Research Article

Diamondoid Hydrocarbons as Maturity Indicators for Condensates from Southern Indus Basin, Pakistan

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Received 13 May 2013; Accepted 5 September 2013

Academic Editor: Alexander Tatarinov

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Diamondoid hydrocarbons have been examined in condensates reservoirized in the Southern Indus Basin using GC-MS. Bulk properties reveal that samples are waxy and low sulfur with the exception of Pakhro and Gopang which are nonwaxy. TIC show bimodal distribution of *n*-alkanes along with high abundance of C_{20+} *n*-alkanes indicating substantial contribution of terrigenous OM in these samples. CPI close to one is consistent with mature nature of oils. The samples show two ranges of Pr/Ph ratios. Those within the range of 2.2–2.7 reflect marine depositional settings for OM while others with Pr/Ph >3 may have originated from terrestrial OM deposited under marine oxic conditions. The cross plot of Pr/*n*- C_{17} versus Ph/*n*- C_{18} indicate type III kerogen as main source of OM deposited under marine to marine oxic conditions. The values of diamondoid based maturity parameters, like methyladamantane index 54.1–75.8% and methyladamantane index 34.9–56.3% indicate high level of thermal maturity corresponding to vitrinite reflectance 1.1–1.6%. No biodegradation is observed in any of these samples as shown by methyladamantanes/adamantane 3.99–5.52 and methyladamantanes/diamantane 2.16–2.99 and supported by high values of API gravity (45.13°–60.02°) and absence of UCM.

1. Introduction

Diamondoids are a group of three-dimensional cyclohexane ring alkanes that have highly symmetrical and strain-free diamond like fused ring structures in chair conformation (Figure 1) [1–3]. This name originated from the word “adames,” the Greek letter for diamond, after the discovery of these compounds from Czechoslovakian petroleum [4]. The simplest of these polycyclic diamondoids is adamantane followed by its homologues diamantanes, trimantanes, tetramantanes, pentamantanes, and hexamantanes [5]. Diamondoids in petroleum and sediment extracts are extremely stable compounds. These are generally more stable than any other hydrocarbon class in geological samples, hence more resistant to alteration processes like biodegradation and maturation [3, 5–11]. Because of these properties diamondoids have been used in evaluating geochemistry of source rocks and crude oils including biodegradation and thermal maturity of high maturity crude oils and condensates [9–14]. Sassen and Post used $\delta^{13}C$ values of diamondoids for establishing

oil to source correlation of condensates [15]. Jalees et al. used diamondoids and biomarkers to study the effect of maturity and biodegradation on crude oils and condensates [16]. Dahl et al. proposed diamondoid hydrocarbons as indicators of oil cracking [12]. Others researchers used methyladamantane and methyladamantane indices as maturity parameters for high maturity oils [9, 16, 17]. The most commonly used technique to analyze diamondoids is gas chromatography-mass spectrometry (GC-MS). Recently, Liang et al. used GC-MS-MS and Li et al. used two-dimensional gas chromatography with time of flight mass spectroscopy (GC × GC-TOFMS) for identification and characterization of diamondoids in condensates [18, 19]. These techniques enabled these authors to identify di- and tri-methyladamantanes more effectively.

In this study we have used diamondoids along with *n*-alkanes and isoprenoid parameters to evaluate geochemistry and thermal maturity of condensates from the Southern Indus Basin which is difficult to find otherwise because of extremely low concentration of biomarkers in these samples.

TABLE I: Geological and bulk properties of the condensate samples.

Sr. number	Sample name	Depth (ft) ¹	Reservoir formation ¹		°API	% S	PP (°C)	Waxy/nonwaxy	CPI	Pr/Ph	Pr/ <i>n</i> -C ₁₇	Ph/ <i>n</i> -C ₁₈
			Name	Age								
1	Resham	NA	NA	NA	45.13	<0.1	1	Waxy	1.05	2.77	0.21	0.08
2	Dhamrakhi	8142	L. Goru	Cretaceous	47.59	<0.1	4	"	1.05	4.46	0.28	0.07
3	Baloch	5744	L. Goru MS	Cretaceous	50.37	<0.1	4	"	1.02	2.17	0.19	0.08
4	Unnar	NA	L. Goru MS	Cretaceous	48	<0.1	1	"	1.05	2.46	0.17	0.09
5	Shah	9849	L. Goru MS	Cretaceous	47.54	<0.1	3	"	1.01	2.50	0.21	0.09
6	Pasahki East	NA	L. Goru MS	Cretaceous	46.19	<0.1	4	"	1.04	2.58	0.19	0.08
7	Pakhro	10515	L. Goru BS	Cretaceous	55	<0.1	<-10	Nonwaxy	0.93	1.94	0.11	0.04
8	Gopang	NA	NA	NA	60.02	<0.1	<-10	"	0.84	4.49	0.34	0.11

¹Data from Oil and Gas Development Corporation Limited (OGDCL); CPI: $2(C_{23} + C_{25} + C_{27} + C_{29})/[C_{22} + 2 * (C_{24} + C_{26} + C_{28}) + C_{30}]$ [29]; waxy and nonwaxy on the basis of PP ≥ 1 and <1 ; L. Goru MS: lower Goru massive sand; L. Goru BS: lower Goru basal sand; NA: not available.

FIGURE 1: Structure and numbering of adamantane (I) and diamantane (II).

2. Experimental

2.1. Samples Details. Eight condensates samples collected from different oil fields of the Southern Indus Basin were analyzed in this study. The location of sample wells is shown in Figure 2, while geological information is listed in Table I. A brief geological description of the study area is outlined below and described in more detail by Wandrey et al. [20]. The basin is bounded to the north by the Middle Indus Basin, to the northwest by the Sulaiman Fold Belt, and the Kirthar Fold Belt in the southwest (Figure 2). The hydrocarbon expulsion, migration, and entrapment occurred mainly during Eocene to Miocene time. Source rocks have been identified in Cretaceous and Eocene successions. The Early Cretaceous shales of Sembar and Goru Formations have been recognized as source for the bulk of hydrocarbons charging several oil and gas fields in the Southern Indus Basin. Sembar shales contain mixed type II and type III kerogen and are thought to be deposited under shallow marine depositional conditions [21]. Upper Cretaceous Goru sands and Eocene carbonates are the main reservoirs in the Southern Indus Basin [20–23]. The condensate samples used in this study belong to the Cretaceous reservoirs of Lower Goru Formation.

2.2. Physicochemical Analysis. API gravity, pour point, and sulfur content were determined using ASTM methods [24–26]. Details are described elsewhere [27].

2.3. Separation of Compound Classes by Liquid Chromatography. Condensate samples were fractionated into saturates, aromatics, and polar fractions using liquid column chromatography employing a standard method described elsewhere [28]. In brief, sample (30 mg) dissolved in *n*-hexane (500 μ L) was introduced onto the top of activated silica gel column that has been activated at 250°C for overnight. Saturated hydrocarbon fractions were eluted with three bed volumes of *n*-hexane, aromatic fractions with three bed volumes of mixture of *n*-hexane: dichloromethane (9:1), and the polars with three bed volumes of 1:1 mixture of dichloromethane and methanol. Saturated fractions were analysed by gas chromatography-mass spectrometry (GC-MS).

2.4. Gas Chromatography-Mass Spectrometry. GC-MS analysis was performed using a Hewlett-Packard (HP) 5973 Mass Selective Detector Interfaced to a HP6890 gas chromatograph, which was fitted with a DB-5 capillary column (J and W Scientific, 60 m, 0.25 mm internal diameter, 0.25 μ m). The GC oven was programmed from 40°C to 310°C at a heating rate of 3°C/min with initial and final hold times of 1 and 30 minutes, respectively. The MS source and quadrupole temperatures were at 230°C and 106°C, respectively. Samples were dissolved in *n*-hexane and injected in a pulsed splitless mode using an autosampler. Helium was used as the carrier gas at a linear velocity of 27 cm/s with the injector operating at constant flow. The MS was operating with ionization energy 70 eV, source temperature 180°C, and electron multiplier voltage 1800 V. Data was acquired in a full scan mode from mass range of 50 to 550 amu.

3. Results and Discussion

3.1. Bulk Properties. The crude oils are classified as heavy, medium, and light on the basis of API gravity values $\leq 20^\circ$,

FIGURE 2: Map showing location of condensates wells within the Southern Indus Basin.

20–40°, and 40–45°, respectively, while condensates have API gravity values > 45° [29]. The samples analyzed in this study have API gravity values between 46 and 60° (Table 1) and are classified as condensates.

Pour point (PP) is generally associated with paraffinicity or waxy nature of crude oils. The term high paraffinic reflects high concentration of C_{20+} n -alkanes in petroleum. Crude oils derived from terrigenous OM generally have high paraffinic content and high PP. Figure 3 and data listed in Table 1 show that the analyzed samples having high concentration of C_{20+} n -alkanes have high values of PP up to 4°C and are waxy in nature, so all the samples except Pakhro and Gopang are waxy condensates, while those having low concentration of C_{20+} n -alkanes show low PP and are nonwaxy in nature, for example, Pakhro and Gopang.

Sulfur compounds are undesirable in crude oils and its products because of extra cost incurred on sulfur removal and environmental problems associated with sulfur compounds. The crude oils are termed as sour or sweet on the basis of sulfur content >1% and <1%. The sulfur content of analyzed samples is extremely low (<0.1%) rendering these samples as sweet and commercially valuable.

3.2. n -Alkanes and Isoprenoids Distributions. The distribution pattern of n -alkanes provides useful information on the source of OM, thermal maturity, and biodegradation.

Total ion gas chromatograms of waxy condensates described above show bimodal distribution of n -alkanes (Figure 3), thereby reflecting that source generating these oils has high contribution of terrestrial OM. The absence of UCM indicates that the samples have not undergone biodegradation. Carbon preference index (CPI) of samples is close to one indicating that these samples are high maturity condensates [30] (Table 1). Oil derived from terrigenous OM show marked predominance of C_{27} , C_{29} , and C_{31} n -alkanes which is lost at high maturity level. The analyzed samples do not show odd or even predominance of n -alkanes and exhibit uniform distribution. This feature is attributed to high thermal maturity of these samples.

Pristane to phytane (Pr/Ph) ratios in crude oil and source rocks within oil window reflect redox potential in the depositional environment and nature of OM [31]. Most marine and organic rich sediments have Pr/Ph ratios in the range of 0.8–2.5, which show a gradual increase with increasing maturity within this range, although marine OM usually has Pr/Ph ratio <1.5 at high maturity levels, while terrigenous OM input under oxic conditions shows ratios >3 [29]. Lower values (<0.8) typify anoxic commonly hypersaline or carbonate environment, particularly if it is accompanied by high sulfur content [32–34]. Pr/Ph ratios of six samples (Sr. number 1–6) are 2.2 to 2.77 and indicate significant contribution from terrigenous OM input under marine depositional settings.

FIGURE 3: Total ion chromatograms from GC-MS analysis showing distribution of *n*-alkanes and isoprenoids (Pr and Ph) in condensates from the Southern Indus Basin. C₈–C₃₃ represents *n*-alkanes with carbon atoms 8–33. Pr and Ph = Pristane (Pr) and Phytane (Ph) are C₁₉ and C₂₀ regular acyclic isoprenoids which elute after C₁₇ and C₁₈ *n*-alkanes.

Higher value of 3.95 has been observed for Gopang, which is 60° API and < –10°C PP condensate, and high value of Pr/Ph reflects very high thermal maturity as well as substantial contribution from terrigenous source of OM input under oxic conditions for this sample. Similarly high Pr/Ph ratio (3.98) for Dhamrkhi is consistent with an origin from source rocks having substantial contribution of terrestrial OM and deposited under marine oxic conditions.

The Pr/*n*-C₁₇ ratios have been used to differentiate OM under swamp environment (<1.5) from those found under marine environments (<0.5) although this ratio is affected by maturity [35–37]. The Pr/*n*-C₁₇ ratios of analyzed samples are in a close range of 0.11–0.34 and indicate marine depositional conditions of OM. The Pr/*n*-C₁₇ versus Ph/*n*-C₁₈ plot proposed by Shanmugam provides useful information regarding thermal maturity, biodegradation,

FIGURE 4: $\text{Pr}/n\text{-C}_{17}$ versus $\text{Ph}/n\text{-C}_{18}$ plot showing high maturity and substantial contribution of type III organic matter in source rocks of these samples.

FIGURE 5: Mass spectra of peaks 1, 5, 18, and 23 (Figure 6) assigned as 1-methyladamantane, adamantane, 4-methyldiamantane, and diamantane on the basis of the literature data [9, 10].

and depositional conditions of OM [35]. Increased thermal maturity results in decreased isoprenoid/*n*-alkane ratio due to fast release of *n*-alkanes compared to isoprenoids. On the other hand biodegradation results in increased isoprenoid/*n*-alkane ratios due to fast removal of *n*-alkanes prior to isoprenoids. The Southern Indus Basin condensates show extremely low values of $\text{Pr}/n\text{-C}_{17}$ and $\text{Ph}/n\text{-C}_{18}$ in

the range of 0.11–0.34 and 0.04–0.11, respectively (Table 1). The samples have gathered towards the lower left corner of the plot suggesting high thermal maturity for the samples (Figure 4). The source of OM is mainly type III kerogen deposited under marine oxic conditions which is likely to generate waxy oils or condensates under high thermal conditions.

FIGURE 6: Single ion chromatograms m/z 135, 136, 149, and 163 and 177 m/z 187, 188, and 201 showing distribution and elution order of adamantanes and diamantanes in a representative condensate sample (Gopang). Refer to Table 2 for identity of peaks.

TABLE 2: Diamondoid hydrocarbons identified in Southern Indus Basin condensates.

Peak number	Compound	Abbreviation	Molecular formula	Base peak (m/z)	M^+ (m/z)
1	1-Methyladamantane	1-MA	$C_{11}H_{18}$	135	150
2	2-Methyladamantane	2-MA	$C_{11}H_{18}$	135	150
3	1-Ethyladamantane	1-EtA	$C_{12}H_{20}$	135	164
4	2-Ethyladamantane	2-EtA	$C_{12}H_{20}$	135	164
5	Adamantane	A	$C_{10}H_{16}$	136	136
6	1,3-Dimethyladamantane	1,3-DMA	$C_{12}H_{20}$	149	164
7	1,4-Dimethyladamantane (<i>cis</i>)	1,4-DMA	$C_{12}H_{20}$	149	164
8	1,4-Dimethyladamantane (<i>trans</i>)	1,4-DMA	$C_{12}H_{20}$	149	164
9	1,2-Dimethyladamantane	1,2-DMA	$C_{12}H_{20}$	149	164
10	2,6-Dimethyladamantane + 2,4-dimethyladamantane	2,6-DMA + 2,4-DMA	$C_{12}H_{20}$	149	164
11	1,3,5-Trimethyladamantane	1,3,5-TMA	$C_{13}H_{22}$	163	178
12	1,3,6-Trimethyladamantane	1,3,6-TMA	$C_{13}H_{22}$	163	178
13	1,3,4-Trimethyladamantane (<i>cis</i>)	1,3,4-TMA	$C_{13}H_{22}$	163	178
14	1,3,4-Trimethyladamantane (<i>trans</i>)	1,3,4-TMA	$C_{13}H_{22}$	163	178
15	1-Ethyl, 3,5-dimethyladamantane	1-Et, 3,5-DMA	$C_{14}H_{24}$	163	192
16	1,3,5,7-Tetramethyladamantane	1,3,5,7-TeMA	$C_{14}H_{24}$	177	192
17	1,2,5,7-Tetramethyladamantane	1,2,5,7-TeMA	$C_{14}H_{24}$	177	192
18	4-Methyldiamantane	4-MD	$C_{15}H_{22}$	187	202
19	1-Methyldiamantane	1-MD	$C_{15}H_{22}$	187	202
20	3-Methyldiamantane	3-MD	$C_{15}H_{22}$	187	202
21	1-Ethyldiamantane	1-EtD	$C_{16}H_{24}$	187	216
22	2-Ethyldiamantane	2-EtD	$C_{16}H_{24}$	187	216
23	Diamantane	D	$C_{14}H_{20}$	188	188
24	4,9-Dimethyldiamantane	4,9-DMD	$C_{16}H_{24}$	201	216
25	1,2-Dimethyldiamantane + 2,4-dimethyldiamantane	1,2-DMD + 2,4-DMD	$C_{16}H_{24}$	201	216
26	4,8-Dimethyldiamantane	4,8-DMD	$C_{16}H_{24}$	201	216
27	3,4-Dimethyldiamantane	3,4-DMD	$C_{16}H_{24}$	201	216
28	Dimethyldiamantane 1	*NI	$C_{16}H_{24}$	201	216
29	Dimethyldiamantane 2	*NI	$C_{16}H_{24}$	201	216

*NI: not identified.

3.3. Assignment of Diamondoid Hydrocarbons. Diamondoids in the condensate samples have been analyzed and identified by GC-MS. These compounds were identified by comparing their mass spectra and relative retention time (Figures 5 and 6) with the previous studies [2, 3, 9–11, 13, 38]. The structure and numbering of adamantane and diamantane are shown in Figure 1. Adamantanes and diamantanes were examined using m/z 135, 136, 149, 163, and 177 and m/z 187, 188, and 201, respectively. Figure 6 shows the distribution and elution order of adamantanes and diamantanes in a representative sample, while Table 2 enlists identity and mass spectral properties of different isomers.

3.4. Diamondoid Hydrocarbons as Indicators of Thermal Maturity. Diamondoids are highly stable compounds under thermal conditions. Therefore these compounds have been used to estimate thermal maturity of highly mature samples including condensates [9, 10, 13]. The use of diamondoid

hydrocarbons as maturity indicator is based on the relative stability of different isomers under different thermal conditions. For example, 1-methyladamantane (1-MA) is thermally more stable than 2-methyladamantane (2-MA) due to methyl at bridgehead and tertiary position in the former, and hence its concentration increases with maturity. Similarly 4-methyldiamantane (4-MD) is more stable compared to 1-methyldiamantane (1-MD) and 3-methyldiamantane (3-MD). Chen et al. introduced methyladamantane index (MAI) and methyldiamantane index (MDI) to distinguish different maturity levels [9, 10]. They proposed that samples of vitrinite reflectance (R_o) 1.1–1.3% have MAI values between 50 and 70% and MDI values between 30 and 40%. Similarly samples with R_o values 1.3–1.6% were shown to have MAI 70–80% and MDI 40–50%, while those with R_o values 1.6–1.9% showed MAI 80–90% and MDI 50–60%. Samples of even higher maturities ($R_o > 1.9$) have MAI > 90% and MDI > 60% [9, 10]. The values of indices MAI and MDI thus provide

TABLE 3: Parameters based on diamondoid hydrocarbons.

Sr. number	Name of oil	MAI%	MDI%	MA/A	MD/D
1	Resham	60.8	37.3	4.91	2.99
2	Dhamrakhi	58.7	34.9	4.87	2.65
3	Baloch	64.8	41.8	4.57	2.55
4	Unnar	54.1	48.4	3.99	2.16
5	Shah	65.2	40.7	4.51	2.43
6	Pasahki East	70.9	40.4	4.82	2.55
7	Pakhro	75.8	52.0	5.52	2.35
8	Gopang	64.1	56.3	4.49	2.22

MAI% = $(1\text{-MA}/1\text{-MA} + 2\text{-MA}) \times 100$ [9, 10]; MDI% = $(4\text{-MD}/1\text{-MD} + 3\text{-MD} + 4\text{-MD}) \times 100$ [9, 10]; MA/A = $1\text{-MA} + 2\text{-MA}/A$ [11]; MD/D = $1\text{-MD} + 3\text{-MD} + 4\text{-MD}/DIA$ [11].

FIGURE 7: Cross-plot of MAI% and MDI% for Southern Indus Basin condensates showing high thermal maturity corresponding to R_o 1.1–1.3 for Resham, Baloch, and Dhamrakhi and R_o 1.3–1.6 for Unnar, Shah, Gopang, Pasahki East, and Pakhro [9, 10].

guidelines for maturity determination particularly for high maturity samples including condensates. The distribution and relative abundances of adamantane, methyladamantanes, diamantane, and methyladamantanes in a representative sample (Gopang) are shown in Figure 6, while values of MAI and MDI are listed in Table 3. Among the samples suit Dhamrakhi with MAI 58.7% and MDI 34.9% is the least mature and Pakhro with MAI 75.8% and MDI 52% is the most mature (Table 3). Cross-plot of MAI and MDI is shown in Figure 7 which indicates that the Southern Indus Basin condensates, Resham, Baloch, and Dhamrakhi, with MAI 58.7–64.8% and MDI 34.9–41.8%, have thermal maturities equivalent to R_o 1.1–1.3 and Unnar, Shah, Gopang, Pasahki East, and Pakhro, with MAI 54.1–75.8% and MDI 40.4–56.3%, have higher maturities corresponding to reflectance range 1.3–1.6.

3.5. Biodegradation. Diamondoids are highly resistant to biodegradation. The stability of these compounds allows to use these compounds as fingerprints for the assessment of biodegradation. The ratios methyladamantanes/adamantane (MA/A) and methyladamantanes/diamantane (MD/D) have

been applied to assess biodegradation of crude oil [11]. Higher values of MA/A up to 16 indicate progressive level of microbial activity and in-reservoir biodegradation. MA/A is sensitive to even initial stages of biodegradation, and values > 6.3 have been observed for slightly biodegraded oils. However the value increases with progressive increase in level of biodegradation. On the other hand MD/D values are not affected by slight to moderate biodegradation; however slight change in MD/D ratio (> 3.5) has been observed at severe levels of biodegradation (level 8) [11]. The values of MA/A and MD/D for the analyzed samples are listed in Table 2 which range from 3.99 to 5.52 and 2.16 to 2.99, respectively. These values are lower than the limits described for biodegradation suggesting that no biodegradation has taken place in the Southern Indus Basin condensates. Moreover, *n*-alkanes profile and absence of UCM also support nonbiodegraded nature of these samples.

4. Conclusions

- Bulk properties of samples reveal that six samples (Sr. no. 1–6) with API gravity 45–50° and PP 1–4°C are waxy condensates, while two (Sr. no. 7–8) with API 55 and 60 and PP $< -10^\circ\text{C}$ are nonwaxy condensates.
- Bimodal distribution of *n*-alkanes and high abundance of C_{20+} *n*-alkanes suggests terrigenous source of OM for the condensates, while Pr/Ph ratios 2.2–2.77 and 3.95–3.98 suggest marine to marine oxic environment of deposition for the samples.
- Isoprenoid/*n*-alkane ratios and Pr/*n*- C_{17} versus Ph/*n*- C_{18} plot suggest marine to marine oxic depositional conditions and type III kerogen as main source of OM which is likely to generate waxy oils or condensates under high thermal conditions.
- Diamondoid-based maturity parameters (MAI and MDI) have indicated that samples have attained high levels of thermal maturity corresponding to vitrinite reflectance 1.1–1.6%.
- Absence of UCM and ratios of MA/A and MD/D indicate that samples are nonbiodegraded.

Abbreviations

A:	Adamantane
MA:	Methyladamantane
D:	Diamantane
MD:	Methyldiamantane
MAI:	Methyladamantane index
MDI:	Methyldiamantane index
PP:	Pour point
CPI:	Carbon preference index
OM:	Organic matter
UCM:	Unresolved complex mixture
GC-MS:	Gas chromatography-mass spectrometry.

Acknowledgment

The authors are thankful to Oil and Gas Development Company Limited (OGDCL), Pakistan, for providing the condensate samples and geological data.

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