

Geochemical Investigation of Crude Oils from Different Oil Fields of the Potwar Basin

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Summary: Crude oils (12) from the Potwar Basin, have been analyzed to obtain geochemical information on source and depositional environment of organic matter, maturation, biodegradation and geochemical correlation. Bulk and molecular parameters have recognized three groups of petroleum within the study area, Group I of heavy oils, Group II of medium to light oils and Group III, comprising of a single oil Adhi, of light oil. Based on samples location in ternary diagram, Group I oils were classified as paraffinic naphthenic (PN), while Groups II and III were classified as paraffinic (P) oils.

Gas chromatographic (GC) fingerprints of Group II and III oils showed full suite of n-alkanes, low isoprenoid to n-alkane (Pr/nC17 and Ph/nC18) ratios, absence of UCM (unresolved complex mixture) and higher saturates/aromatics ratios. These features suggested non-biodegraded nature of these samples. Most of the oils of Group I were affected by light to moderate biodegradation on account of these parameters. Carbon Preference Index (CPI) and Odd Even predominance (OEP) 1.0 for Group II and Adhi and <1.0 for Group I oils revealed slightly lower thermal maturity of the latter. Terrestrial to aquatic ratios (TAR) suggested that all the samples contained mixed organic matter (OM) with predominant contribution of marine geolipids for Groups I & II and terrestrial OM for Group III. Pristane to phytane (Pr/Ph) ratios ≤ 1 along with high sulfur content suggested typical marine carbonate dysoxic sediments generating Group I oils, while Pr/Ph > 1 and very low sulfur content recommended oxic depositional settings for Group I oils and Adhi. The differences in the location of Joyamair and Minwal on geochemical plots were interpreted to difference in thermal maturity compared to other oils of this group.

Introduction

The Potwar Basin is the main source of hydrocarbons in northern Pakistan. It is structurally deformed portion of the Indian Plate during the Indo-Eurasian plate collision and by the overthrust of the Himalayas, in sedimentary sequences of widely-varying ages (e.g., Precambrian and Tertiary) to occur in close proximity of each other. Petroleum of very different properties has been produced from stratigraphic units of Cambrian to Miocene ages that occur within a distance of few kilometers. Although there are some studies discussing source rocks and petroleum systems in the basin [1-3], however, oil to source correlations and defining petroleum systems in the basin require comprehensive geochemical study.

The application of geochemical parameters in petroleum exploration has been elaborated significantly in the present study. The parameters suitable for geochemical characterization range from bulk properties to molecular ratios [4-6]. Bulk properties are useful for initial screening; however, molecular parameters based on individual

hydrocarbon ratios provide an insight to assess thermal maturity and biodegradation of hydrocarbons [6-11]. The notion behind the approach is that same source material and environment of deposition produces petroleum with similar chemical signatures. This similarity is transmitted in crude oils produced from common source rocks provided hydrocarbons are not affected by secondary processes [12, 13]. In this study both bulk and molecular parameters have been used to investigate geochemical characteristics of petroleum from different oil fields of the Potwar Basin.

Results and Discussion

Bulk Properties

The crude oils analyzed in this study are listed in Table-1. The properties like American Petroleum Institute (API) gravity, Reid vapor pressure (RVP), sulfur content and Kinematic viscosity (KV) have been used for broad grouping of samples. The

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Table-1: Geological and bulk parameters of crude oils.

Sr. No.	Sample Name	Reservoir			Properties					
		Formation		Depth (m)	Temp (°F)	Specific Gravity	API	S (%)	RVP (Psi)	KV (cSt)
		Name	Age							
Group III										
1	Adhi	Khewra/Tobra	Cambrian	2256	-	0.77	51	0.05	9	< 1
Group I										
2	Chak Naurang	Khewra/Tobra	Cambrian	2563	-	0.936	20	1.7	4	-
3	Joyamair	Sakesar	Eocene	2025	182	0.956	16	2.1	1.7	-
4	Kal-I	Khewra	Cambrian	2720	125	0.944	20	1.8	4.39	9.04
5	Minwal	Sakesar	Eocene	2021	172	0.956	16	2.0	1.6	-
6	Rajian	Khewra	Cambrian	3645	-	0.936	20	-	-	-
7	Fimkassar	Sakesar	Eocene	2888	-	0.877	29.4	1.64	3.8	10.1
Group II										
8	Bhangali	Sakesar	Eocene	3700	482	-	32	0.1	4.2	4.1
9	Dhurnal	Chorgali/Sakesar	Eocene	4096	-	0.833	38	0.15	6.5	-
10	Missa Keswal	Chorgali	Eocene	2187	-	0.833	38	0.2	3.9	1.6
11	Pindori	Sakesar	Eocene	3953	273	0.801	41	0.04	7.3	1.4
12	Turkwal	Chorgali	Eocene	4000	-	0.874	30	0.7	3.2	-

API: American Petroleum Institute gravity 60/60 °F, S: Sulfur content; RVP: Reid vapour pressure at 100 °F; KV: Kinematic viscosity at 40 °C, -: no data/ not determined

crude oils Chak Naurang, Joyamair, Kal, Minwal Rajian and Fimkassar, discovered in Cambrian and Eocene reservoirs, show characteristics of heavy oils, *i.e.*, low values of API gravity (16-20°), RVP (< 2 Psi), high values of KV (9-10 cSt) and sulfur content (~2 %). These properties are strongly dependent on molecular composition and indicate low levels of light hydrocarbons. The processes like in-reservoir biodegradation or evaporative fractionation could be the likely causes of reduced levels of light hydrocarbons. The other oils, Bhangali, Dhurnal, Missa Keswal, Pindori and Turkwal, demonstrate different properties, *i.e.* high API gravity (32 to 41°), RVP (3.2 to 7.2 Psi) and low values of sulfur content ($\leq 0.2\%$ except Turkwal), KV (1-4 cSt). These parameters therefore suggest the presence of significant amounts of low molecular weight hydrocarbons (LMWHCs) and non-biodegraded nature of petroleum. The properties of single oil 'Adhi' are different from other two groups and resemble to condensates, *i.e.*, very high API gravity (51°), RVP (9

Psi), extremely low sulfur content (0.05%) and KV. Since condensates are usually generated from more mature source rocks and reservoirs under high temperature and typically undergo extensive migration; they are likely to contain elevated levels of LMWHCs. On the basis of these data, at least three groups of petroleum with distinct physicochemical properties could be identified within the study area. Group I of heavy oils, Group II of medium to light oils and Group III, representing a single oil Adhi, of very light oil.

Geochemical Characterization

Types of Crude oils and Correlations

The relative percentages of saturates, aromatics, NSOs and asphaltenes (NSOs: nitrogen, sulfur and oxygen containing compounds) was used to distinguish different types of crude oils (Table-2). Higher relative proportions of saturates are present in

Table-2: Geochemical data of crude oils.

Sr. No.	Name	Sats	Aros	NSO+Asp	Sats	Pr	Pr	Ph	Pr+nC ₁₇	CPI	OEP	TAR	nC ₃₁
		1	2	3	Aros	Ph	nC ₁₇	nC ₁₈	Ph+nC ₁₈				nC ₁₉
Group III													
I	Adhi	58	12	30	4.8	2.6	0.4	0.2	1.06	1.0	1.0	0.5	0.49
Group I													
3	Chak Naurang	35	37	28	1.0	1.1	1.1	0.86	1.52	0.98	0.92	0.3	0.4
5	Fimkassar	45	33	22	1.4	0.9	1.04	0.71	1.29	0.99	0.95	0.3	0.26
6	Joyamair	15	39	46	0.4	1.1	0.94	0.68	0.90	0.9	0.91	0.4	0.31
7	Kal-I	37	24	39	1.5	1.3	1.6	0.8	1.27	0.99	0.95	0.4	0.18
8	Minwal	19	33	48	0.6	1.1	1.0	0.98	0.96	0.96	0.89	0.5	0.37
11	Rajian	35	32	33	1.1	1.3	1.3	0.7	1.42	0.98	0.92	0.3	0.25
Group II													
2	Bhangali	56	18	26	3.1	1.5	1.17	0.74	1.21	1.0	1.0	0.3	0.2
4	Dhurnal	63	19	18	3.3	1.4	0.9	0.7	1.28	1.0	1.0	0.3	0.6
9	Missa Keswal	59	23	18	2.6	2.2	0.8	0.3	1.10	0.99	1.02	0.3	0.02
10	Pindori	45	26	29	1.7	1.6	0.90	0.51	1.16	1.0	0.98	0.2	0.16
12	Turkwal	64	20	16	3.2	1.7	1.0	0.5	1.12	0.98	0.92	0.3	0.04

crude oils of Group II and Adhi, whereas most of the oils of Group I contains competitive concentrations of all three compound classes. Alternatively saturate/aromatic ratio is the maximum in Adhi, intermediate in Group II and minimum in Group I oils. When these results were plotted on ternary diagram (Fig. 1), different groups of petroleum showed clear differentiation, Group I oils were located in the paraffinic naphthenic (PN) region, while Group II oils and Adhi were clustered in paraffinic (P) region of the plot. Ternary diagram therefore provides a mean to distinguish different types of crude oils on the basis of major compound classes and to establish correlation between the samples. The difference in the location of Joyamair and Minwal was interpreted to difference in maturity.

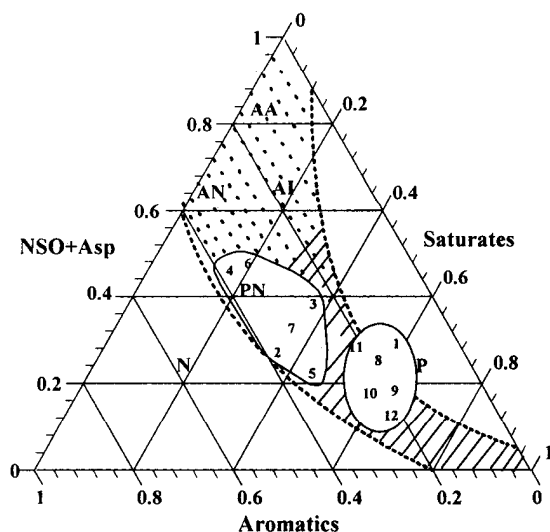


Fig. 1: Ternary plot between saturates, aromatics and NSO+asphaltenes showing crude oil types and correlation. Nos 1-12 denote crude oils, refer to Table 1 for the identity of crude oils; P: Paraffinic; PN: Paraffinic naphthenic; N: Naphthenic; AI: Aromatic intermediate; AN: Aromatic naphthenic and AA: Aromatic asphaltic.

1-3: Sats: saturates; Aros: aromatics; NSO: nitrogen, sulfur and oxygen containing compounds; Asp: asphaltenes, obtained by silica gel chromatography; 4 : saturates/aromatics ratio; 5 : Pr (Pristane)/Ph (Phytane); 6: Pristane/ *n*-heptadecane; 7: Phytane/*n*-octadecane; 8: Pristane+*n*-heptadecane/Phytane+*n*-octadecane; 9: Carbon Preference Index: $(C_{23}+C_{25}+C_{27}+C_{29})/(C_{25}+C_{27}+C_{29}+C_{31})/2(C_{24}+C_{26}+C_{28}+C_{30})$; 10: Odd Even Predominance:

$(C_{25}+6C_{27}+C_{29})/(4C_{26}+4C_{28})$; 11: Terrestrial to Aquatic Ratio: $(C_{27}+C_{29}+C_{31})/(C_{15}+C_{17}+C_{19})$, parameters 5-12 calculated from *n*-alkane and isoprenoids peak areas, refer to Fig. 3 for peak identity.

Biodegradation

Biodegradation is microbial alteration of various classes of hydrocarbons present in petroleum. When biodegradation occurs in petroleum reservoirs, it affects the hydrocarbon composition, fluid properties and oil geochemistry [14, 15]. The unresolved complex mixture (UCM) is useful indicator of petroleum biodegradation [16].

Fig. 2 shows representative gas chromatograms (GCs) of saturated hydrocarbon fraction from each group. The GCs of Group II and Adhi are typical of non-biodegraded crude oils as indicated by full suite of *n*-alkanes, absence of UCM and low isoprenoids to *n*-alkane ratios. The values of Pr/*n*C₁₇ and Ph/*n*C₁₈ are 0.4 and 0.2 for Adhi and 0.8-0.9 and 0.3-0.7 for Group II oils (Table-2). These oils have shown high API gravity and low KV. Since these features are typical of non-biodegraded petroleum, therefore Adhi and Group II oils are non-biodegraded. The lack of *n*-alkanes in early retention window of the chromatograms is due to evaporative loss during procedural operations. Moreover, oils within Group II show good correlation in terms of above parameters.

The GC of Group I oil (Fig. 2) shows low abundance *n*-alkanes relative to isoprenoids and presence of UCM. Their Pr/*n*C₁₇ and Ph/*n*C₁₈ ratios are comparatively higher (0.9-1.3 and 0.7-0.98 respectively) reflecting that most of the oils this group have undergone low to moderate level biodegradation resulting in partial loss of *n*-alkanes prior to isoprenoids [17]. The fluid properties, like low API gravity and high KV, are also consistent with biodegraded nature of these oils.

Cross plot of API gravity versus S content has been used to distinguish different groups of petroleum (Fig. 3). Most oils of Group II and Adhi cluster into non-biodegraded region of the plot, while Group I oils assemble into biodegraded region of the plot, Turkwal (sample No. 12) is borderline case.

Thermal Maturity

Carbon Preference Index (CPI) and Odd Even Predominance (OEP) in specified carbon

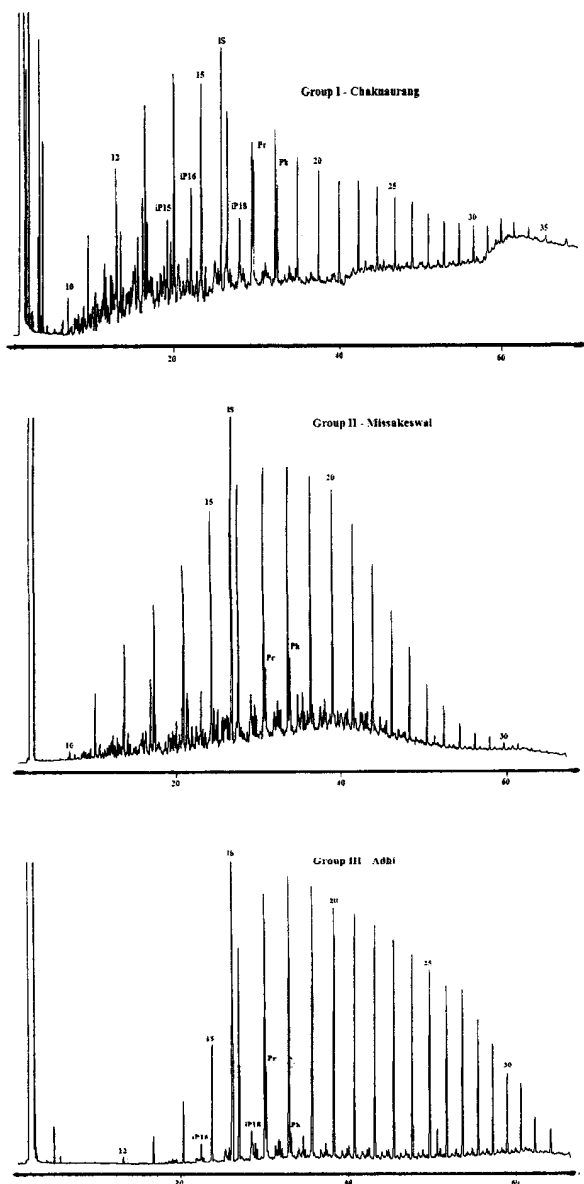


Fig. 2: Capillary gas chromatograms of representative sample from each group. Peaks C_{12} to C_{35} are *n*-alkanes; iP_{15} : 2,6,10-trimethyldodecane also called farnesane; iP_{16} : 2,6,10-trimethyltridecane; iP_{18} : 2,6,10-trimethylpentadecane also called norpristane; iP_{19} : 2,6,10,14-tetramethylpentadecane, common name Pristane (Pr); iP_{20} : 2,6,10,14-tetramethylhexadecane, common name Phytane (Ph); IS: Internal standard fluorene.

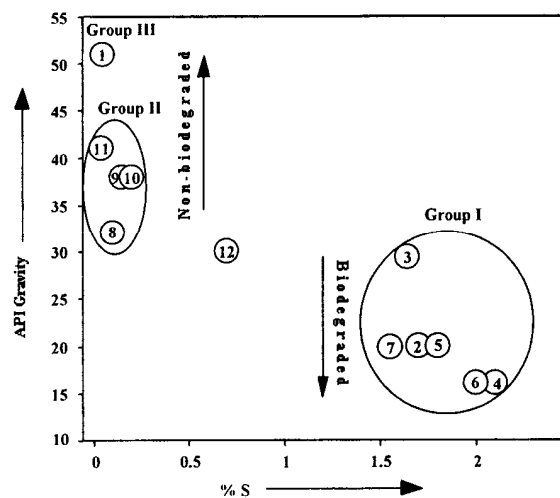


Fig. 3: API gravity versus S content graph differentiated biodegraded and non-biodegrade oils. Oils within a group have been encircled.

number range have been used to infer thermal maturity [7, 18]. The values significantly above (odd preference) or below (even preference) 1.0 indicate thermally immature organic matter, whereas value of 1.0 is typical of thermally mature oil or source rock extract. The crude oils of Group I and two samples of Group II (Missakeswal and Turkwal) show CPI and OEP < 1.0, which indicate relatively low thermal maturity of these samples. Since bitumen related to carbonate source rocks commonly show even carbon number predominance and CPI and OEP less than one [6], therefore option of carbonate lithology of source rocks cannot be ruled out. Among the sample suite, Joyamair and Minwal exhibit minimum CPI and OEP suggesting low maturity. The CPI and OEP of remaining oils of Group II and Adhi is 1.0, which is consistent with thermally mature OM. Although Adhi has shown substantial terrestrial contribution (next section) however odd predominance of C_{27} to C_{31} *n*-alkanes was not observed to have an effect on carbon preference indices. Maturity indicators therefore reveal lower relative maturity of Group I compared to Adhi and Group II oils.

Source and Depositional Environment

The ratio of the pristane to phytane is used to assess redox conditions of the sediments during

diagenesis [11]. The phytol side chain of chlorophyll or phytanyl ether lipids from bacterial cell wall are widespread sources of pristane and phytane. Oxidative or reductive pathway from any source leads to the formation of pristane and phytane [8]. Higher values (3-5) have been observed for oxic, probably near-shore deltaic type environments and indicate terrigenous source of OM; while low wax oils from marine source rocks show Pr/Ph in the range of 1-3, very low values (< 0.8) typify anoxic, commonly hypersaline environment. Oils from carbonate sources demonstrate low Pr/Ph ratios, low carbon preference indices and high sulfur contents [6].

Pr/Ph ratios of Group I oils are in the range of 0.9-1.3. The oils have shown slight even predominance of *n*-alkanes (*i.e.* CPI and OEP < 1) and high sulfur content. These results suggest dysoxic depositional conditions and marine carbonate source rocks for Group I oils [19]. Higher value 2.6 was observed for Adhi, which indicate more oxic environment. The source rocks contained probably mixed terrestrially-influenced OM because nC_{31}/nC_{19} and TAR close to 0.5 were observed (Table-2). For Group II oils, Pr/Ph ratios are in the range of 1.4 to 2.2. These oils have shown low values of nC_{31}/nC_{19} and TAR (<0.3). These results indicate that crude oils are derived from marine source rocks deposited under oxic depositional conditions.

The parameter, $Pr+nC_{17}/Ph+nC_{18}$, suggested by Alexander *et al.* [20], was calculated to provide an additional evidence for correlation, because this parameter is less affected by maturity. The values of parameter show some variations for different groups. For example, 1.3 to 1.5 for Group I oils (excluding Joyamair and Minwal which are known to have low maturity), 1.1 to 1.2 Group II oils and 1.06 for Adhi (Table-2). These data provide an additional evidence that crude oils within a group are derived from same source material and depositional environment.

The amount of sulfur present in petroleum is a useful indicator of hydrocarbon generating sequence. It has been shown that high sulfur content is associated with anoxic sequences and those subjected to low thermal exposure [21]. The crude oils of Group I show high sulfur content (~2 wt %) which suggest more anoxic sequences generating these oils than Group II. Among the sample suite, Adhi appears to have been generated from the most

oxic sequences as shown by extremely low sulfur content (0.05%) and high Pr/Ph ratio.

Terrigenous to Aquatic Ratios (TARs) and Source of Organic Matter

n-Alkanes are derived from algal, microbial and higher plant sources. The predominance of C_{27} , C_{29} and C_{31} *n*-alkanes has been associated with land plant sources of OM [19]. Algal contribution, in contrast, is indicated by the predominance of C_{15} , C_{17} and C_{19} *n*-alkanes [22, 23]. TAR measurements are therefore useful to determine relative contribution of land plant versus aquatic OM. Values >1 indicate more terrigenous input relative to aquatic source and vice versa.

TAR values of Group I oils 0.3 to 0.4 (Table-2), are consistent with marine source of OM. These results together with even carbon preference indices (CPI and OEO < 1.0), high sulfur content and low Pr/Ph ratios (Tables-1 and 2). These data suggest that marine carbonate sediments deposited under dysoxic environment, are likely source rocks for these oils. Most of the oils of Group II show TAR values 0.3, which suggest marine source of OM. These oils have shown low sulfur content, comparatively higher Pr/Ph ratios with no odd or even predominance of *n*-alkanes. These results reflect that marine sediments deposited under oxic environments are likely source rocks for these oils. For Group III oil (Adhi) TAR is 0.5, indicating an increasing contribution of land-plant derived OM compared to other two groups. High Pr/Ph ratio and extremely low sulfur content are consistent with considerable oxicity of source rocks producing Adhi. The distribution of TAR values is also in good agreement with that of nC_{31}/nC_{19} .

Experimental

Samples

The samples analyzed in this study belong to the Potwar Basin. Fig. 4 shows the location of study area while Table-1 enlists geological and bulk properties of the samples.

Physicochemical Analysis

The parameters, API gravity, sulfur content, Reid Vapor Pressure (RVP) and Kinematic Viscosity

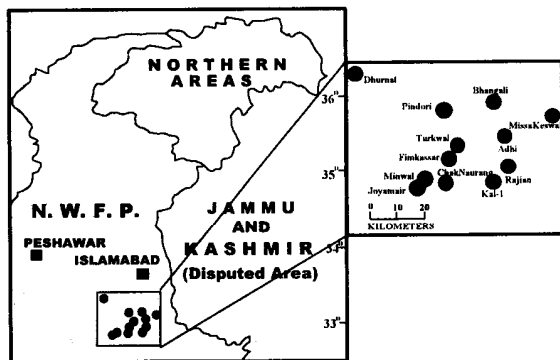


Fig. 4: Location of study area on the map of Pakistan.

(KV) were determined according to IP and ASTM standard methods [24-28]. The details of procedures are as follows:

Specific Gravity and API Gravity [24]

The specific gravity was determined using glass hydrometer of specification E 100 (Zeal, UK) at room temperature. The results were converted to standard temperature 60/60°F using ASTM standard table [25]. API gravity was calculated using formula:

$$\text{API gravity} = \frac{141.5}{\text{Sp. gravity } 60/60^\circ\text{F}} - 131.5$$

Sulfur Content [26]

The percentage of sulfur was determined using sulfur meter (RX-350S, Tanaka Scientific Ltd., Japan). The method consisted of three steps; combustion of sample, absorption of oxidized sulfur into absorbent solution and titration. The combustion assembly consisted of a round furnace having openings at both ends to hold a quartz tube. The exit end of the quartz tube was connected to flask containing 50 ml of absorbent solution (H_2O_2 : H_2O ; 1:19). The furnace was turned ON to attain temperature 900 °C. The sample (100 mg) was loaded to ceramic boat, which was then placed in the quartz tube and combustion was continued for 30 minutes. After absorption, the solution was titrated against 0.05 M NaOH using 3-4 drops of methyl purple indicator (0.1% alcoholic solution) to green end point. The sulfur content was calculated using the formula: $S \% = 1.603 \times M \times V/W$

where M and V: molarity and volume of NaOH; and W: weight of sample in g.

Reid Vapor Pressure [27]

Reid vapor pressure was determined by RVP apparatus (Seta-Stanhope, UK). The crude oil sample was taken in the liquid chamber of the apparatus, which was immersed in a water bath maintained at 37.8 °C (100°F). The vaporized portion of crude oil raised into air chamber above the oil. The increase in pressure in the air chamber was measured by a pressure gauge.

Kinematic viscosity [28]

The Kinematic viscosity (KV) of crude oil was measured at 40 °C using a reverse flow glass viscometer (STANHOP-SETA Ltd. England). The sample was taken in the viscometer up to the mark with the help of a suction pump. The mouth of viscometer was capped and it was immersed in viscosity bath maintained at temperature 40 °C for one hour. The cork was then removed and time of free flow of sample from one mark to other was noted. The same procedure was adopted for measurement of kinematic viscosity at 50 °C. The Viscosity was calculated using formula:

$$\text{KV (cSt)} = \text{Time of flow (sec)} \times \text{viscometer constant.}$$

where viscometer constant at 40 °C = 1.035

Organic Geochemical Analysis

Isolation of Compound Classes by Liquid Chromatography

Crude oils were separated into alkanes, aromatics, NSO and asphaltene fractions by column chromatography using silica gel as adsorbent employing a previously reported method [29]. In brief, a glass column (40 cm x 1cm i.d.) was packed with a slurry of silica gel (5 g) in *n*-hexane (20 ml). The sample (50 mg) in *n*-hexane (500 μl) was introduced onto the column. The alkanes were eluted with *n*-hexane, the aromatics with mixture of 95:5 *n*-hexane: diethyl ether, the NSO compounds with methanol and asphaltenes with chloroform. 15 ml solvent or solvents mixture was used for each elution. The fractions were recovered after evaporation of the

solvent on a rotary evaporator and then under nitrogen to avoid oxidation.

GC-FID Analysis

The alkane fractions were analyzed by capillary GC-FID Shimadzu 14-B series (Japan) gas chromatograph, equipped with a Flame Ionization Detector (FID) and fused silica capillary column, coated with methyl silicon (OV-1) 30m x 0.25 mm i.d film thickness 0.25 μm . The sample (1 μl) containing fluorene as internal standard was injected in split less mode at 60°C. Detector (FID) and injector temperature were 280°C and 250°C, respectively. The oven temperature was programmed from 60°C to 300°C at 4°C/min. The initial and final temperatures were maintained for 1 and 5 minutes respectively. Nitrogen at linear velocity of 2 ml/min was used as carrier gas. The data was collected from retention time 0-70 minutes using Shimadzu CLASS-GC10 version 2.00 software and data acquisition system.

The sample preparations were as follows: (a) Alkane solution: 10 mg/ml cyclohexane. (b) Internal standard solution: 1mg fluorene/3 ml cyclohexane. (c) 50 μl each of (a) and (b) were mixed and 1 μl was injected to GC column.

Conclusions

Geochemical analysis of twelve crude oils has uncovered at least three groups of petroleum within the study area. Group I oils were derived from marine carbonate source rocks, deposited under dysoxic conditions. These samples exhibited low thermal maturity.

Group II oils were also derived from marine-influenced source rocks, however sediments were deposited under oxic conditions. The source rocks of Group III oil were deposited under more oxic conditions and contained terrestrially-influenced OM. Maturity indicators demonstrated higher thermal maturity of Adhi and Group II compared to Group I oils. Group II and III oils were non-biodegraded while most of the oils of Group I were affected by light to moderate biodegradation.

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