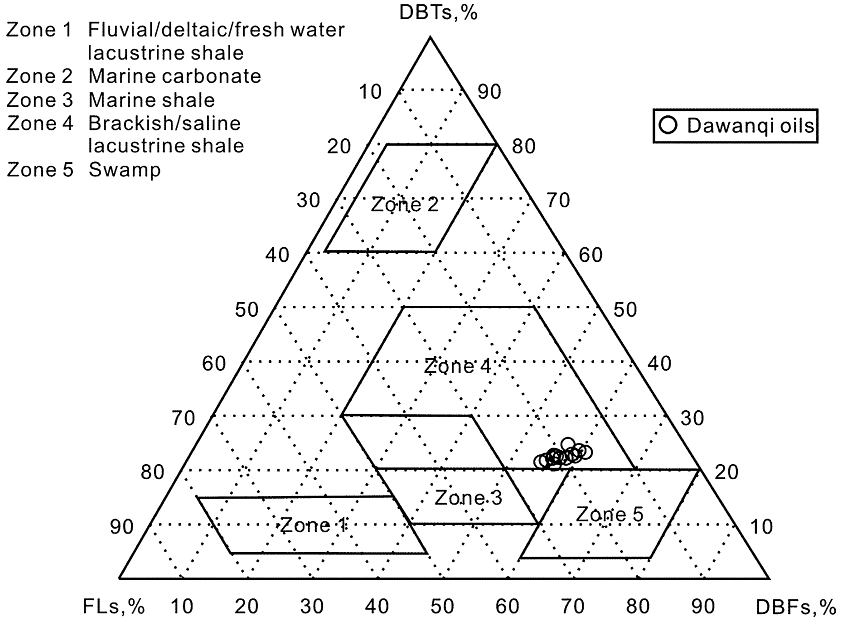


Fig. 3 Ternary diagram showing the proportion of dibenzothiophenes (DBTs), fluorenes (FLs), and dibenzofurans (DBFs) from Dawanqi oils

(from Type II to Type IV), the relative abundance of straight-chained alkanes and branched alkanes decreased gradually; five-membered cycloalkanes and six-membered cycloalkanes increased gradually (Fig. 6; Table 3). Biodegradation resulted in the preferential depletion of straight-chained alkanes and branched alkanes.

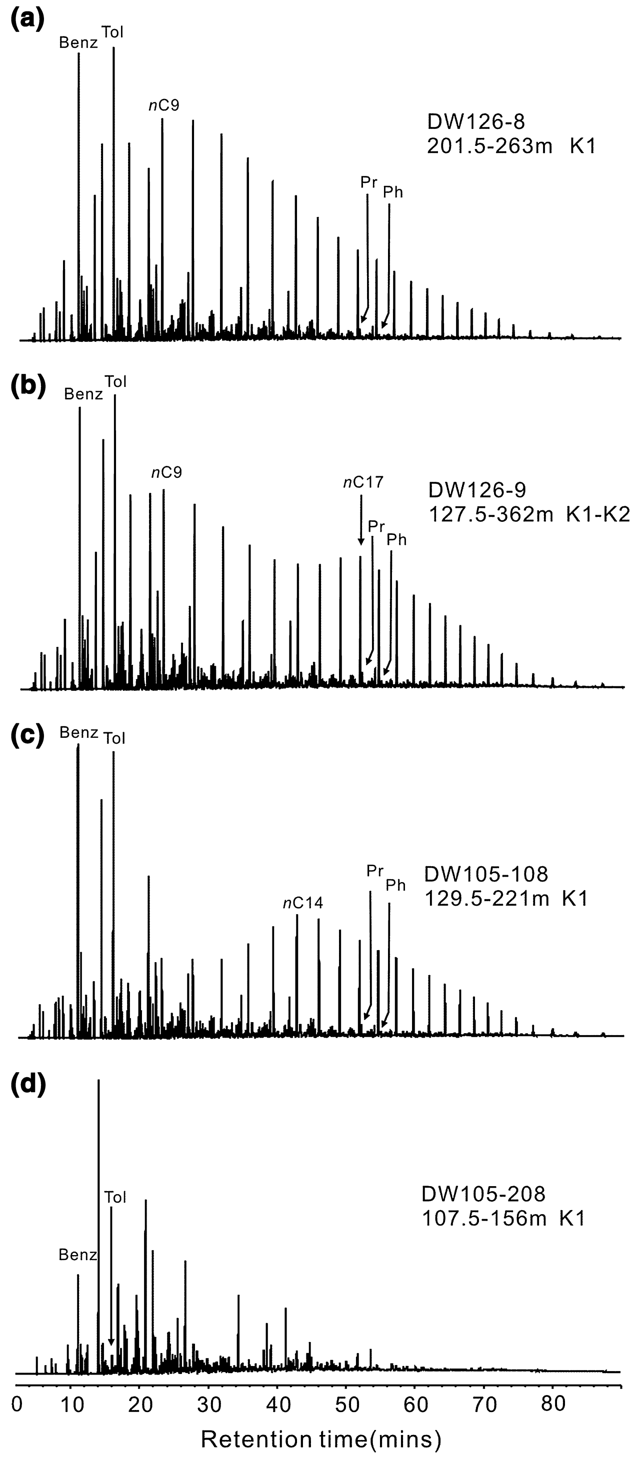


Fig. 4 Whole oil gas chromatogram of different types oils from the Dawanqi Oilfield, Tarim Basin

4.2.2 Branched alkanes

A total of four methyl-, six dimethyl- and one trimethyl-substituted C_6–C_7 alkanes were detected in oils from the Dawanqi Oilfield (Fig. 2; Table 1). The relative abundance of these branched C_6–C_7 alkanes exhibited regular distribution during biodegradation.

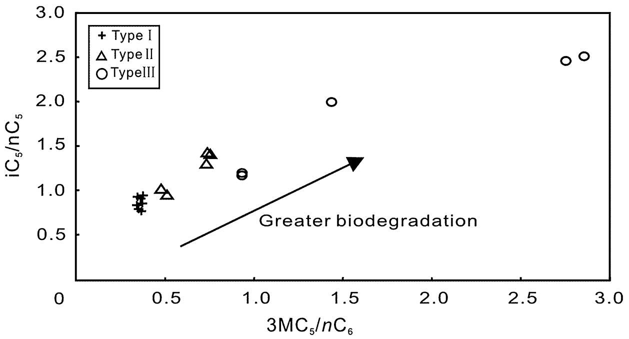


Fig. 5 Plot of $3MC_5/nC_6$ vs iC_5/nC_5 of crude oils from Dawanqi Oilfield

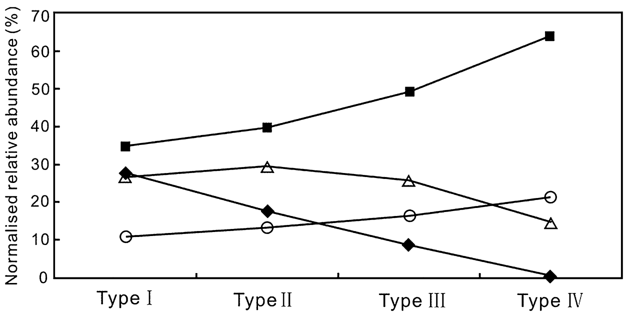


Fig. 6 Graph of the average relative content of C_6–C_7 straight-chained alkanes, branched alkanes, five-membered cycloalkanes and six-membered cycloalkanes for Dawanqi oils (*filled diamond* straight-chained alkane; *open diamond* branched alkane; *open circle* five-membered cycloalkane; *filled square* six-membered cycloalkane)

As shown in Fig. 7, with increasing biodegradation, the relative abundance of $2MC_6$ decreases gradually. The relative amounts of $2MC_5$ and $3MC_6$ almost remained unchanged in type I and type II, while decreasing in type III and type IV. $3MC_5$ show a marked increasing trend with greater biodegradation until type IV oils. Dimethylalkanes and trimethylalkanes exhibit a steadily increasing trend, especially $2,3DMC_5$. In branched C_6–C_7 alkanes, biodegradation resulted in the prior depletion of $2MC_6$, whereas $2,3DMC_5$ is the most resistant to biodegradation.

The ternary diagram of C_6–C_7 monomethylalkanes, dimethylalkanes, and trimethylalkanes also shows a similar distribution (Fig. 8). With increasing biodegradation, the relative contents of monomethylalkanes decrease and dimethylalkanes increase. For trimethylalkanes, because only $2,2,3TMC_4$ was detected in Dawanqi oils by GC analysis technique, the proportions of the trimethylalkanes range from 1.06 % to 4.42 %, with relatively lower values. The relative contents of trimethylalkanes also show a slight increasing trend. As already mentioned by George et al. (2002) and Yang et al. (2015), the degree of alkylation is

Table 3 Group compositions of C_6–C_7 light hydrocarbon and relevant ratios

Well no.	Straight-chained alkane (%)	Branched alkane (%)	Five-membered cycloalkane (%)	Six-membered cycloalkane (%)	$2MC_5$/ $3MC_5$	$2MC_6$/ $3MC_6$	Oil type
DW105-192	28.41	26.66	10.39	34.54	1.28	0.91	I
DW105-182	27.99	27.09	10.68	34.24	1.31	0.91	I
DW105-197	27.93	27.52	10.48	34.08	1.30	0.90	I
DW1-10-1	27.89	26.46	10.50	35.16	1.27	0.90	I
DW105-179	27.89	27.70	10.73	33.69	1.32	0.92	I
DW107-1	27.69	26.92	10.62	34.77	1.30	0.92	I
DW1-30	27.63	27.05	10.45	34.87	1.27	0.91	I
DW126-8	27.36	25.68	11.26	35.70	1.28	0.91	I
DW1-3-2	27.30	26.60	10.93	35.17	1.28	0.91	I
DW109-5-3	27.28	27.00	10.91	34.81	1.31	0.91	I
DW126-7	27.22	24.90	11.19	36.70	1.26	0.90	I
DW109-5-1	27.00	26.46	11.06	35.47	1.30	0.90	I
DW126-9	21.81	26.54	12.43	39.22	1.18	0.71	II
DW126-6	20.81	27.95	12.74	38.49	1.23	0.68	II
DW117-6	15.72	31.70	13.52	39.06	1.28	0.64	II
DW117-7	15.66	31.82	13.47	39.05	1.28	0.64	II
DW105-34	14.11	29.41	13.96	42.53	1.15	0.62	II
DW105-145	11.83	25.69	15.17	47.31	0.85	0.74	III
DW105-108	11.83	25.66	15.09	47.42	0.85	0.74	III
DW105-79	9.37	25.51	16.27	48.86	0.66	0.65	III
DW105-20-2	5.30	25.45	17.58	51.66	0.58	0.53	III
DW105-20-1	5.11	25.77	17.48	51.64	0.58	0.52	III
DW105-208	0.29	14.58	21.13	64.00	0.16	0.26	IV

one of the primary controlling factors for the biodegradation of C_6–C_7 LHs. Generally, branched C_6–C_7 alkanes are more resistant to biodegradation when more alkylated. There is, however, a particular case: although $2,2,3TMC_4$ has a relative higher alkylation degree, $2,3DMC_5$ is more resistant to biodegradation than $2,2,3TMC_4$.

The position of alkyls on the carbon skeleton is also one of critical factors controlling the rate of biodegradation, which is mainly reflected in the variation of the $2MC_5$/$3MC_5$ and $2MC_6$/$3MC_6$ ratios in Dawanqi oils (Fig. 9; Table 3). In non-degraded oils (type I oils), there are higher relative ratios of $2MC_5$/$3MC_5$ and $2MC_6$/$3MC_6$ (1.26–1.32 and 0.90–0.92). With increasing biodegradation, these two ratios show a remarkable decreasing trend (0.16–1.28 and 0.26–0.74), which indicates that the $2MC_5$ and $2MC_6$ are more susceptible to biodegradation than the $3MC_5$ and $3MC_6$. Isomers of the bilateral methyl groups are more prone to bacterial attack relative to the mid-chain isomers (George et al. 2002; Yang et al. 2015). However, no similar characteristics in susceptibility to biodegradation were found within other branched C_6–C_7 alkanes, implying that the biodegradation did not progress sufficiently for other analogue ratios of branched alkanes.

4.2.3 Cycloalkanes

A total of eight C_6–C_7 cycloalkanes, including six five-membered cyclcoalkanes and two six-membered cyclohexanes, were detected (Fig. 2; Table 1). In the Dawanqi samples, no obvious changes occured in the relative abundance of the C_6–C_7 cycloalkanes during biodegradation, which implies that such a biodegradation scale could not sufficiently affect these compounds.

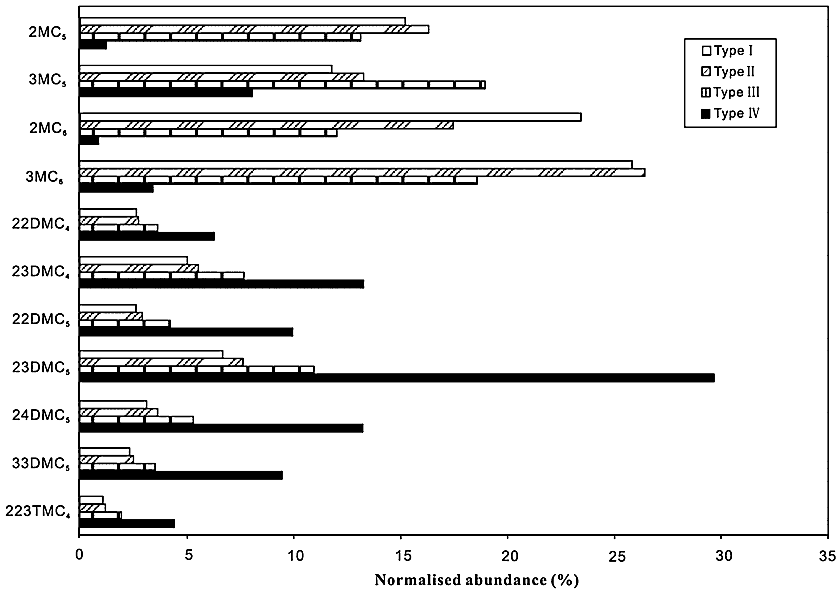
4.3 Light hydrocarbon parameters

Based on the above study, the variation of C_6–C_7 LHs may affect common LH parameters.

4.3.1 Mango's light parameters K1 and K2

Mango (1987) determined that four isoheptanes had fixed roles in different petroleum systems, $K1 = (2MC_6 + 2,3\text{-}DMC_5)/(3MC_6 + 2,4DMC_5) \approx 1.0$, regardless of the concentrations in the oils. Subsequently, Mango (1990, 1992, 1994) posed a steady-state catalytic process and the parent-daughter scheme was established and modified for the

Fig. 7 Bar charts of the average relative content of branched C_6–C_7 alkanes for Dawanqi oils



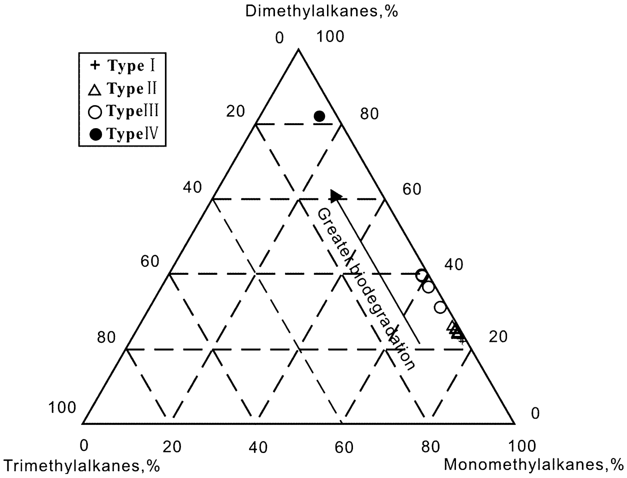


Fig. 8 Ternary diagram of C_6–C_7 monomethylalkanes, dimethylalkanes and trimethylalkanes for Dawanqi oils

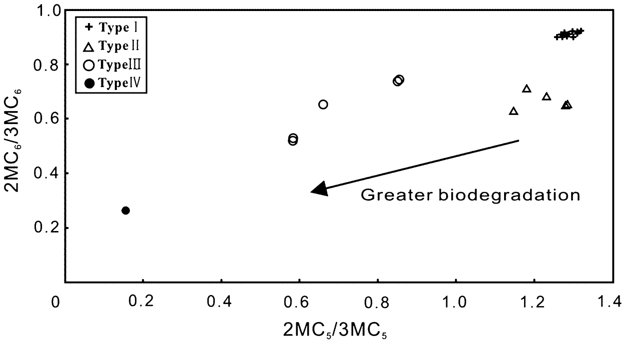


Fig. 9 Plot of $2MC_5/3MC_5$ vs $2MC_6/3MC_6$ of crude oils from Dawanqi Oilfield

formation of C_7 hydrocarbons. Based on the scheme, the second invariance ratio was predicted, $K2 = (2{,}2DMC_5 + 2{,}3DMC_5 + 2{,}4DMC_5 + 3{,}3DMC_5 + 2{,}2{,}3TMC_4)/(2MC_6 + 3MC_6 + 1{,}1DMCYC_5 + 1{,}c3DMCYC_5 + 1{,}t3DMCYC_5)$. Generally, analogous oil genesis sets should have similar K1 and K2 values.

In non-degraded oils (type I oils), Mango parameter K1 is approximately 1.04–1.05, and K2 is approximately 0.25–0.26. In type II and type III oils, Mango parameters show relatively low K1 values (0.81–0.99) and relatively high K2 values (0.29–0.59). The K1 values are affected very little in type II and type III oils. In typeIV oils, there are higher relative Mango parameters of K1 and K2 (1.83 and 1.14). Biodegradation could affect Mango parameters K1 and K2 (Fig. 10; Table 4).

4.3.2 Heptane value and isoheptane value

Thompson (1979) proposed two LH parameters: the Paraffin index 1, of which the formula is: $\text{Isoheptane Value} = (2MC_6 + 3MC_6)/(1{,}c3DMCYC_5 + 1{,}t3DMCYC_5 + 1{,}t2DMCYC_5)$ and the Paraffin index 2, which can been expressed as: $\text{Heptane Value} = nC_7 \times 100/(CYC_6 + 2MC_6 + 1{,}1DMCYC_5 + 3MC_6 + 1{,}c3DMCYC_5 + 1{,}t3DMCYC_5 + 1{,}t2DMCYC_5 + nC_7 + MCYC_6)$. The distribution of non-degraded samples from the Dawanqi Oilfield show that Dawanqi oils belong to mature oils. With increasing biodegradation, the values of *n*-heptane and isoheptane decrease gradually (Fig. 11; Table 4).

Thompson (1983) proposed that when the heptane value is 0–18 and isoheptane value is 0–0.8, a crude oil is

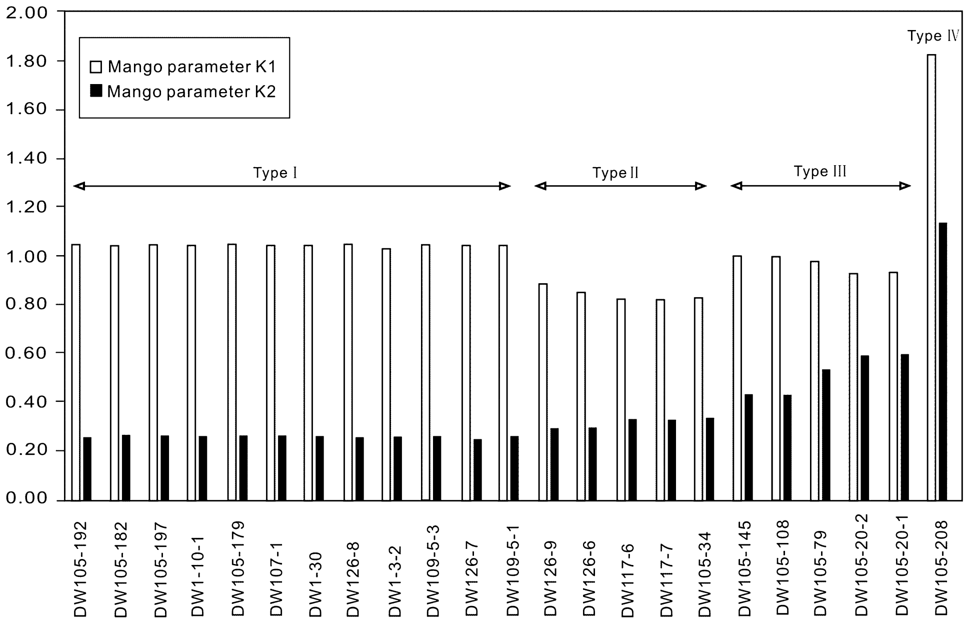


Fig. 10 Bar charts of Mango parameters K1 and K2 for oil samples from Dawanqi Oilfield

Table 4 Geochemical parameters list of C_6–C_7 hydrocarbons

Well no.	Mango parameters		*n*-Heptane value	Isoheptane value	CA indix	MCH indix	Oil type
	K_1	K_2					
DW105-192	1.04	0.26	27.26	3.31	40.79	49.21	I
DW105-182	1.04	0.26	26.39	3.08	39.61	49.72	I
DW105-197	1.04	0.26	26.21	3.15	39.73	49.82	I
DW1-10-1	1.04	0.26	26.97	3.21	41.96	49.64	I
DW126-9	0.88	0.29	20.88	2.53	46.52	55.42	II
DW126-6	0.85	0.29	19.53	2.51	46.42	55.77	II
DW117-6	0.81	0.32	13.78	2.24	47.51	61.14	II
DW117-7	0.81	0.32	13.61	2.23	47.50	61.39	II
DW105-145	0.99	0.42	10.19	1.50	55.59	66.43	III
DW105-79	0.98	0.53	8.22	1.05	58.93	67.98	III
DW105-20-2	0.93	0.59	4.77	0.87	65.07	70.65	III
DW105-20-1	0.92	0.59	4.55	0.89	65.05	71.04	III
DW105-208	1.83	1.14	0.26	0.06	78.27	74.05	IV

catergorized as “Biodegraded”. However, in the Dawanqi oils, only three biodegraded oils are in the “Biodegraded” zone determined by Thompson (1983) (Fig. 11; Table 4). Here, because the biodegraded samples belong to slight or minor biodegraded oils (ranks 1 or 3 on the degree of biodegradation scale) as described before, the values of *n*-heptane and isoheptane from the Dawanqi Oilfield can better reflect and determine “Biodegraded” zone. As shown in Fig. 11, when the heptane value is 0–21 and the isoheptane value is 0–2.6, the crude oil can be catergorized as within the “Biodegraded” zone.

4.3.3 Methylcyclohexane index and cyclohexane index

The C_6 and C_7 oil correlation ternary diagram has been widely used to gain geochemical information (Hu et al. 1990; Dai 1992, 1993; Odden et al. 1998; Odden 1999; Jarvie 2001; Hu and Zhang 2011). Based on these diagrams, the indices of methylcyclohexane (MCH index) and cyclohexane (CA index) have been developed by many scholars as optimum indices for parent material type and maturity (Hu et al. 1990; Dai 1992, 1993; Hu and Zhang 2011). The formula of these two parameters are: MCH

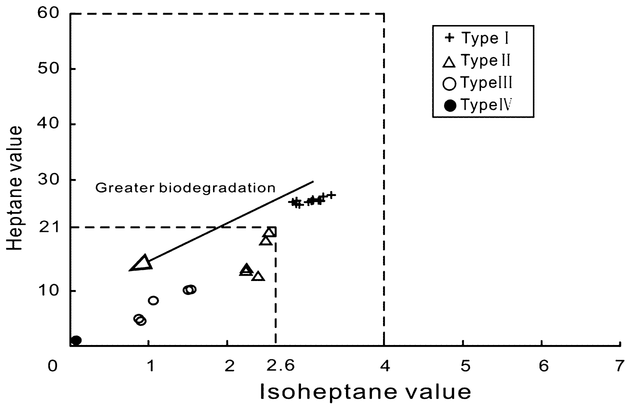


Fig. 11 Correlation of the the isoheptane and heptane values of crude oils from Dawanqi Oilfield, contrasting with the Thompson model (1983)

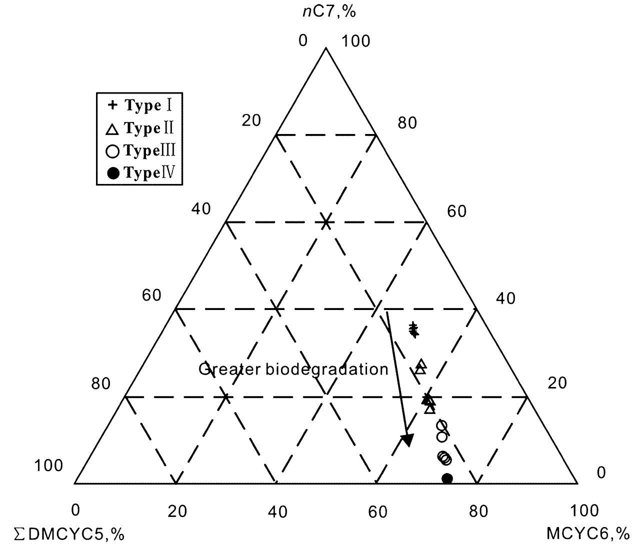


Fig. 12 Ternary diagram of methylcyclohexane ($MCYC_6$), dimethylcyclopentanes ($\sum DMCYC_5$) and *n*-heptane (nC_7) for Dawanqi oils

index = $MCYC_6/(nC_7 + MCYC_6 + 1{,}1DMCYC_5 + 1{,}c3DMCYC_5 + 1{,}t3DMCYC_5 + 1{,}t2DMCYC_5) \times 100$, CA index = $CYC_6/(nC_6 + CYC_6 + MCYC_5) \times 100$. Parent materials from humic kerogen show the distribution pattern of the MCH index as >50 % and the CA index as >27 %, while those from sapropelic kerogen show the distribution pattern of the MCH index as <50 % and the CA index as <27 %.

The ternary diagram of the C_7 LHs show that the relative content of methylcyclohexane is 49 %–74 %, which is higher than those of dimethylcyclopentane (14 %–26 %) and *n*-heptane (0 %–36 %). Correspondingly, the ternary diagram of C_6 LHs show that the relative content of cyclohexane is 40 %–78 %, which is higher than those of methylcyclopentane (13 %–24 %) and *n*-hexane (1 %–47 %). Most of oil data is distributed in the position of methylcyclohexane and cyclohexane, which indicates that the Dawanqi oils maybe originate from terrigenous source rock. We can also see that the MCH index and CA index increase obviously with increasing biodegradation, which is caused by the preferential degradation of straight-chained alkanes (Figs. 12, 13; Table 4).

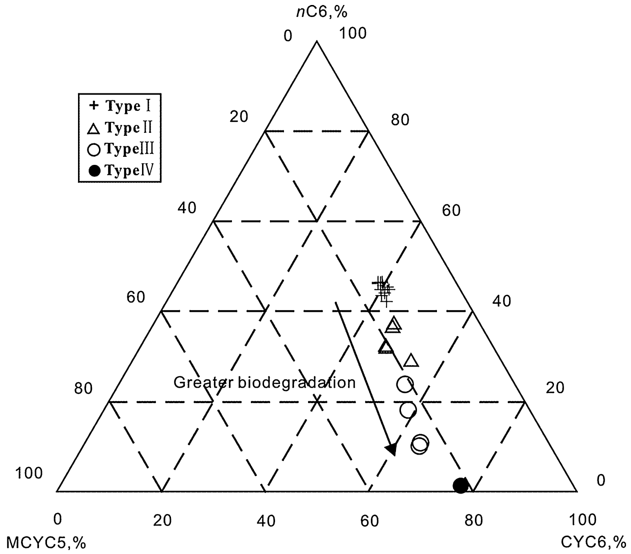


Fig. 13 Ternary diagram of cyclohexane (CYC_6), methylcyclopentane ($MCYC_5$) and *n*-hexane (nC_6) for Dawanqi oils

All the above discussions indicate that LH parameters should be applied cautiously for the biodegraded oils.

5 Conclusions

1. Whole oil gas chromatograms show that Dawanqi crude oils have four distribution types. Type I oils are non-degraded oils. Type II oils and Type III oils belong to slight biodegraded oils (rank 1 on the degree of biodegradation scale), and Type IV oils belong to minor biodegraded oils (rank 3 on the degree of biodegradation scale).
2. Biodegradation resulted in the preferential depletion of straight-chained alkanes, followed by branched alkanes. In slight and minor biodegraded oils, such biodegradation scale could not sufficiently affect C_6–C_7 cycloalkanes.
3. For branched C_6–C_7 alkanes, biodegradation resulted in the preferential depletion of $2MC_6$. $2{,}3DMC_5$ is the most resistant to biodegradation. With increasing biodegradation, the relative contents of monomethylalkanes decrease, whereas dimethylalkanes and trimethylalkanes increase. The degree of alkylation is one of the primary controlling factors of the biodegradation of C_6–C_7 LHs.

Generally, branched C_6–C_7 alkanes are more resistant to biodegradation when more alkylated However, there is a particular case: although 2,2,3TMC$_4$ has a relative higher alkylation degree, 2,3DMC$_5$ is more resistant to biodegradation than 2,2,3TMC$_4$.

4. With increasing biodegradation, the ratios of 2MC$_5$/3MC$_5$ and 2MC$_6$/3MC$_6$ show a remarkable decrease, which indicates that 2MC$_5$ and 2MC$_6$ are more susceptible to biodegradation than 3MC$_5$ and 3MC$_6$. Isomers of bilateral methyl groups are more prone to bacterial attack relative to mid-chain isomers. The position of alkyls on the carbon skeleton is also one of critical factors controlling the rate of biodegradation.
5. During biodegradation, Mango's LH parameters K1 values decrease and K2 values increase, the values of *n*-heptane and isoheptane decrease, and the indices of methylcyclohexane and cyclohexane increase. LHs parameters should be applied cautiously for the biodegraded oils. Because biodegraded samples belong to slight or minor biodegraded oils, the values of *n*-heptane and isoheptane from the Dawanqi Oilfield can better reflect and determine "Biodegraded" zone. When the heptane value is 0–21 and the isoheptane value is 0–2.6, the crude oil is categorized as within "Biodegraded" zone.

Acknowledgments The work was financially supported by the National Natural Science Foundation of China (Grant No. 41272158 and 41172136).

References

BeMent WO, Levey RA, Mango FD (1994) The temperature of oil generation as defined with a C_7 chemistry maturity parameter (2,4-DMP/2,3-DMP ratio). In: First joint AAPG/AMPG Hedberg research conference. Geological Aspects of Petroleum System, 2–6 Oct 1994, Mexico City (Oral Presentation)

Canipa-Morales NK, Galan-Vidal CA, Guzman-Vega MA, Jarvie DM (2003) Effect of evaporation on C_7 light hydrocarbon parameter. Org Geochem 34:813–826

Chung HM, Walters CC, Buck S, Bingham B (1998) Mixed signals of the source and thermal maturity for petroleum accumulations from light hydrocarbons: an example of the Beryl Field. Org Geochem 29:381–396

Connan J (1984) Biodegradation of crude oils in reservoirs. Adv Pet Geochem 1:299–335

Dai JX (1992) Identification and distinction of various alkane gases. Sci China B 35:1246–1257

Dai JX (1993) Identification of coal formed gas and oil type gas by light hydrocarbons. Pet Explor Dev 20:26–32 **(in Chinese with English abstract)**

Fisher SJ, Alexander R, Kagi RI, Oliver GA (1998) Aromatic hydrocarbons as indicators of biodegradation in North Western Australian reservoirs. In: Purcell PG, Purcell RR (eds), The sedimentary basins of Western Australia 2. Proceedings of Petroleum Exploration Society of Australia Symposium, Perth, pp 185–194

George SC, Boreham CJ, Minifie SA, Teerman SC (2002) The effect of minor to moderate biodegradation on C_5 to C_9 hydrocarbons in crude oils. Org Geochem 33:1293–1317

Graham SA, Hendrix MS, Wang LB, Homewood P (1993) Collision successor basins of western China, impact of tectonic inheritance on sand composition. Geol Soc Am Bull 105:323–344

Halpern HI (1995) Development and applications of light-hydrocarbon-based star diagrams. AAPG Bull 79:801–815

Haven HLT (1996) Applications and limitations of Mango's light hydrocarbon parameters in petroleum correlation studies. Org Geochem 24:957–976

Hu GY, Zhang S (2011) Characterization of low molecular weight hydrocarbons in Jingbian gas field and its application to gas sources identification. Energy Explor Exploit 29:777–796

Hu TL, Ge BX, Zhang YG, Liu B (1990) The development and application of fingerprint parameters for hydrocarbons absorbed by source rocks and light hydrocarbons in natural gas. Pet Geol Exp 12:375–393 **(in Chinese with English abstract)**

Jarvie DM (2001) Williston basin petroleum systems: inferences from oil geochemistry and geology. Mt Geol 38:19–41

Jiang ZX, Li LX, Song Y, Tian FH, Zhao MJ, Wang HJ, Zhao ZX (2010) Control of neotectonic movement on hydrocarbon accumulation in the Kuqa Foreland Basin, west China. Pet Sci 7:49–58

Li MJ, Wang TG, Zhong NN, Zhang WB, Sadik A, Li HB (2013) Ternary diagram of fluorenes, dibenzothiophenes and dibenzofurans: indicating depositional environment of crude oil source rocks. Energy Explor Exploit 31:569–588

Liang DG, Zhang SC, Chen JP, Wang FY, Wang PR (2003) Organic geochemistry of oil and gas in the Kuqa Depression, Tarim Basin, NW China. Org Geochem 34:873–888

Liu WH, Zhang DW, Zheng JJ, Chen MJ, Wang XF, Gao B (2005) A preliminary discussion on geochemical dynamic tracing of oil/gas reservoir ring process—taking Dawanqi structure in Kuqa Depression as an example. Oil Gas Geol 26:716–717 **(in Chinese with English abstract)**

Mango FD (1987) An invariance in the isoheptanes of petroleum. Science 237:514–517

Mango FD (1990) The origin of light hydrocarbons in petroleum: a kinetic test of the steady-state catalytic hypothesis. Geochim Cosmochim Acta 54:1315–1323

Mango FD (1992) Transition metal catalysis in the generation of petroleum: a genetic anomaly in ordovician oils. Geochim Cosmochim Acta 10:3851–3854

Mango FD (1994) The origin of light hydrocarbon in petroleum: ring preference in the closure of carbocyclic rings. Geochim Cosmochim Acta 58:895–901

Masterson WD, Dzou LIP, Holba AG, Fincannon AL, Ellis L (2001) Evidence for biodegradation and evaporative fractionation in West Sak, Kuparuk and Prudhoe Bay field areas, North Slope, Alaska. Org Geochem 32:411–441

Odden W (1999) A study of natural and artificially generated light hydrocarbons (C_4–C_{13}) in source rocks and petroleum fluids from offshore mid-Norway and the southernmost Norwegian and Danish sectors. Mar Pet Geol 16:747–770

Odden W, Patience RL, Van Graas GW (1998) Application of light hydrocarbons (C_4–C_{13}) to oil/source rock correlations: a study of the light hydrocarbon compositions of source rocks and test fluids from offshore Mid-Norway. Org Geochem 28:823–847

Palmer SE (1993) Effect of biodegradation and water washing on crude oil composition. In: Engel MH, Macko SA (eds) Organic geochemistry, principles and applications. Plenum, New York, pp 511–533

Peters KE, Walters CC, Moldowan JM (2005) The biomarker guide. Cambridge University Press, Cambridge

Philippi GT (1975) The deep subsurface temperature controlled origin of the gaseous and gasoline-range hydrocarbons of petroleum. Geochim Cosmochim Acta 39:1353–1373

Tang XY, Yang SC, Hu SB (2014) Thermal and maturation history of Jurassic source rocks in the Kuqa foreland depression of Tarim Basin, NW China. J Asian Earth Sci 89:1–9

Thompson KFM (1979) Light hydrocarbons in subsurface sediments. Geochim Cosmochim Acta 43:657–672

Thompson KFM (1983) Classification and thermal history of petroleum based on light hydrocarbon. Geochim Cosmochim Acta 47:303–316

Volkman JK, Alexander R, Kagi RI, Woodhouse GW (1983) Demethylated hopanes in crude oils and their applications in petroleum geochemistry. Geochim Cosmochim Acta 47:785–794

Welte DH, Kratochvil H, Rullkötter J, Ladwein H, Schaefer RG (1982) Organic geochemistry of crude oils from the Vienna Basin and an assessment of their origin. Chem Geol 35:33–68

Williams JA (1974) Characterization of oil types in Williston Basin. AAPG Bull 58:1243–1252

Yang L, Zhang CM, Li MJ, Du JX (2015) Influence of slight biodegradation on C_7 hydrocarbons in crude oils: a case study of Dawanqi Oilfield in Tarim Basin. Geochimica 44:485–492 **(in Chinese with English abstract)**

Zhang CM, Li ST, Zhao HJ, Zhang J (2005) Applications of Mango's light hydrocarbon parameters to petroleum from Tarim Basin, NW China. Appl Geochem 20:545–551

Zhang SC, Zhang B, Zhu GY, Wang HT, Li ZX (2011) Geochemical evidence for coal-derived hydrocarbons and their charge historyin the Dabei Gas Field, Kuqa Thrust Belt, Tarim Basin, NW China. Mar Pet Geol 28:1364–1375

Zhao MJ, Song Y, Liu SB, Qin SF (2003) The diffusion influence on gas pool: Dawanqi Oilfield as an example. Nat Gas Geosci 14:393–397

Zou YR, Zhao CY, Wang YP, Zhao WZ, Peng PA, Shuai YH (2006) Characteristics and origin of natural gases in the Kuqa Depression of Tarim Basin, NW China. Org Geochem 37:280–290