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Characterization of Aromatic Hydrocarbons in Dhurnal oil from Northern Indus Basin

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Summary: A molecular study of aromatic hydrocarbons in a crude oil from northern Indus basin was carried out using liquid chromatography and capillary GC-FID techniques. The study revealed high concentration of aromatic compounds (~ 20% of crude oil). The identification of compounds was made consulting with the literature data. The concentration of individual compounds was calculated by using internal standard method. Kovat indices of 56 compounds using OV-1 column have been reported for reference. Biomarker parameters like, Pr/Ph, Pr/n-C_{17} and Ph/n-C_{18} ratios have been applied to assess depositional conditions and any sign of biodegradation; these parameters revealed that Dhuranl is a typical non-biodegraded crude oil and was generated under oxic sedimentary conditions. High concentration of alkyl naphthalenes (mono-, di-, tri- and tetramethylnaphthalens) is the products of sedimentary reactions during catagensis and metagensis. The ratios of β-substituted isomers to the α-substituted isomers of alkylnaphthalenes and alkylphenanthrenes were used to assess maturity, which revealed high maturity level of crude oil.

Introduction

Polycyclic aromatic hydrocarbons are ubiquitous compounds found in ancient and recent sediments [1]. Their distribution in petroleum, coals and sediments is highly variable due to the complex nature of biogenic origin and thermal alteration. The occurrence of aromatic hydrocarbons that have non-isoprenoidal structure has led to the suggestion that such compounds are the products of sedimentary reactions [2-3]. These hydrocarbons are formed by aromatization of alicyclic system or from saturated hydrocarbons by cyclization followed by aromatization. Such type of reactions occurs during catagensis and metagensis.

Occurrence of aromatic hydrocarbons in crude oil and sediments has been described by different researchers [2, 4-11]. The principal application of C_{10}+ aromatic hydrocarbons in petroleum geochemistry has been as maturity indicator. The most common approach exploits measuring changes in the relative abundance of different isomers including methyl phenanthrenes, di- and trimethyl-naphthalenes and methyl dibenzothiophenes [2, 12-13]. Another widely used aromatic hydrocarbon based maturity parameter measure the abundance of monoaromatic steranes relative to triaromatic steranes [14].

As petroleum is a complex mixture of thousands of hydrocarbons. Following techniques are commonly adopted to isolate and analyze aromatic hydrocarbons. Preparation of sample by removing free sulfur followed by column chromatography for separation of saturated, aromatics and NSO (nitrogen, sulfur, oxygen) fractions. Fractionation of total aromatics according to ring size prior to GC analysis further reduces the complexity of the mixture. Aromatic hydrocarbons are separated into mono- di- and triaromatic fractions by high performance liquid chromatography (HPLC) or TLC. These fractions still contained several series of compounds. The individual compounds are separated and identified by capillary GC-FID and GC-MS techniques.

In this study, a crude oil sample from northern part of upper Indus basin has been analyzed for aromatic hydrocarbons using GC-FID and related techniques. Kovat indices of 56 compounds have been reported and 29 compounds have been identified. Application of aromatic hydrocarbons as maturity parameters has been suggested.

Results and Discussion

Bulk parameters

API gravity is inversely related to specific gravity. This property is used to assess commercial value and thermal maturity of crude oil. Generally API gravity in the range of 40 shows high

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commercial value and high maturity of the oil. During thermal maturation heavier components of the oil undergo cracking, resulting an increase in API gravity. However API gravity is affected by factors like biodegradation, migration, organic matter input and water washing etc. API gravity 38 (Table-1) reveals the significant high maturity level of Dhurnal oil.

Saturated Hydrocarbons

The distribution of n-alkanes and isoprenoids in saturated fraction is shown in Fig. 1A. The chromatogram is typical non-biodegraded crude oil with no loss of n-alkanes or isoprenoids. Pristane to Phytane ratio 2 is indication of oxic depositional conditions (Table-2) of organic matter, similarly Pr/n-C_{17} and Ph/n-C_{18} ratio less than 1 indicates non-biodegraded nature of crude oil.

Aromatic Hydrocarbons

The distribution of both saturated and aromatic hydrocarbons in same retention window under same program has been shown (Fig. 1 A & B) for identification and determination of Kovat indices of aromatic hydrocarbons.

Identification and quantification

Kovat indices (*KI*) have been calculated using methyl silicone column (OV-1) for aromatic hydrocarbons according to method described in the literature [15]. Kovat [16] derived an equation (1) for determination of retention indices of unknown compounds with reference to retention time of known compounds. In this study the retention times of n-alkanes has been used as reference for calculation of *KI* of the unknown aromatic hydrocarbons.

$$KI = 100\{K+\log(t_{Rx}/t_{Rk})/\log(t_{Rk+1}/t_{Rk})\} \quad \ldots\ldots\ldots.(1)$$

Where K is the carbon number of earlier n-alkane, t_{Rk} and t_{Rk+1} are the retention time of earlier and latter n-alkane, while the t_{Rx} is the retention time of desired aromatic hydrocarbons.

The concentration of aromatic hydrocarbons was calculated using their peak areas with reference to standard phenanthrene peak area by following method:

$$\text{Conc. of compound (ng)} = \frac{\text{Conc. of Std. Phen.} \times \text{peak area of desired compound}}{\text{Peak area of phen.}}$$

Table-3 shows the Kovat indices and concentration of aromatic hydrocarbons identified in this study.

Geosynthesis of aromatic hydrocarbons

Aromatic hydrocarbons are widespread constituents of geological materials and are believed to be derived partly from nonaromatic natural precursors by cyclization and aromatization reactions [17-19]. The origin of alkyl aromatics in sediments and oils is not well defined. A high relative abundance of alkyl substituted aromatic hydrocarbons compared to non-alkylated compounds is attributed to sedimentary

Table 1: Bulk and Geochemical data of Dhurnal oil

Sample		Bulk Properties				Relative percentages		
Name	Formation	Sp. Gravity 60/60°	API gravity	Sulfur (Wt %)	Sats.	Aros.	NSOs	Asp.+ Resin
Dhurnal-1	Sakesar	0.841	38	0.17	62.9	19.1	4.3	13.7

Sats: Saturated hydrocarbon fraction
Aros: Aromatic hydrocarbon fraction
NSOs: Nitrogen, sulfur and oxygen containing compounds
Asp: Asphaltenes

Table-2: Saturated and aromatic hydrocarbons parameters of Dhurnal oil.

Saturated		Naphthalene (ng/g)		Phenanthrenes			
Pr/Ph	2.0	Naphthalene	0.017	Phenanthrene	0.294	MPI 1	1.20
Pr/n-C_{17}	0.82	DMN[a]	0.296	∑MP/P	4.67	MPI 2	1.43
Ph/n-C_{18}	0.5	TMN[b]	0.597	MPR: 2MP/1MP	1.22	MPI 3	1.18

a: β-isomer of Dimethylnaphthalene [2,6-DMN]+[2,7-DMN]
b: [1,3,7]+[1,3,6]+[1,4,6]+[1,3,5] TMN
∑MP=MP1+MP2+MP3+MP9
MPI 1 = 1.5(2MP+3MP) / P+1MP+9MP
MPI 2 = 3(2MP) / P+1MP+9MP
MPI 3 = [2MP]+[3MP] / [1MP]+[9MP]

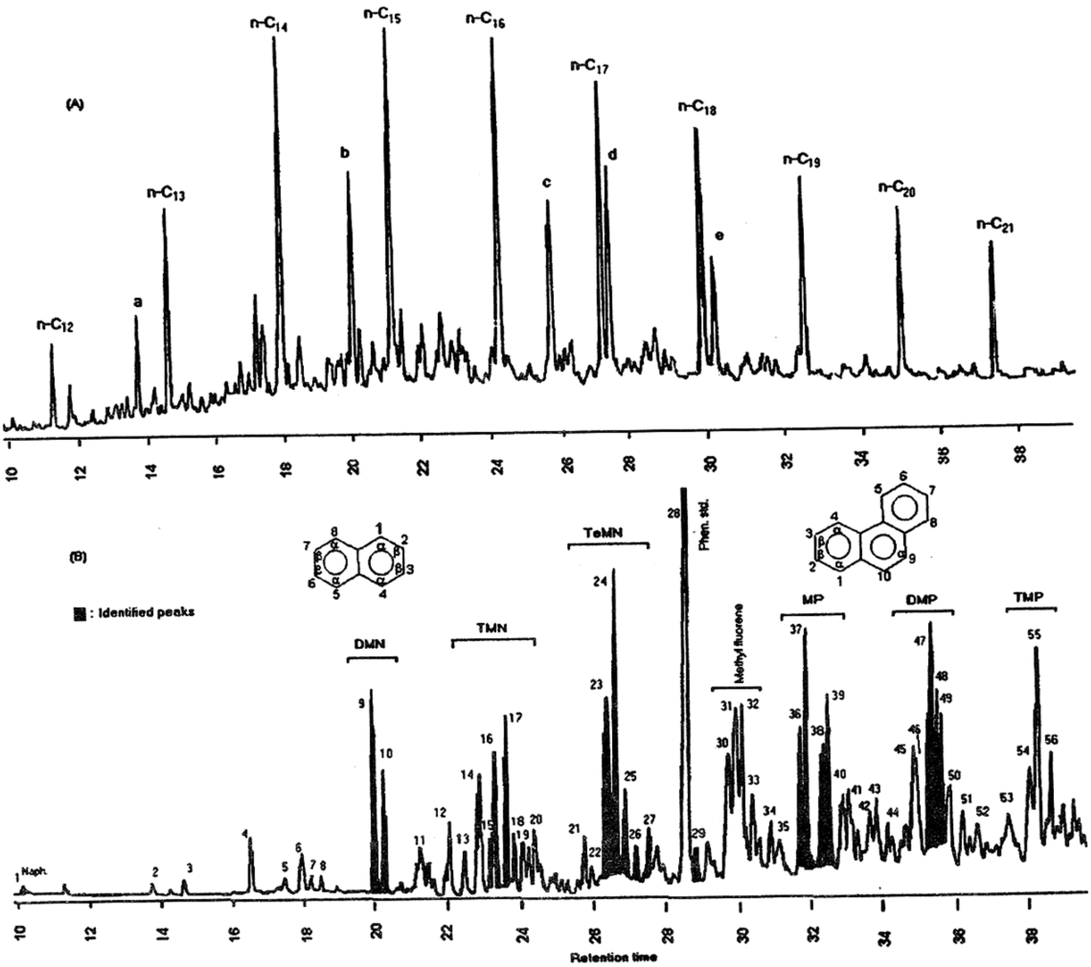

Fig. 1: Gas chromatograms of Dhurnal oil (A) Saturated fraction; peaks n-C12 to n-C21 are n-alkanes with carbon number 12 to 21, a: 2,6,10-trimethylundecane; b: 2,6,10-trimethyltridecane; c: nor-pristane; d: 2,6,10,14-tetramethyl pentadecane (pristane); e: 2,6,10,14-tetramethyl hexadecane (phytane), (B) Aromatic fraction; numbers on peaks refer to Table 3; Naph: naphthalene; DMN: Dimethylnaphthalene; TMN: Trimethylnaphthalene; TeMN: Tetrame-thylnaphthalene; MP: Methylphenanthrene, DMP: Dimethyl phenanthrene; TMP: Trimethyl phenanthrene.

maturation processes like degradation of biogenic precursors under thermal stress and dehydrogenation and alkylation processes. The identification and distribution of sedimentary alkyl aromatics by alkylation processes has been demonstrated for phenols [20], benzenes [5], naphthalene [11], phenanthrene [8, 20], and anthracenes [21].

The aromatic fraction of Dhurnal oil contained higher concentration of alkyl naphthalenes (di-, tri-, and tetramethylnaphthalens) as compared to naphthalene (Fig. 2B). It has been shown that methyl substitution to parent naphthalene takes place during thermal alteration. Bastow *et al.* [11] observed that alkyl naphthalene readily undergo electrophilic substitution reaction at specific positions when treated with methyl donor under laboratory conditions. This has been interpreted as evidence for sedimentary methylation process. Dimethyl and trimethyl naphthalenes (DMN & TMN) could have

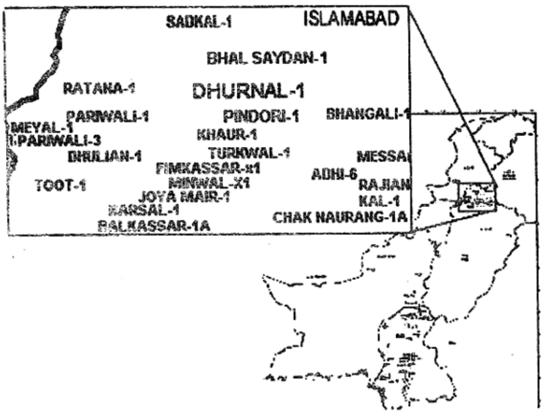

Fig. 2: Location of Dhurnal oil field in Northern Indus basin

been formed by the same sequence of alkylation reactions.

Alkylphenanthrenes (Fig. 1B) are present in significant concentration as compared to parent phenanthrene. These compounds could be derived by the aromatization of tricyclic diterpenoids of resinous plants, particularly retene or by the dehydrogenation of alkylated dihydrophenanthrene [5, 21, 22]. Presence of higher concentration of methyl & dimethyl substituted phenanthrenes shows that the methylation of parent compound during thermal alteration is favorable sedimentary process.

Thermal maturation

Assessment of thermal maturation using aromatic hydrocarbons has been demonstrated by

Table-3: Kovat Indices for Aromatic hydrocarbons in Dhurnal crude oil

Peak identity		Kovat indices	Identification	Concentraion (ng/g of oil sample)
Carbon number*	Peak number**	(Column OV-1)		
11	1	1168	Naphthalene	0.017
12	2	1276	–	0.014
13	3	1300	–	0.02
"	4	1359	–	0.074
"	5	1385	–	0.026
"	6	1398	–	0.085
14	7	1406	–	0.026
"	8	1416	–	0.023
"	9	1463	2,6+2,7-DMN	0.296
"	10	1471	1,3+1,7+1,6DMN	0.172
15	11	1500	–	0.105
"	12	1528	–	0.0107
"	13	1541	–	0.061
"	14	1555	–	0.217
"	15	1564	1,3,7-TMN	0.088
"	16	1568	1,3,6-TMN	0.239
"	17	1578	1,4,6+1,3,5-TMN	0.27
"	18	1584	–	0.09
"	19	1592	–	0.075
16	20	1602	–	0.098
"	21	1650	–	0.098
"	22	1657	–	0.05
"	23	1672	1,3,5,7-TeMN	0.52
"	24	1680	1,3,6,7-TeMN	0.532
"	25	1688	1,2,4,6+1,2,4,7-TeMN	0.198
"	26	1698	2,3,6,7-TeMN	0.101
17	27	1711	1,2,6,7-TeMN	0.148
"	28	1752	Phenanthrene	0.294
"	29	1759	Anthracene	0.097
"	30	1791	–	0.34
"	31	1799	–	0.476
18	32	1803	–	0.257
"	33	1817	–	0.183

Table-3: Continued.

Peak identity		Kovat indices (Column OV-1)	Identification	Concentraion (ng/g of oil sample)
Carbon number*	Peak number**			
"	34	1835	–	0.111
"	35	1844	–	0.136
"	36	1868	3-MP	0.301
"	37	1875	2-MP	0.441
"	38	1891	9-MP	0.269
"	39	1896	1-MP	0.362
19	40	1912	–	0.183
"	41	1919	–	0.232
"	42	1935	–	0.04
"	43	1944	–	0.169
"	44	1963	–	0.084
"	45	1983	–	0.098
"	46	1991	–	0.451
20	47	2011	1,3+3,9+2,10-DMP	0.63
"	48	2018	1,6+2,9+2,5-DMP	0.488
"	49	2030	1,7-DMP	0.233
"	50	2046	–	0.127
"	51	2063	–	0.124
"	52	2072	–	0.044
"	53	2096	–	0.229
21	54	2123	–	0.246
"	55	2133	–	0.431
"	56	2149	–	0.263

* Carbon number of earlier n-alkane

** Refer to Figure 2(B)

–: not identified

different authors [2, 6, 12, 17]. It has been observed that with increasing maturity the relative abundance of structurally more stable β-isomers increases compared to less stable α-substituted isomers in methyl naphthalenes and methyl phenanthrenes [11, 21]. The concentration of Naphthalene and its methyl substituted isomers in Dhurnal oil is shown in Table -2. In dimethyl naphthalene region, 1,8-DMN and 1,5-DMN (both α-substituted isomer) are absent. Alexander *et al.,* [7] reported that the relative abundance of 1,8-DMN was a sensitive indicator of thermal maturity of sediments. The β-dimethyl naphthalene (2,6-, 2,7-DMN) are present in high concentration 0.296 ng/g (Table-2). Same trend was observed for TMN (Table-2) and TeMN. In all methyl substituted naphthalenes, the TeMN region shows highest concentration and six isomers of TeMN were identified (Fig. 1B and Table-3). Organic matter from low mature samples have 1,2,5,6-TeMN and 1,2,3,5-TeMN as the most abundant isomers where as with increase in maturity the 1,3,5,7-TeMN and 1,3,6,7-TeMN isomers showed greater abundance. In TeMNs of Dhurnal oil the 1,3,5,7-TeMN and 1,3,6,7-TeMN are present in higher concentration which reveals conversion of less stable isomers to stable isomers that indicate the higher thermal maturity of crude oil. Other isomers are in low concentration or absent especially compounds with substitution at position 1 and 8. Both these positions in DMN and TMN are also absent shows the unfavorable substitutions during sedimentary processes.

The abundance of methylphenanthrene relative to phenanthrene (∑MP/P, Table-2) reflects the diagenetic evolution of alkylated compounds. Smith *et al.,* [21] carried out methylation of phenanthrene in laboratory heating experiments, they observed that at lower temperature the 9-position (α-) is more activated than 2 and 3 positions (β-), but as temperature increases more predominant methylation occurs at 2 and 3 positions of phenanthrene. In Dhurnal oil 2methylphenanthrene (2MP), 3MP and 1MP are present in higher concentrations. Regarding the methylphenanthrene, different ratios have been used in petroleum geochemistry as thermal maturity indices [5]. Pervious studies have reported a relative increase in abundance of 2MP and 3MP relative to

9MP and 1MP when maturity increases [2]. These ratios in the case to present study (Table-2) show the abundance of stable isomers. Methylphenanthrene indices (MPI) are molecular maturity parameters which have been developed from studies on coals and source rocks [2, 4]. MPI is dependent on phenanthrene and methylphenanthrene homologues with increasing maturity; α-methylphenanthrenes are gradually converted to more stable β-methylphenanthrenes. In Dhurnal oil, MPI 1, 1.20 and MPI 2, 1.43 (Table-2) indicated the oil has reached to highest level of thermal maturation. The methylphenanthrene ratio (MPR) value more than 1 also favors the MPI indications. Dimethyl-phenanthrene trend is same as of methylphenan-threne. All these results reveal the high thermal maturity of Dhurnal crude oil.

Experimental

The crude oil sample belongs to Dhurnal oil field (Fig. 2), located in Potwar Plateau of northern Indus basin (Punjab basin). The oil sample is associated with rocks of Tertiary age. The geological Formation of Dhurnal oil is Sakesar [23].

Sample preparation

Crude oil sample was prepared for column chromatography by removing free sulfur. A column of fine precipitated copper (1g) was prepared in pasture pipette. Sequential washing was done with methanol, dichloromethane and n-hexane. Oil sample (100 mg dissolved in n-hexane) was passed through column. Any free sulfur present in oil chemically combined with copper and retained in the column. The crude oil was quantified to calculate weight %age of sulfur.

Fractionation by Liquid Chromatography

Sulfur free oil sample was fractionated by column chromatography. Silica gel 60 (70-230 mesh, Merck) was activated at 250°C for 12 hours. Column was packed using 5g of activated silica gel in n-hexane. The crude oil (50mg) in n-hexane (500µL) was introduced onto the column. Saturated hydrocarbons were eluted with three bed volume of n-hexane. Second elution for aromatics was performed with three bed volume of mixture of n-hexane: diethyl ether (95:5) and NSO and asphaltenes + resin were eluted with three bed volume each of methanol and chloroform respectively. The fractions were dried under the flow of nitrogen to constant weigh and quantified. Aromatic fraction was further separated into mono-, di-, and tri-aromatic fractions by thin layer chromatography. TLC plate (0.5mm thickness) was coated with alumina (Merck). It was activated at 120°C for 12 hours prior to use. Naphthalene and phenanthrene were used as standard for identification of di- and triaromatic regions respectively. n-Hexane was used as solvent in the tank and specific aromatic regions were identified using UV lamp. The fractions were recovered by extracting di- and tri-aromatic regions of plate with dichloromethane and were quantified.

Capillary GC-FID Analysis

The sample dilution and analytical condition for capillary GC-FID were made as follows:

Internal standard solution was prepared by dissolving 10 mg of Phenanthrene in 10 mL of n-hexane; so each µL of solution contained 1ng of phenanthrene. For GC-FID analysis 4mg of aromatic fraction was dissolved in 200 µL of *n*-hexane and 50µL of above prepared standard phenanthrene solution was added to it for quantification. Similarly 4 mg / 200 µL dilution were made for GC analysis of saturated hydrocarbons. Analysis of both saturated and aromatic fractions was carried out, using a Schimadzu GC-14B series (Japan) gas chromatograph with fused silica capillary column (30m×0.25mm i.d.) coated with methyl silicone (OV-1). The samples (each 1µL) were injected in a splitless mode at 60 °C. Detector (FID) and injector temperatures were 290 °C and 280 °C respectively. The oven temperature was programmed from 60 °C to 290 °C at the rate of 4 °C/min. The final temperature was maintained for 5 minutes. Nitrogen at a linear velocity of 2 mL/min. was used as the carrier gas.

Conclusions

Hydrocarbon composition of a crude oil has been determined using LC and GC techniques. Presence of full suit of n-alkanes and isoprenoids in saturated fraction showed non-biodegraded nature of crude oil. Pristane to phytane ratio >1 revealed the oxic depositional environment of organic matter. GC-FID analysis and Kovat indices have indicated higher concentration of methyl substituted naphthalenes and phenanthrenes. These compounds are suggested to be originated from non-aromatic biogenic precursors via clay catalyzed sedimentary reactions during diagensis and catagensis. Molecular thermal maturation parameters e.g. Methylphenanthrene indices (MPI 1, 1.20 and MPI 2, 1.43) and Methylphenanthrene ratio (MPR >1) indicated that Dhurnal crude oil reached their higher stage of thermal maturation. The higher concentration 1,3,5,7-TeMN and 1,3,6,7-TeMN supports the suggestion of higher thermal maturity of organic matter.

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