Hydrocarbon Composition of Crude Oils from the Oldest Formation of the Punjab, Pakistan

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Abstract. Four crude oils from the oldest formation of the Punjab basin were analyzed for the hydrocarbons. These crude oils belong to two sedimentary basins namely the Punjab Basin and Sindh Basin. The samples were analyzed for chemical fossils using a range of chemical methods and instrumental techniques. Quantification and characterization of isolated compounds were carried out using data from the literature and reference compound. Gas chromatograms (GC) of the saturated hydrocarbon fractions of crude oils were characterized by a striking series of peaks, eluting between the n-alkanes mainly in the C_{20}-C_{26} range. Optimized GC resolution showed that each peak is a co-elution of subpeak which corresponds to a complex series of monomethylalkanes. The hydrocarbon composition in terms of depositional environment, levels of maturation, and the nature of the primitive microorganisms which existed during ancient times were interpreted.

Keywords: crude oils, monomethylalkanes, microorganisms, hydrocarbons, sedimentary basin

Introduction

The oldest rocks in Pakistan are of Precambrian age, which form the basement of the lower Paleozoic sediments and in certain cases serve as the source of terrigenous clastics for the younger rocks in adjoining areas. The Punjab basin was a large desiccating basin with marine replenishment and increasing clastic input. The occurrence of oil shales within the sequence suggests restricted conditions during periods of reduced desiccation and enhanced biological activity. Available evidences indicate that rocks of certain geological ages are much richer in petroleum than those of other ages.

Numerous hydrocarbons have been observed in cores and ditch samples of wells, drilled in the Salt Range Formation, however, the oil is very heavy and viscous and not considered to be of commercial importance. The disseminated bitumen found in the late Precambrian Nonesuch Formation of northern Michigan suggests possible presence of hydrocarbons in Precambrian time (Levorsen, 1972).

Hydrocarbon composition of crude oils. The hydrocarbon fractions of oils contain mainly aliphatic and aromatic hydrocarbons. In addition to these true hydrocarbons, there are also small amounts of aromatic hydrocarbon-like-compounds containing sulphur, oxygen or nitrogen atoms (Bowden *et al.,* 2006).

Aliphatic hydrocarbons. These are normal alkanes extending to C_{40} or more with higher concentrations around C_6-C_8. Acyclic isoprenoidal alkanes are important constituents

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particularly pristane and phytane. Acyclic alkanes < 15 C_5 are gases under normal surface conditions, while those up to C_{15} are liquids. The n-alkanes with > C_{15} atoms tend to be viscous liquids grading into solid waxes. Major cycloalkanes include cyclohexane and cyclopentane series with alkyl chains of carbon number range similar to the n-alkanes. Cycloalkanes are generally with more than one ring system such as the alkylperhydronaphthalene (Sandison *et al.*, 2003).

Aromatic hydrocarbons. Low molecular weight alkylbenzenes are generally the most abundant hydrocarbons. Alkylnaphthalenes and the alkylphenanthrenes, are usually present but larger polycyclic aromatic hydrocarbons such as chrysene are less abundant.

Heterocyclic hydrocarbons. Sulphur containing compounds like benzothiophene, dibenzothiophene, naphthobenzothiophene are usually present in oils.

Parameters based on GC analysis. Gas chromatographic study of saturated hydrocarbon is principally carried out to determine n-alkane and isoprenoid distribution. Identification of compound represented by various peaks is carried out by comparison of retention time with the known ones (time required for components to emerge from the column). Biomarker and non-biomarker parameters based on GC are as follows:

(a) The molecular weight distribution of n-alkanes in low, medium and high molecular weight region gives indication of their origin (Olivella *et al.*,2006). n-Alkane distribution reflects the composition of the biological matter and the depositional

environment and their overall distribution swifts to lower molecular weight regions with increasing maturity of source rocks.

(b) Monomethylalkanes mid-chain branching is found in the components of various plants and animals. Living organisms tend to produce specific isomers of monomethylalkanes (Barber *et al.*, 2001). Evolutionary considerations strongly suggest that biological contribution from higher organisms are unlikely during the Precambrian (Pr) or early Phanerozoic (Ph) era in contrast to input from microbial sources.

(c) Carbon preference index (CPI) is a numerical means of representing odd-over-even predominance in *n*-alkane distribution in a particular carbon number range.

(d) Light hydrocarbon ratios have been used for many years to classify crude oils (Obermajor *et al.*, 2002).

(e) Acyclic isoprenoid, pristane/phytane ratio has been shown to change with thermal maturation (Dawson *et al.*, 2005).

Materials and Methods

Sample collection. Four crude oil samples used in this study were procured from commercial wells of the sedimentary Punjab Basin (Upper Indus Basin). Samples of crude oil PA to PD (Table 1) were sampled using standard sampling procedure (ASTM D-270). Prior to detail investigation, the quality and the commercial value of crude oil sample were determined using physicochemical properties (Quddus

et al.,1995). Table 2 lists the data pertaining to the properties of crude oil samples used in this study.

Sample fractionation. The crude oil samples were fractionated into saturated aromatic and nitrogen, sulfur and oxygen (NSO) fractions by column chromatography on silica gel. Glass column (40 cm x 1.2 cm i.d) was packed with 5 g freshly activated silica gel (105 °C, 24 h) in *n*-hexane (20 ml). The crude oil sample (100 mg) in *n*-hexane (50 µl) was introduced onto the column. The saturated fraction was eluted with three bed volumes of *n*-hexane, the aromatics with three bed volumes of 95:5 (*n*-hexane: diethylether) and NSO with three bed volumes of methanol. The fractions were recovered by careful evaporation of the solvent on a sand bath followed by the removal of residual solvent under nitrogen. The fractions were collected in pre-weighed sample bottles. This procedure was repeated twice.

Urea adduction. Further separation of the alkanes into two fractions, *n*-alkanes plus simply branched/cyclic alkanes, was achieved with urea. Saturated solution of urea was prepared in hot methanol using excess of urea. The saturated fraction (30 mg), dissolved in 1 ml of 1:1 mixture of cyclohaxane and acetone was taken in 50 ml centrifuge tube. Saturated solution of urea was added to the sample, drop wise, till appearance of urea crystals.

The sample was centrifuged for 5 min. The solvent was evaporated under the slow stream of nitrogen gas. Again

Table 1. Location, geological ages, source input of crude oils and petroleum reservoir characteristics

Sample	Formation	Basin	Probable age of source	Reservoire depth (M)
PA	Jutana	Punjab (Upper Indus)	Early cambrian	2063.5-2065
PB	Khewra	Punjab (Upper Indus)	Early cambrian	2650-2670
PC	Khewra	Punjab (Upper Indus)	Early cambrian	3495-3645
PD	Khewra/Tobra	Punjab (Upper Indus)	Cambrian	2563.5-2590

Table 2. Physicochemical properties of crude oils

Properties	PA	PB	PC	PD
Appearance	Opaque	Opaque	Opaque	Opaque
Colour (Visual)	Brownish black	Black	Black	Black
Density g/cm³ at (60° F)	0.9342	0.9423	0.9111	0.9416
Specific gravity at (60° F)	0.9477	0.9501	0.9121	0.9438
API gravity (60° F)	17.26	21.39	23.80	18.42
Kinematic viscosity (100° F)	3.46	35.4	17.35	88.37
Sulphur content (% by wt.)	1.815	1.729	1.135	1.627
Flash point (°C)	69.00	62.00	65.00	71.00
Pour point (°C)	+23.00	+24.00	+22.00	+25.50

urea solution and solvent mixture (cyclohexane and acetone) were added in 50:50 ratio, and all the above procedure was repeated, three times. After complete adduction, the supernatant solution was decanted.

The solvent was evaporated under low pressure of nitrogen gas resulting in branched hydrocarbons which were further analyzed by gas chromatography flame ionization detector GC-FID.

GC analysis. Gas chromatograms were obtained on a Shimadzu GC-14B series (Japan) instrument, fitted with a 30 m × 0.25 mm i.d. fused silica capillary column, coated with methyl silicone (OV-1). 1 μl of sample was injected in splitless mode at 60 °C. Detector (FID) and injector temperatures were 300 °C and 280 °C, respectively. The oven temperature was programmed from 60 °C to 300 °C at 4 °C/min. Nitrogen at a linear velocity of 28 cm/s was used as the carrier gas. The data was collected from retention time 0-60 minutes.

Results and Discussion

Hydrocarbon composition. Crude oils were fractionated into saturated alkanes, aromatics and NSO components by column chromatography using silica gel. Table 3 shows the results.

$$C_1 - C_{14} = \frac{C_{12} + C_{13} + C_{14}}{C_{12} + C_{13} + \ldots\ldots\ldots + C_{33}}$$

$$C_{15} - C_{25} = \frac{C_{15} + C_{16} + \ldots\ldots\ldots + C_{33}}{C_{12} + C_{13} + \ldots\ldots\ldots + C_{33}}$$

$$C_{26} - higher = \frac{C_{26} + C_{27} + \ldots\ldots\ldots + C_{33}}{C_{12} + C_{13} + \ldots\ldots\ldots\ldots C_{33}}$$

C_x is calculated from peak area in GC

where:

$$C_x = C_{12} \ldots\ldots\ldots C_{33}$$

The relative percentage of each class was used to classify the crude oils. The crude oils with high percentage of acyclic alkanes (> 50%) and less than 1% sulfur have been described paraffinic oils. In order to obtain the percentage of acyclic alkanes, there is a need to separate branched acyclic alkanes. Branched and n-alkanes were separated through urea adduction and 5 °A molecular sieves. Table 3 shows that the PA, PB and PD contains < 50% acyclic alkanes while PC > 60% acyclic alkanes. Further none of the crude oils contains > 50% saturated branched and acyclic compounds. On this bases, none of the samples can be described as naphthenic in nature.

n-Alkane distribution. *Source and biodegradation determination.* The relative abundance of low, medium and high molecular weight n-alkanes in saturated fractions of different crude oils have been applied for the assessment of thermal maturity. The data for the relative abundance of n-alkanes of different molecular weight range is calculated from respective peak areas in the gas chromatograms of the corresponding saturated fractions of crude oils under similar conditions. These data are summarized in Table 3.

Table 3 shows that the relative percentage of higher molecular weight n-alkanes is maximum in PC and is minimum in PD, so the crude oil belonging to PD is the most immature, while the low molecular weight n-alkane percentage is maximum in saturated fraction of PA crude. Therefore, it is the most mature oil.

Relative abundance of low molecular weight n-alkanes shows higher level of maturity, and excess higher molecular weight n-alkane distribution is an indication of lower level of matura-

Table 3. Percentage of each fraction and relative abundance of n-alkanes in crude oil samples

| Samples | Relative percentage (weight %) | | | | | Relative abundance (%) | | |
| | Saturates | | Aromatic | NSO's | ASP* | Low mol. wt. n-alkanes (C_1 to C_{14}) | Med. mol. wt. n-alkanes (C_{15} to C_{25}) | High mol. wt. n-alkanes (C_{26} to higher) |
	n-alkanes	B/C						
PA	21.5	27.6	41.4	4.4	5.1	21.9	69.9	8.2
PB	17.5	27.9	46.5	3.5	4.6	18.8	72.0	9.2
PC	22.6	37.4	34.3	3.8	1.9	17.4	70.1	12.5
PD	20.9	27.6	35.4	5.2	10.9	20.5	72.5	7.0

ASP* (asphaltene) by difference method.

tion, while the high relative abundance of medium molecular weight *n*-alkanes plays intermediate role towards both extremes. All eight samples of the crude oils contain normal distribution of *n*-alkanes; no depletion has been observed in any chromatogram. In terms of biodegradation, these oils are non-degraded (Huang *et al.*, 2004).

Parameters based on GC analysis. The saturated fraction isolated from crude oils was subjected to gas chromatographic analysis. Following geochemical parameters have been calculated using these chromatograms.

1) Pr/Ph ratio: depositional environment determination
2) $Pr/n-C_{17}$ and $Ph/n-C_{18}$ and biodegradation level
3) Carbon preference index (CPI) and odd-even predominance (OEP): thermal maturity determination

Pr/Ph ratio. *Depositional environment determination.* Depositional conditions can be characterized using isoprenoid distribution; the low Pr/Ph ratios (< 1) may indicate that there were anoxic condition at the time of the deposition of the source and a low Pr/Ph ratio can also be the result of phytane derived from archaebacterial lipids while a high Pr/Ph ratio (> 1) suggests oxic environment. The values of this parameter > 1 for all crude oil samples suggest that they are formed in oxic environment (Table 4).

The crude oil samples also contain a distribution of regular acyclic isoprenoids (2,6,10, trimethyldodecane; 2, 6, 10, trimethyltridecane; 2, 6, 10, trimethyltetradecane and norpristane) in small proportion (Bakr and Wilkes, 2002).

$Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios and biodegradation level. The ratio of isoprenoid to *n*-alkane decreases with depth in all types of organic matter with increasing maturation due to the increasing prevalence of *n*-paraffins. Both ratios increase with biodegradation due to loss of these *n*-paraffins. In order to assess maturity of samples, $Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios were calculated from peak area in gas chromatogram (Table 4).

The results show that PA has high maturity while PC is comparatively of low maturity level and biodegradation process is absent.

Carbon preference index (CPI) and odd-even predominance (OEP). *Thermal maturity determination.* CPI and OEP are influenced by the type of organic matter and the degree of maturity. CPI and OEP values were calculated using formula given by Smith and Bend (2004). They used these ratios for calculating the maturity of oils. The CPI values of all crude oils samples are equal to almost one (Table 4). Since mature oils usually do not show any preference for either odd or even carbon, therefore oils in these wells lie in the principal zone of oil formation, in which substantial amounts of new alkanes are generated with less or no odd preference; thus, the progressive disappearance of odd/even predominance is caused with increasing maturation.

Degradation of wax esters experimentally produces odd *n*-alkanes and even *n*-alkanes, which are subsequently converted to even *n*-alkanes (Yanik *et al.,* 2003).

Monomethyl alkanes. Monomethyl alkanes with mid-chain branching are components of various plants and animals. Evolutionary considerations strongly suggest them to be biological contributions from microbial sources. Cyanobacteria and ancient algae are the microorganisms known to produce mid-chain branched monomethyl alkanes. High concentration of these compounds has been observed in ancient sediments and crude oils.

The series of monomethyl alkanes occurs in the $C_{14}-C_{28}$ range of chromatogram, and its most abundant members are in the $C_{20}-C_{26}$ range. Gas chromatograms show bunch of small peaks between *n*-alkanes, which corresponds to a complex series of monomethyl alkanes (Klomp, 1986). Table 5 shows the relative percentage of monomethyl alkanes for some crude oil samples, calculated from their respective peak areas in the gas chromatograms.

Different isomers of monomethylalkanes have been identified by blowing up the region between small *n*-alkanes. Peak identification has been made by comparing the GC-retention time and elution order with the published data (Fowler and Douglas 1987).

Table 4. Pr/Ph, Isopreniod/*n*-alkane ratio, CPI and OEP values of crude oil samples

Samples	Pr/Ph	Isoprenoid / *n*-alkane		CPI value	OEP value
		$Pr/n-C_{17}$	$Pr/n-C_{18}$		
PA	1.47	1.11	0.77	1.05	1.09
PB	1.43	1.09	0.71	1.02	0.99
PC	1.30	1.01	0.62	0.98	1.04
PD	1.33	1.02	0.77	0.99	0.96

Table 5. Relative percentage of monomethyl alkanes in crude oil samples

Samples	Relative percentage			
	C_{20} MMA	C_{22} MMA	C_{24} MMA	C_{26} MMA
PA	0.101	0.092	0.062	0.072
PB	0.091	0.078	0.058	0.069
PC	0.089	0.081	0.061	0.059
PD	0.090	0.072	0.056	0.062

C_x MMA = ΣC_x MMA/$\Sigma C_{12} + C_{13} + ... + C_{33} \times 100$; where: MMA = monomethylalkanes; C_x is calculated from peak areas in GC

Gas chromatograms of the saturated hydrocarbon fractions of the crude oils are characterized by series of mono-methylalkanes (MMAs) eluted between C_{20} - C_{26} range. From the presence of these monomethylalkanes, these compounds are believed to be derived from cyanobacteria and archae-bacteria, the "primitive microorganisms" which prevailed in ancient times.

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