GEOCHEMICAL CHARACTERIZATION OF RESERVIOR FLUIDS FOR CONNECTIVITY AND ALTERATIONS, ADHI OIL FIELD, POTWAR SUB BASIN, PAKISTAN

SYED ABDUL QUDDUS

01-262191-009

A thesis submitted in fulfilment of the
requirements for the award of degree of
Master of Science (Geology)

Department of Earth and Environmental Sciences

BAHRIA UNIVERSITY ISLAMABAD

NOVEMBER 2021

Bahria University

Department of Earth & Environmental Sciences
Islamabad Campus, Islamabad

Dated: 15/12/2021

<u>C e r t i f i c a t e</u>

A thesis submitted by **Mr. Syed Abdul Quddus** to the Department of Earth & Environmental Sciences, Bahria University, Islamabad in partial fulfillment of the requirements for the degree of **Masters in Geology** (Session **2019-2021**).

Committee Member	Name	Signature
Supervisor	Mr. Saqib Mehmood	
Co-Supervisor	Dr. Samina Jahandad	
Internal Examiner	Mr. Tausif Ahmad	
External Examiner	Mr. Syed Habib Shah	
Post Graduate Coordinator	Dr. Muhsan Ehsan	
Head of Department (E&ES)	Dr. Said Akbar Khan	

Thesis Completion Certificate

Scholar's Name:＿＿＿Syed Abdul Quddus＿＿＿＿＿ **Registration No**: 01-262191-009

Programmed of Study:＿MS GEOLOGY

Thesis Title: "GEOCHEMICAL CHARACTERIZATION OF RESERVOIR FLUIDS FOR CONNECTIVITY AND ALTERATIONS, ADHI OIL FIELD POTWAR SUB BASIN PAKISTAN"

It is to certify that the above scholar's thesis has been completed to my satisfaction and, to my belief, its standard is appropriate for submission for examination. I have also conducted plagiarism test of this thesis using HEC prescribed software and found similarity index ＿% that is within the permissible limit set by the HEC for the MS degree thesis. I have also found the thesis in a format recognized by the BU for the MS thesis.

Principal Supervisor's Signature: ＿＿＿＿＿＿＿＿＿＿

Date: November 12, 2021

Name: Mr. Saqib Mehmood

Author's Declaration

I, <u>Syed Abdul Quddus</u> hereby state that my MS thesis titled

<u>"GEOCHEMICAL CHARACTERIZATION OF RESERVOIR FLUIDS FOR CONNECTIVITY AND ALTERATIONS, ADHI OIL FIELD POTWAR SUB BASIN PAKISTAN"</u>

is my own work and has not been submitted previously by me for taking any degree from this university, <u>BAHRIA UNIVERSITY ISLAMABAD</u> or anywhere else in the country/world.

At any time if my statement is found to be incorrect even after my graduation, the University has the right to withdraw/cancel my MS degree.

Name of scholar<u>: Syed Abdul Quddus</u>

Date: <u>November 12, 2021</u>

PLAGIARISM UNDERTAKING

I, solemnly declare that research work presented in the thesis titled "GEOCHEMICAL CHARACTERIZATION OF RESERVOIR FLUIDS FOR CONNECTIVITY AND ALTERATIONS, ADHI OIL FIELD POTWAR SUB BASIN PAKISTAN"

is solely my research work with no significant contribution from any other person. Small contribution / help wherever taken has been duly acknowledged and that complete thesis has been written by me.

I understand the zero-tolerance policy of the HEC and Bahria University towards plagiarism. Therefore, I as an Author of the above titled thesis declare that no portion of my thesis has been plagiarized and any material used as reference is properly referred / cited.

I undertake that if I am found guilty of any formal plagiarism in the above titled thesis even after award of PhD degree, the university reserves the right to withdraw / revoke my PhD degree and that HEC and the University has the right to publish my name on the HEC / University website on which names of scholars are placed who submitted plagiarized thesis.

Scholar / Author's Sign: _____

Name of the Scholar: <u>Syed Abdul Quddus</u>

Dedication

To my beloved Parents and Teachers.

ACKNOWLEDGEMENT

ABSTRACT

Potwar Sub-Basin is a Himalayan foreland fold and thrust belt in the Upper Indus Basin of Northern Pakistan. The Potwar Sub Basin is Pakistan's traditional oil-producing region, the basin has various formations that are essential for oil and gas development in the region, and it is one of Pakistan's most productive hydrocarbon-bearing sedimentary Basins. The Salt Range Formation, Khewra Sandstone, and Patala Formation are all probable source rocks in the Adhi oil field, whereas the reservoir rocks are Khewra Sandstone, Tobra Formation, and Sakesar Limestone. Due to the mismatch of source and depositional environments of organic matter, biomarkers and bulk stable isotopes were previously utilized to evaluate oils in the Potwar Basin of Pakistan. Saturated and Aromatic biomarker distributions were used to classify crude oils from the Potwar Basin, and the results were previously published but we know very little about the source potential and secondary alterations based on Light hydrocarbons characterization of Potwar Sub Basin. The geochemical characterization of Light hydrocarbons of Adhi Oil Field oil samples and their correlation is carried out using Thompson's (1983) and Mango's (1994) parameters. These parameters were used for the assessment of thermal maturity, organic input, source rock identification and secondary alterations. Five oil samples (A-10, A-11, A-15, A-16, A-17) of Adhi oil Field were studied for geochemical characterization. The parameter used for thermal maturity (Thompson's 1983) revealed that the oil samples are normal oils except the sample A-11 which is Mature. The source related parameters indicates that oil samples have the same terrigenous source for hydrocarbons. The secondary alterations assessment parameters showed that none of the oil sample is biodegraded. The Aromaticity versus Paraffinicity and C_7 oil correlation star diagram represent that the oil samples are slightly altered by Evaporative Fractionation.

Table of Contents

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

OM	Organic Matter
nC_5	n-pentane
nC_7	n-heptane
C_7OCSD	C_7 oil correlation star diagram
C_7OTCSD	C_7 oil transformation correlation star diagram
TOL	Toluene
Benz	Benzene
GC	Gas Chromatography
H	Heptane Ratio
I	Iso-heptane Ratio
2MH	2-Methylhexane
3MH	3-Methylhexane
Ma	Million years
OGDCL	Oil and Gas Development Company Limited
PPL	Pakistan Petroleum Limited
POL	Pakistan Oil fields Limited

CHAPTER 1

INTRODUCTION

Potwar Sub-Basin is a Himalayan foreland folds and thrust belt in the Upper Indus Basin of Northern Pakistan. The Potwar Sub Basin is Pakistan's traditional oil-producing region, where Attock Oil Company discovered the first oil from Miocene sands at Khaur-1 in 1915. (Kazmi and Jan 1997). The basin has various formations that are essential for oil and gas development in the region, and it is one of Pakistan's most productive hydrocarbon-bearing sedimentary basins (Kadri, 1995).

The reservoir units in the Potwar sub-basin are Precambrian to Tertiary in age. The principal source of hydrocarbons in the area has been assumed to be the Paleocene Patala Formation, however other areas of petroleum systems might also come up with separate potential source rocks in that basin (Wandrey et al., 2004; Fazeelat et al., 2010). The Precambrian Salt Range Formation, which contains clastic, carbonate, and evaporites dominated strata, is the earliest possible source rock. Similarly, the Tobra, Sardhai, and Chhidru formations in the Permian age have substantially higher TOC values and may perhaps represent source rocks (Quadri and Quadri, 1997).

The research area The Salt Range Formation, Khewra Sandstone, and Patala Formation are all probable source rocks in the Adhi field, whereas the reservoir rocks are Khewra Sandstone, Tobra Formation, and Sakesar Limestone (Siddiqui, Badar et al. 2003).

The application of hydrocarbon geochemical parameters is critical in petroleum exploration. The biomarkers are helpful in determining the organic matter input to sediments and the source rocks from which oil is extracted. Some biomarkers are sensitive thermal maturity indicators, while others can be used to infer the lithology, depositional environment, and chemical composition of petroleum source rocks. Their use in the petroleum sector has aided oil and gas development, particularly in frontier or underexplored basins, by giving critical information regarding crude oil origins and prospective migration paths.

1.1. Location of Study Area

The Adhi field, located between 33° 14' 14" N latitude and 73° 15' 78" E longitude, is a combined project among Pakistan Petroleum Limited (PPL), Oil and Gas Development Company Limited (OGDCL), and Pakistan Oil fields Limited (POL). PPL operates a mining lease in eastern Potwar, some 40 kilometers south of Islamabad. Kal field in the south, Missa Keswal field in the east, Bhangli field in the north, and Turkwal field in the west define the study area (Fig 1.1). Khewra Sandstone, Tobra Formation, and Sakesar Limestone are reservoir rocks in the research area. (Siddiqui, Badar, et al, 2003)
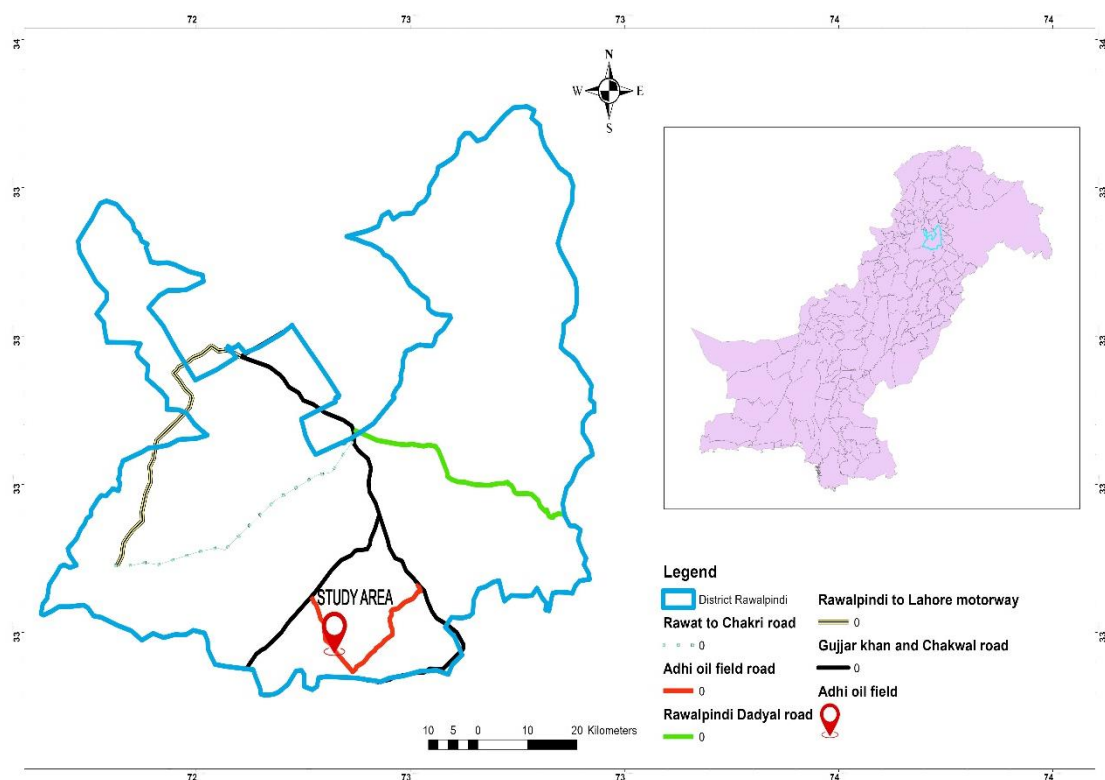
Figure 1. 1: Structural map of the Kohat-Potwar plateau modified after (Petroconsultants, 1996).

1.2. Previous Work

Due to the mismatch of source and depositional environments of organic matter, biomarkers and bulk stable isotopes were previously utilized to evaluate oils in the Potwar Basin (Upper Indus) of Pakistan. (OM) (Asif et al., 2012).

The Potwar Basin is one of Pakistan's most prolific petroliferous provinces, with exploration activity dating back more than a century. Even though for decades debate

on Potwar Basin has been going on (Ahmed and Alam, 2007; Fazeelat et al., 2009, 2011), until recently, the geochemical information of source rocks and crude oils had not been adequately explored.

Saturated and aromatic biomarker distributions were used to classify crude oils from the Potwar Basin, and the results were previously published (Asif et al., 2008). The impacts of biodegradation on hydrocarbons (HCs) and stable H isotopes can be seen in some of these crude oils (Asif et al., 2009). Distributions of stable isotopes and biomarkers carried out in earlier portion of this study to indicate that the basin contains three different types of crude oil, on the basis of differences in the source of organic matter (OM) and the environment of deposition (Asif et al., 2011). In group (A), source rocks contain terrigenous OM and were deposited in a strongly deltaic depositional setting.

In group (B), oils are derived from marine organic matter which was thought to be deposit in a sub-oxic setting of deposition, and only a few of them are biodegradable up to levels 2–3, making them denser (low API) than that of other basin oils. In group (C), comprises of marine/algal OM source rocks deposited in a marine oxic depositional setting with limited terrestrial organic input, and displaying no signs of biodegradation. It's important to note that biodegradation has never been related to this classification scheme, despite the fact that biodegradation affects several group B oils (Asif et al., 2009).

The distribution and relative levels of heterocyclic and polycyclic aromatic hydrocarbons in crude oils from the Potwar Basin back up the prior classification A, B and C.

Group (A) oil has a highly oxic environment for deposition as well as an enrichment in terrestrial organic materials. The abundance of methyl isomers of naphthalene and phenanthrene indicates gymnosperm input. Plant resin contributions to group A oil's organic matter are revealed by diagnostic aromatic biomarkers such as retene, methyl retenes, and cadalene.

Marine oils comprise Groups B and Group C. Organic matter (OM) is divided into two groups based on differences in source and depositional settings. The deltaic depositional setting and terrestrial organic source can be linked to the abundance of

alkyl-fluorenes and alkyl-dibenzofurans, whereas heterocyclic aromatic hydrocarbons are strong indications for depositional habitats. Source rocks produced under marine sub-oxic depositional conditions are rich in S-containing heterocyclic aromatic hydrocarbons, whereas alkyl-fluorenes and S heterocyclic compounds are abundant in marine oxic oils. Potwar Basin oils were clearly divided into three groups based on the distribution of tri-aromatic and methyl tri-aromatic steroids. The virtual abundance and unusual dispersal of these chemicals in Potwar Basin are influenced by their depositional environment and source. The thermal maturity of oils in Potwar Basin reveals a peak for late oil generation window based on biomarkers, aromatic hydrocarbons, and tri-aromatic steroids maturity indicators (Asif et al., 2012).

The focus of the proposed research is to critically investigate the geochemical characterization for secondary alterations assessment and their correlations using light hydrocarbons of Adhi Oil Field Potwar Sub Basin Pakistan.

1.3.   Generation of organic matter

Organic matter is generated by living organisms, either directly or indirectly. Basically, the amount of biological content is proportional to the source rock's potential. Photosynthesis is a process that converts light energy into chemical energy. Because of the favorable conditions, organic-rich sediments prefer to settle on the continental shelf (Tissot and Welte, 1984).

Zooplanktons, phytoplankton, bacteria, and higher plants are the primary sources of organic matter in sediments. Carbohydrate, protein, lipid, and lignin are all components of living creatures. The formation of biogenic hydrocarbons occurs at various depths, pressures, and temperatures (Fig 1.2). During the early stages of diagenesis, microbial methane is produced by microbial decomposition in shallow sediments (Rice et al, 1981; Tissot et al, 1984). The thermogenic methane is produced from deeper source rock with a greater temperature (Davis, 1992; Floodgate et al, 1992). As the depth of burial increases over time, the maturity of organic-rich source rock increases, as does the potential for hydrocarbon formation (Floodgate et al., 1992).

1.4. Origin of oil and its composition

According to Alfred Treibs, the porphyrin discovered in crude oils has a structure similar to chlorophyll, a green pigment found in cyanobacteria and various plants, implying that oil was produced by overburden pressure and rising temperatures on plants and algae in sediments (Prashnowsky,1980). Crude oil comprises a wide range of elements with varying shapes, sizes, molecular weights, and solubilities. Crude oil is made from organic matter, which is found in sedimentary rocks and is converted to oil and gas by thermal alteration. Crude oil is made up of organic molecules with varying molecular weights, sizes, shapes, compositions, and solubilities. Crude oil is primarily made up of carbon and hydrogen in proportions of 85 percent and 13%, respectively, and this fraction is referred to as hydrocarbon. In crude oil, there is a small nonhydrocarbon fraction (2%) made up of N, S, O molecules, trace elements, and metal porphyrin. Alkanes, aromatics, and naphthenes make up the hydrocarbon proportions of oil, whereas asphaltenes and resins make up the non-hydrocarbon parts.

1.5. Light Hydrocarbons

Light hydrocarbons are major constituents of oil and gas and have a wide geochemical relevance (Yu et al., 2014), however there is currently no commonly agreed definition for them. Dai Jinxing defined light hydrocarbons as gasoline hydrocarbons with a boiling range of less than 200°C, or C5–10 alkanes, which include certain gas-associated condensate oil and light oil (Dai,1993a). Light hydrocarbons are defined by Guo et al. (2009), Mango (1997), Odden (1999), and Shen et al. (2011) as C4–7, C1–9, C1–13, andC5–10 alkanes, respectively
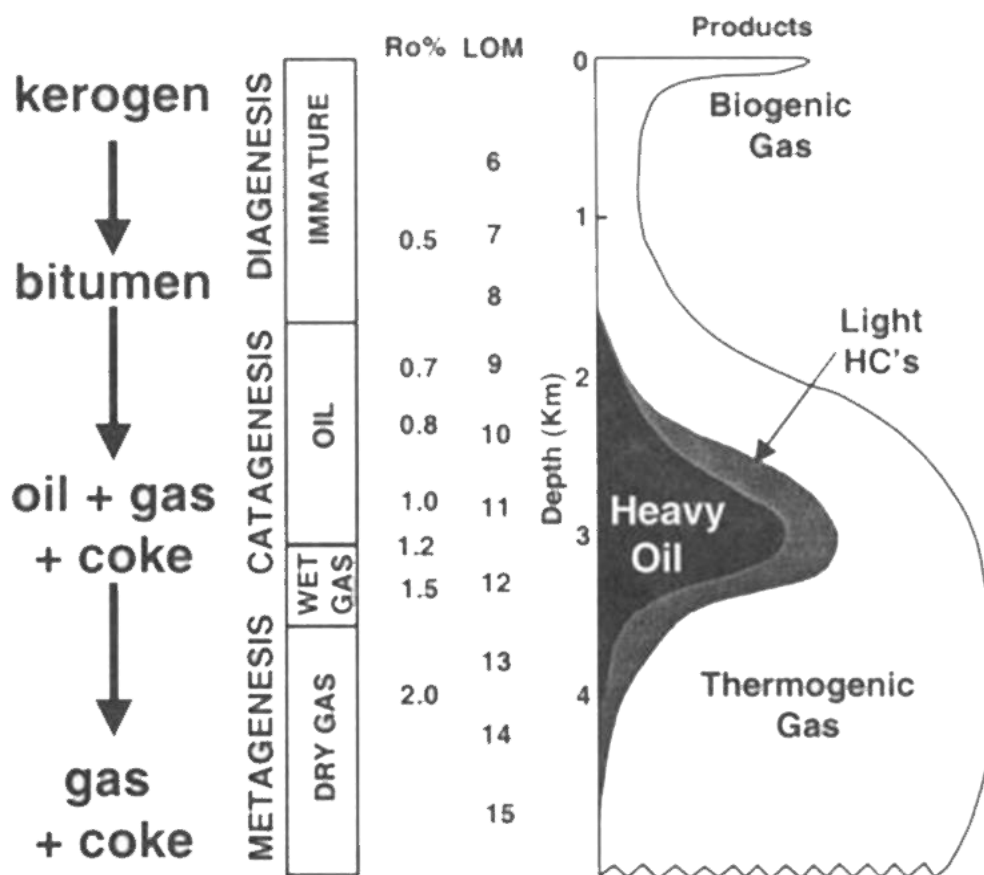
Figure 1. 2: Kerogen is converted to liquid and gaseous hydrocarbons through thermal maturation. At top of oil window, vitrinite reflectance, typical depth, and level of maturity (LOM) at which these reactions occur are displayed.

In source rock an organic material type determines the light hydrocarbon composition at first. Normal alkanes are abundant in kerogens formed from dasycladales remnants, so those found in profound lakes deposits and marine carbonates. Kerogens derived from greater land plant waste, which are coal and fluvial shales, have higher cycloparaffin and aromatic hydrocarbon concentrations. The thermal maturity of basic oils is proportional to the number of light hydrocarbons present. Light hydrocarbons may make up less than 15% of low-maturity, early ejected oils, Marine oils in the mid-oil window typically include 25 to 40 percent light hydrocarbons, Light hydrocarbons make up nearly 100 percent of high-maturity or phase-separated condensates. The heat breakdown of high molecular weight molecules into tiny hydrocarbons causes these alterations. Observations of wellbore strata, oil and condensate because of a number of thermal stresses are the basis of given ratios, whether in source or reservoir rocks. Others are built on assumptions about light hydrocarbon production. In common, ratios for maturation compare or

express putative reactant-product interactions between distinct thermally stable isomers (or sets of isomers).

Secondary physical, chemical, and/or microbiological manners can substantially modify the volume and content of light hydrocarbons. Course where oil undertakes phase parting introducing methane to reservoir is evaporation fractionation and water-washing or aqueous fractionation are examples of physical approaches. In basins with largely perpendicular migration through faults and salt-and mud-diapirs, phase separation mechanisms are especially essential. TSR, a chemical process in which sulphate oxidizes hydrocarbons to produce H2S, CO2, and pyrobitumen, can significantly alter the molecular and isotopic light hydrocarbon ratios. Biodegraded oils (common in reservoirs with temperatures below 80°C) have a distinct light hydrocarbon distribution that is depleted in these molecules because microorganisms selectively catabolize regular and branched paraffin hydrocarbons.

Correlating oils and condensates has been done for many years using light hydrocarbon compositions and isotopic ratios. Light H/C are distinguished genetically related similar to biomarkers. This information is essential for predicting migration paths within the petroleum system. Because they are quickly impacted by secondary processes, light hydrocarbons have capability of high-resolution oil-oil correlation, which is utilized to indicate the continuity of reservoir (Clifford C. Walters 1, Gary H. Isaksen and Kenneth E. 2003).

1.6. Soluble organic matter (Biomarkers)

Resins, saturated, aromatic hydrocarbons, and asphaltenes, collectively known as bitumen, make up soluble organic matter, which is a viscous mixture. Biomarkers are organic substances that are inherited from live organisms and preserve their structure with slight alterations, such as terpanes and steranes. In the discipline of analytical geochemistry, many novel techniques were developed in the 1960s. Gas chromatography mass spectrometry, in combination with GC and a multiple ion detector, was the most essential technology for studying small components in hydrocarbons. Biomarkers were coined by Eglinton and Calvin in 1967 to describe these tiny components (Philip. 2003).

1.7. Thermal Maturity

Biomarkers can also be used to determine the oil's maturity and provenance. Kimble (1972) discovered that differing levels of thermal maturity in shale resulted in varied results for specific parameters. Tricyclic terpanes, TS/ (TS+TM), Diasteranes/ (Diasteranes + Regular steranes), and oleanane are a few of the thermal maturity parameters. With specific source input, the - isomers display comparatively low levels when the samples are immature. Another parameter that increases as the maturity level of the 22S epimer grows is 22S/(22S+22R) (Philip, 2003).

Rice et al. (1981) classified the stages of hydrocarbon maturation as diagenesis, catagenesis, and metagenesis (Fig 1.3). The "golden zone" is defined as the temperature range between 60- and 120-degrees Fahrenheit, which is ideal for hydrocarbon production (Buller et al., 2005; Nadeau, 2011).
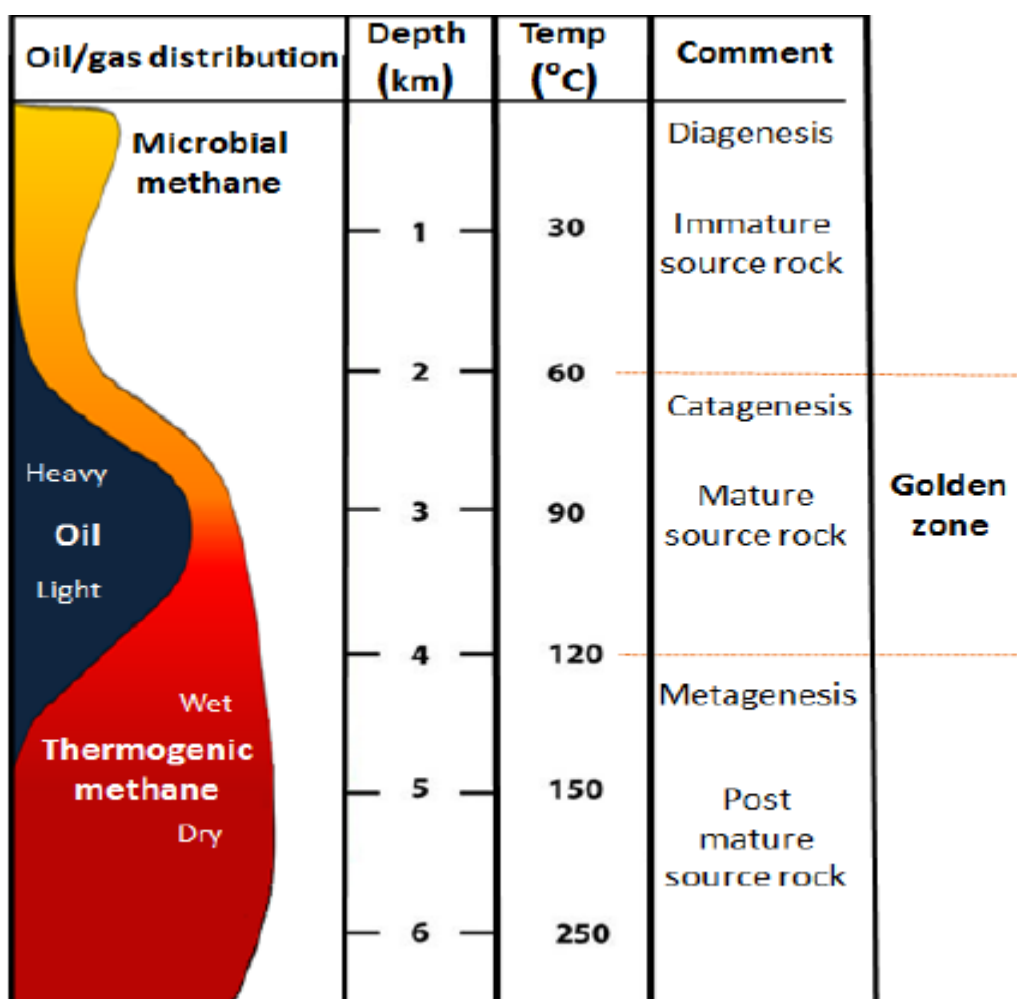
Figure 1. 3: Microbial gas, oil, and thermogenic gas all have different temperature conditions.
Modified from: (Earle, 2015; Perrodon, 1983; Rice et al, 1981)

1.8. Biodegradation

Connan first discovered variations in the crude oil due to biodegradation in 1984. The most biodegradable alkanes are linear alkanes, which get more complicated as the linear alkane structure decreases. N-alkanes are the most sensitive to biodegradation, followed by iso-alkanes, and finally cyclo-alkanes; bulky biomarkers are biodegraded at a later stage, and loss of these alkanes is represented in chromatogram by a shift in the base line known as unresolved complex mixture (UCM).

1.9. Migration

Lighter molecules travel faster than complex molecules, oil that has travelled a long distance will include a high proportion of lighter hydrocarbons. Isotopic shifts in oil occur due to migration, according to Silverman (1965). Any change in oil values could be attributable to migration, primarily due to poor preservation of organic matter. The maturity related steranes parameters are / (+) and 20S/ (20S+20R). According to Philip (2003), linear benzo(a)carbazole migrates more faster than nonlinear benzo(c)carbazole, therefore any change in carbazole isomer ratio is due to migration.

1.10. Objectives

The objectives of the study are following:

a) Evaluation of thermal maturity of oil.
b) Assessment of secondary alterations/transformations in reservoir.
c) Assessment of reservoir connectivity within an oilfield.

CHAPTER 2

REGIONAL GEOLOGY AND TECTONICS

The Potwar Sub Basin lies about 100 kilometers north of the Salt Range. It symbolizes the southern boundary of the Himalayan collision zone. About 50-65 Ma ago, the Indian and Eurasian Plates collided, resulting in the orogeny of Himalayas. This mountainous belt is about 2500 km long. It is the most impressive and youngest product of continental-continental collision (Gansser, 1964; & Fraser et al, 2001). About 130 million years ago, the Indian Plate split from Gondwana and began its northward voyage (Johnsone et al, 1976), followed by subsequent recession of Neo-Tethys in between Indian and Eurasian Plates at that time (McKanzie & Sclater, 1976). This movement resulted in subduction of Neo-Tethys oceanic plate forming Nuristan, Kandahar and Kohistan-Ladakh arcs (Traloar and Izat, 1993 & Searlle, 1991). That island arc formation lasted about 40 Ma (Peterson et al, 1985) and caused cessation of back arc basin. Andean type continental margin formed as Kohistan and Ladakh island arc then collided with Eurasian plate (Coward et al, 1986). According to Powall, (1979). Neo-Tethys continuous subduction beneath the Kohistan and Ladakh Island Arc devoured the prominent margin of Indian Plate and it collided with the remaining part of Island Arc.

The boundary of Indian plate with Kohistan Island arc is Main Mantle Thrust (MMT) and thrust fault in between Kohistan Island Arc and Eurasian plate is Main Karakorum Thrust (MKT) (Taherkheli et al., 1979). Regions of NW Himalayan folds and thrusts belts is bounded by MMT and SRT from north and south and its westward extension of Marwat, Surghar, Manzai and Bhittani ranges. Hazara-Kashmir Syntaxis and Nanga Parbat Harmosh marks the NE frontier. Southeast directed thrusts and strike-slip faults mark the western boundary (Kazmi and Jan 1997).
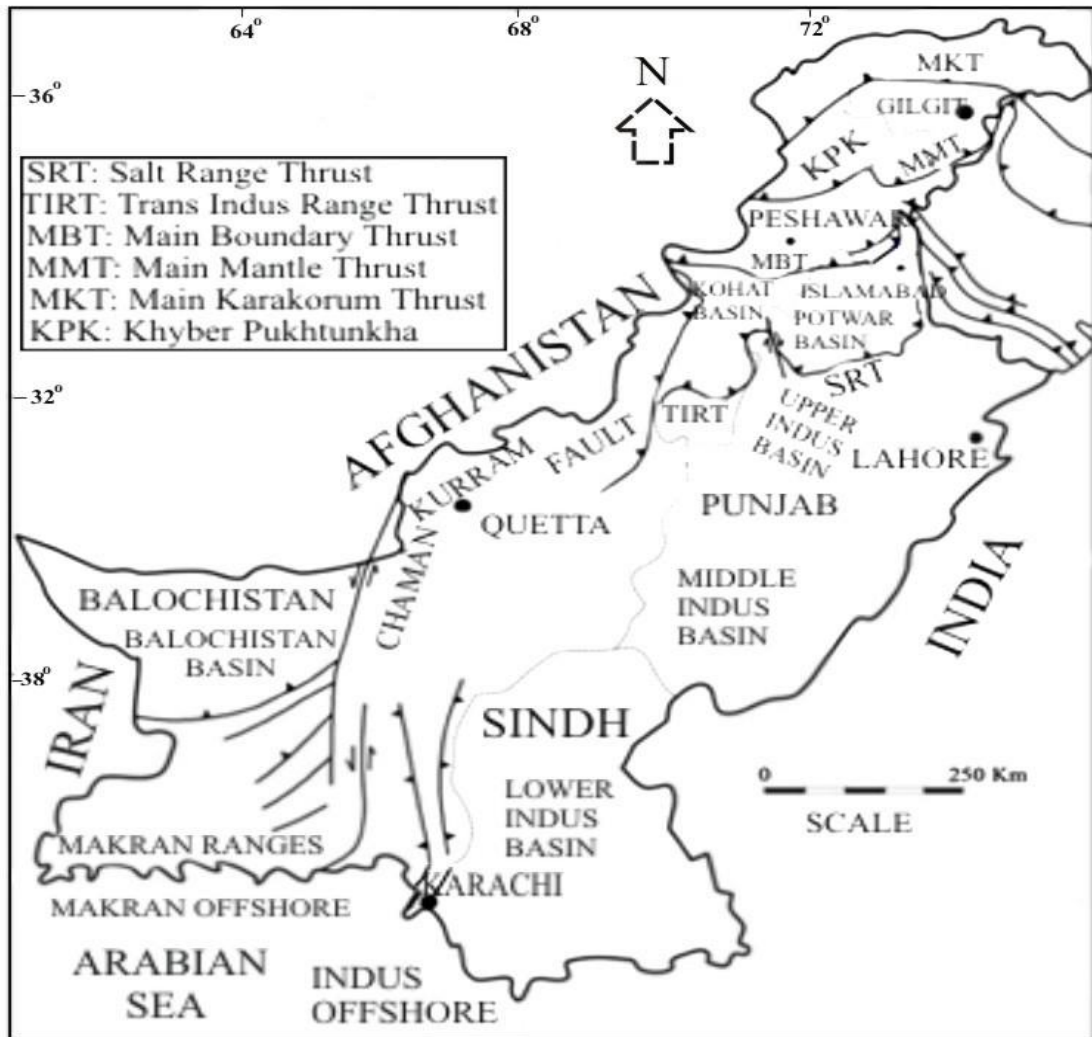
Figure 2. 1: Tectonic map of Pakistan (Kazmi and Rana, 1982)

Based on different orogenic history, tectonic features and geological environments, Pakistan has been sub-divided into different tectonic zones; Himalayan fold and thrust belt, Kohistan-Ladakh magmatic arc, Karakoram block, Indus platform and foredeep, Chagai magmatic arc, Kakar-Khorasan flysch basin and Makran accretionary zone, Baluchistan fold and thrust belt and Pakistan offshore. Himalayas are also subdivided into different tectonic domains based on distinctive stratigraphy and physiography (Kadri, 1995). Figure 2.1 shows the regional tectonics of Pakistan.

2.1 Geology and Tectonics of Kohat-Potwar Fold and Thrust Belt

Collision of Eurasian and Indian plate made a complex structure in Potwar sub basin (Farah, Lawrence et al. 1984). Himalayas are outstandingly over thrusted at north as well northeast because of the collision due to successive detachments of deep surfaces from the Cambrian, resulting in a sequence of faulted and normal anticlines.

Himalaya's uplift resulted in fast deposition of sediments in the Indus Basin and resulted in thick shale and clay sequence of Murree Formation. Indus basin partitioned in three parts namely (Upper Indus basin, Central and Lower Indus basin) (Zaighum and Mallick, 2000). Kohat and Potwar basin separated by Indus River and are part of Upper Indus Basin (Paracha, 2000; Hylland et al, 1988) (Fig2.2).

Potwar sub basin and Kohat sub basin are two sub-divisions of the Upper Indus basin. In Pakistan, In Pakistan, the Potwar sub-basin is situated on the northern edge of the Indian plate. Sargodha High and Jacobabad-Khairpur are arbitrarily bounded by the Upper Indus basin. Thin Eocene calcareous-siliciclastic sediments from the Indian plate and thick Miocene-Pliocene Molasse deposits from the Indus Foredeep fill the basin, followed by thick Miocene-Pliocene Molasse sediments from the Indus Foreland basin. The Potwar folded region is reflected a favorable region for hydrocarbon occurrence due to its structural design. Hydrocarbon has been discovered in a number of reservoirs in this subbasin, which has a number of structural leads. A map of regional temporal structure for the Base Miocene level was created to recognize the structural flair, fault natures, decollement stages, and tectonics for deeper strata that are conformable (Aamir, Siddiqui, and others, 2005).
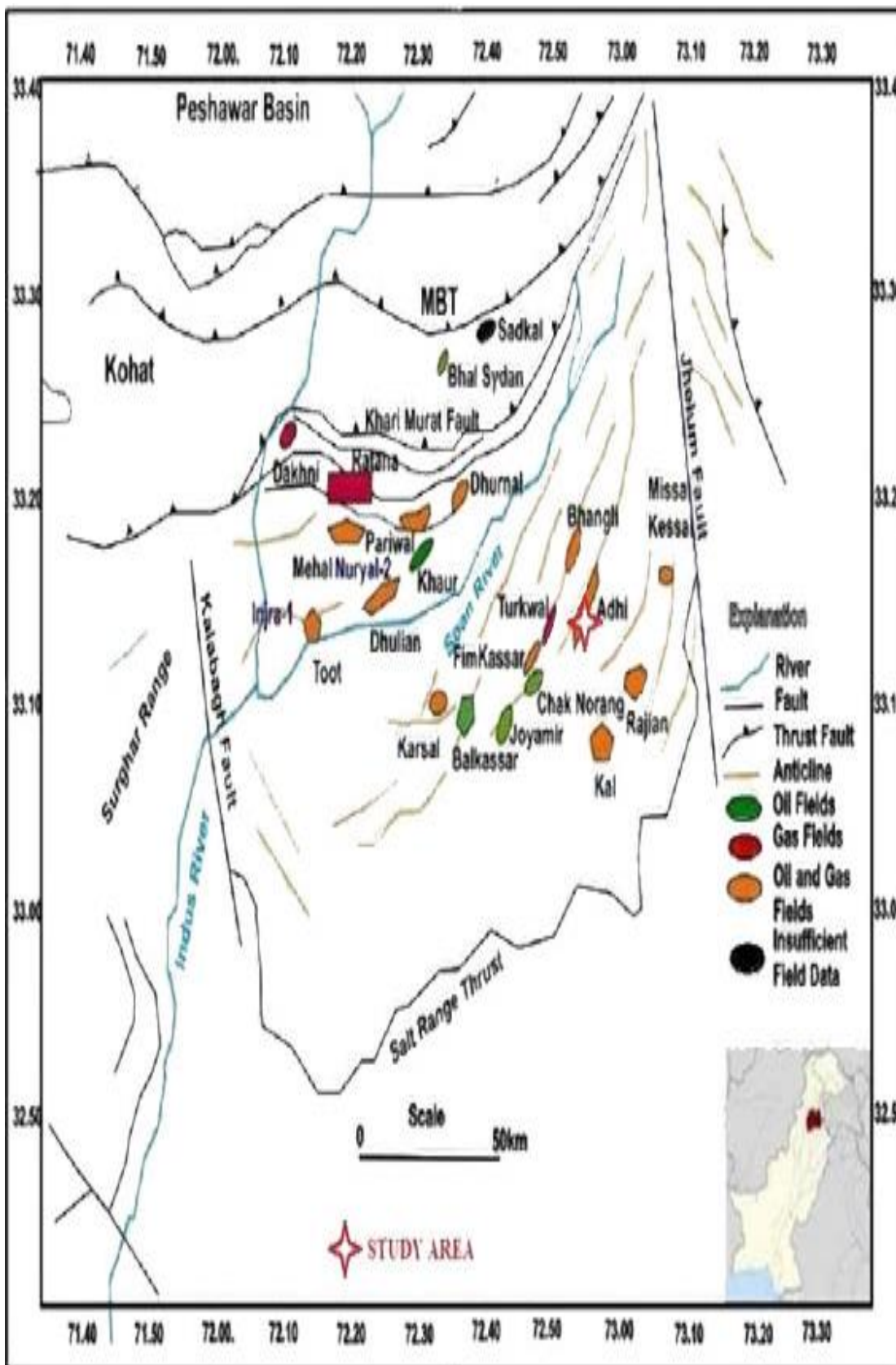
Figure 2. 2: Regional Tectonic map of the Potwar Sub Basin, showing the study area (Raza,1992)

2.2   Stratigraphic Sequence

The Potwar Sub Basin's geologic succession spans to the depth of roughly 6100m, with the oldest rocks being the Infra-Cambrian Salt Range Formation, and the most recent rocks being the Siwaliks Group (Fig 2.3). The sedimentation in this area from Paleozoic to Mesozoic was mostly driven by the Sargodha High's repetitive uplifting and tilting. This activity could have induced depositional cracks and erosion, the Pre-Paleogene series erosional wedge edges that may be found all over the basin are the result of this process. Earliest deposits are Infra-Cambrian evaporates, which have helped to loosen most of the basin's compressional movement (Cheema 1977).

In a coastal to shallow marine setting, early to middle Cambrian clastic rocks with thicknesses up to 610 m were deposited. Permian succession has a thickness of around 762 meters and are mostly made up of glacial, fluvial, and estuary clastic and shallow marine carbonates. Shallow water sediments can be found all the way up to the Late Cretaceous (Fatmi and AN 1973). The erosional wedges are thought to have formed as a result of a massive uplift that stripped away Cretaceous through Permian strata stretching east to west throughout the basin. It is thought that this occurred near the end of the Cretaceous period. The wedges were overstepped by a marine incursion in the early Paleocene, producing in thick deposits of Paleocene and Eocene superficial marine carbonates above the whole area (+1100m). These vast and massive carbonates are basin's primary oil accumulation reservoir.

The Himalayan orogenic process elevated and distorted these pre-existing rocks in the late Eocene (Gee and Gee 1989). A continuous succession of molasses in the organic foredeep quickly filled the Potwar Basin. Over-pressured molasse deposits are across the basin, trapping a major amount of the sediments of Pre-Eocene in oil window and acting as a large over-pressured unit (Shah 1977).

QUAT	PLEIS		Lithology	Source	Reservoir	Seal
TERTIARY	PLIO-CENE	Siwalik Group				🔵
	MIOCENE	Rawalpindi Group				
	EOCENE	Chorgali Fm			🟢	🔵
		Sakesar Lst			🟢	
		Nammal Fm				
	PALEOCENE	Patala Fm		🔴		
		Lockhart Fm				
		Hangu Fm				
CRETACEOUS	E	Lumshiwal Fm				
		Chichali Fm		🔴		
	L					
JURASSIC	M	Samana Suk Fm				
		Shinawri Fm				
	E	Datta Fm			🟢	🔵
TRIASSIC	L	Kingriali Fm				
	M	Tredian Fm				
	E	Mianwali Fm				
PERMIAN	LATE	Chhidru Fm				
		Wargal Fm				
		Amb Fm				
	EARLY	Sardhai Fm		🔴		
		Warccha Fm			🟢	
		Dandot Fm				
		Tobra Fm			🟢	
CAMBRIAN		Baghanwala Fm				
		Jutana Fm				
		Kussak Fm				
		Khewra Sandstone			🟢	
PRE-CAMBRIAN		Salt Range Fm		🔴		

Figure 2. 3: Generalized stratigraphic column of Potwar sub-basin, with possible source, reservoir and seal rocks (Fatmi & AN, 1973)

2.3 Petroleum system of Potwar Basin

Petroleum system comprises of six components,

 (1) Source rock

(2) Reservoir rock

(3) Trap

(4) Seal rock

(5) Time

(6) Generation and migration of oil from source rock

In the Kohat-Potwar region generally there is complete depositional record from Pre Cambrian to recent. There is thick deposit of carbonates in the Salt Range Formation overlain by evaporites. There is potential of possible source rock and oil shows have noticed in the evaporites section (Iqbal and Shah, 1980). The Salt Range Formation is overlain by thick deposits of marine shales and massive sandstones of Cambrian sequence (Jehlum group), which are reservoir at Adhi, Chak Naurang, Missa Keswal and Rajien Fields (Khan et al., 1986). The shelf carbonate sequence of Permian Wargal Formation has produced oil in Dhurnal oil field. Dhulian field in the northwest of Potwar Sub-Basin is producing oil and gas from Jurassic Datta Formation. The Paleocene-Eocene sequence (Patala, Nammal, Sakesar) has been very productive in the basin of about eight oil fields are producing from Sakesar Formation. In the Kohat-Potwar region there is repetition of strata, source, and reservoir rocks due to extensive folding and faulting causes oil from different sources to mix with each other.

2.4 Source rocks

There are several potential source rocks in the Potwar Sub-Basin includes Salt Range Formation (Pre Cambrian), Wargal, Chhidru Formation (Permian), Lockhart Formation (Paleocene), Patala Formation (Eocene) (Quadri and Quadri, 1996). TOC range of Patala Formation is reported at 0.5% to 3.5% averaging 1.4% with mixed type II and III kerogen, TOC values of Wargal and Lockhart Formations are 1 and 1.4% respectively (Jaswal et al., 1997).

2.5 Maturation

Thermal maturity of source rocks in Kohat-Potwar region varies from 0.3 to more than 1.6% (Wandrey et al., 2004). The vitrinite reflectance equivalent thermal maturity of source rocks of Tertiary sequence like Patala and Lockhart ranges from 0.62 to 1.0% in Potwar Sub Basin (OGDC, 1996). Vitrinite reflectance values ranges from 0.6 to 1.1% for Cretaceous rocks like Chichali and Lumshiwal, 0.5 to 0.9% for Jurassic rock like Datta and Shinwari and for Permian rocks like Wargal, Sardhai and Chhidru it ranges from 0.65 to 0.95% (Tobin and Claxton, 2000).

2.6 Generation and migration

The source rocks of Cambrian to Cretaceous age (Wargal, Sardhai, Chhidru, Datta and Shinwari Formations) most likely started generation and migration of petroleum from Late Cretaceous age, for source rocks earlier than Late Cretaceous its generation and migration began from Pliocene to Recent age (OGDC, 1996). In Potwar-Kohat region due to extensive faulting and assembling of multiple source and reservoirs rocks the migration of oil in the region is chiefly for short distances vertically up dip through faults and fractures into the adjacent reservoir rocks (Wandrey et al., 2004).

2.7 Reservoir rock

In the Potwar Sub-Basin there are several reservoir rocks, but majority of production comes from Eocene carbonates. Oil in the region has been produced from Khewra, Kussak and Jutana Formation of Cambrian age, Tobra, Amb and Wargal Formations of Permian age, Datta Formation (Jurassic), Lumshiwal (Cretaceous), Paleocene Formations of Lockhart and Patala and Eocene age Formations of Nammal, Bhadrar, Chorgali and Sakesar, and Murree Formation (Miocene) (Petroconsultants, 1996). Approximately 60% of oil reservoirs are carbonates and porosity in the carbonate rocks in the area is mainly due to tectonically induced fractures on strike with structural trends (Jaswal et al., 1997).

2.8 Traps and seals

In Kohat-Potwar region, primarily two styles of traps have been identified up to date which are overturned faulted anticlines and fault block traps like shales of Datta Shinwari and Patala Formations or pop-up structures of Salt Range Formation the most recent trap formation event started at approximately 5 and 2 Ma (Jaswal et al., 1997). In the basin the strike of the Acticlinal features is approximately parallel to the plate-collision zone generally oriented in east-northeast and south-southwest direction. Shale and clays and interbedded shales of Datta and Patala formation and rock sequence of Siwalik and Rawalpindi group act as seals in the basin (Wandrey et al., 2004).

2.9 Petroleum System of study area

2.9.1   Source Rocks

The Precambrian Salt Range Formation and Paleocene age Patala Formation are responsible for the hydrocarbon formation in the study area.

2.9.2   Reservoir Rocks

The Cambrian Khewra Sandstone, Permian Tobra Formation and Eocene Sakesar Carbonate's act as reservoir in the study area.

2.9.3   Seal Rocks

The shale of the Cambrian Kussak Formation, shale of Warcha/Dandot of Permian and Muree Formation of Miocene age act as seal rocks.

2.9.4   Traps

Thin-skinned tectonics created faulted anticlines, pop up, and positive floral structure over Pre-Cambrian salt, resulting in traps. The Kussak, Warcha/Dandot, and clays and shales from the Murree Formation deliver effective perpendicular and horizontal seals to reservoirs of Eocene with which they come into contact. (Shah 1977) (Figure 2.4)

AGE	FORMATION	TOPS BKB,m	SYMBOL	LITHOLOGY	
P L I O C E N E	NAGRI	315		Sandstone with interbeds of claystone	
	CHINJI	917		Red clay with gray sandstone	
M I O C E N E	KAMLIAL	969		Red to purple sandstone & clay with intra-formational conglomerates	
	MURREE	2289		Red to purple clay & ss with intra-formational & basal conglomerates	
E O C E N E	BHADRAR	2338		Limestone & Shale	**RESERVIOR**
	SAKESAR	2437		Limestone	**RESERVIOR**
	NAMMAL	2460		Limestone	
PALEOCENE	PATALA	2472		Shale	**SOURCE**
	LOCKHART	2485		Limestone & Marl	**RESERVIOR**
	HANGU	2502		Sandstone & Shale	
PERMIAN	WARCHA/ DANDOT	2548		Sandstone & Shale	
	TOBRA	2571		Conglomerates & Sand	**RESERVIOR**
CAMBRIAN	JUTANA	2615		Dolomite & Shales	
	KUSSAK	2652		Shale & Sandstone	
	KHEWRA	2778		Sandstone & Shale	**RESERVIOR**
PRE-CAMB	SALT RANGE	TD 2810		Shale, Marl & Gypsum with interbeds of anhydrite, dolomite & salt.	**SOURCE ?**

Figure 2. 4: Generalized Stratigraphy of Adhi Oil Field (Siddiqui, Badar et al. 2003)

CHAPTER 3

METHODOLOGY

Methodology includes following steps:
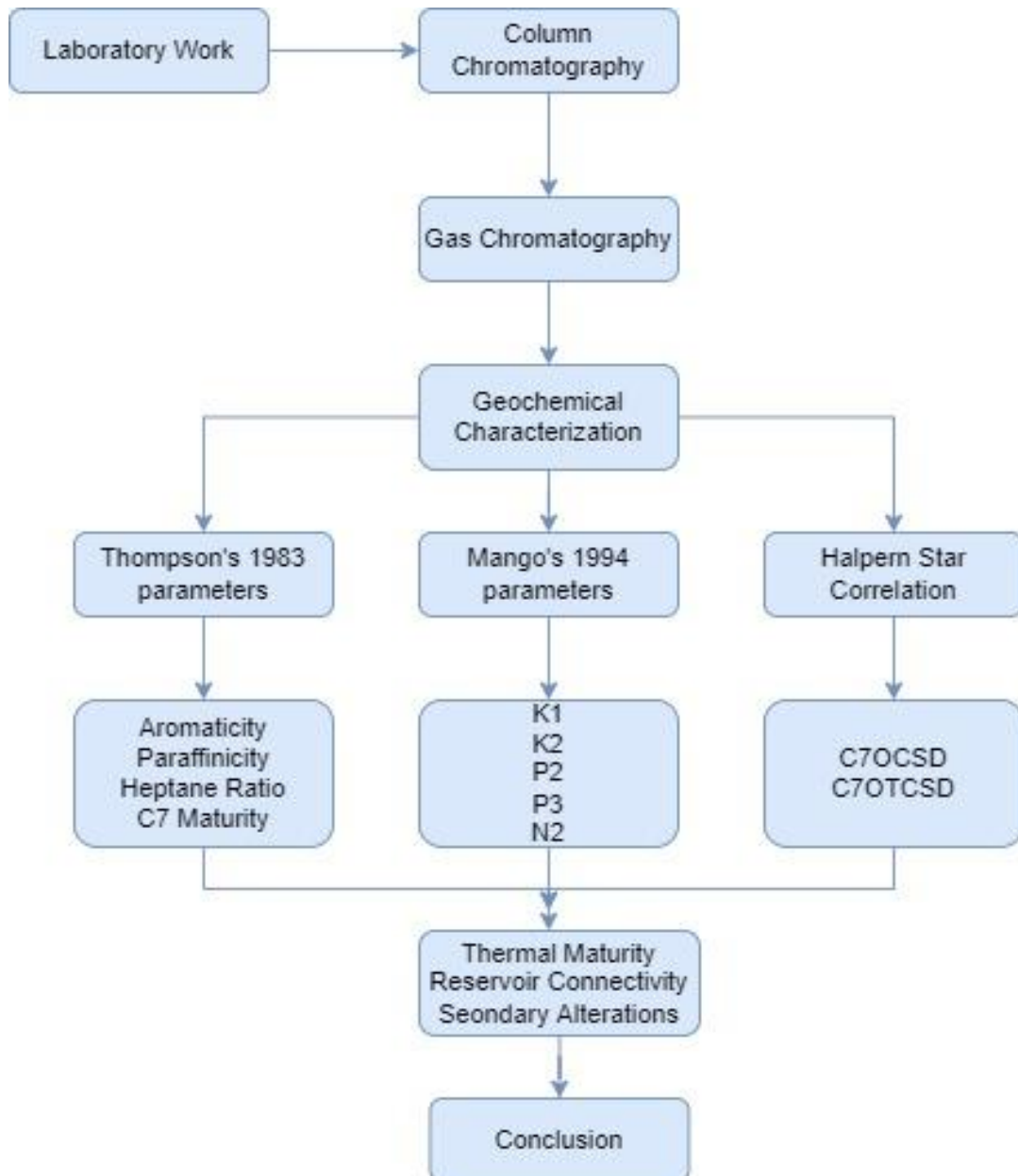
Figure 3. 1: Methodology used for geochemical characterization and transformations correlation of Light Hydrocarbons for Adhi oil field oil samples.

3.1 Laboratory work

Laboratory work comprises of the detailed geochemical analysis of oil samples.

3.1.1   Column Chromatography

Column chromatography was used to discrete the saturated and aromatic hydrocarbon portions of the oil (Figure 3.2). Columns were created by filling disposable 5.0-mL serological pipettes with gel slurries of alumina, silica-type 923 and silica-type 62. The US Geological Survey website has the summarized column preparation and oil column chromatography techniques (2004). By wringing crushed rock samples in the solvent overnight and then repeating this process until the solvent extract was clear, the rock samples were extracted with dichloromethane. At room temperature the asphaltenes were precipitated overnight using pentane. Columns were made by filling disposable serological pipettes (5.0-ml) by silica gel. Saturated hydrocarbons were fractionated with pentane with 15 mL, aromatics with 40 mL of a 90:10 pentane/dichloromethane mixture, and polars with an 87:13 chloroform/methanol mixture. A Micro mass Optima mass spectrometer linked to a Carlo Erba Model 1100 elemental analyzer was used to evaluate saturated hydrocarbon and aromatic hydrocarbon percentage d13C values. In the elemental analyzer, 0.1 mg of saturated and aromatic hydrocarbons were inserted in tin capsules and combusted at 1000°C to generate CO_2 for mass spectrometer analysis. All carbon isotope ratios are calculated using the Peedee Belemnite standard.

Figure 3. 2: Column chromatography apparatus.

3.1.2 Gas Chromatography

The whole oil analysis and saturated segments were analyzed by gas chromatography (GC-FID) by a Perkin Elmer Auto XL gas chromatography (Figure 3.3). A 100 m fused silica capillary column was used (100m × 0.25mm i.d.; 0.25μm thickness). The temperature programing was from initial temperature of 40°C that was raised up to 300°C, at ramp 4°C/min was used. Injector set at 300°C was operated in split mode for whole oil (50:1) while saturated fraction was analyzed using split less mode. Flame ionization detector (FID) for analysis of hydrocarbons was set at 310°C. Injection volume for whole oil was 0.2 µl while for saturated hydrocarbons 1 µl. Helium used as mover gas set at flow rate of 0.5mL/min.

Figure 3. 3: Gas chromatograph along with FID detector.
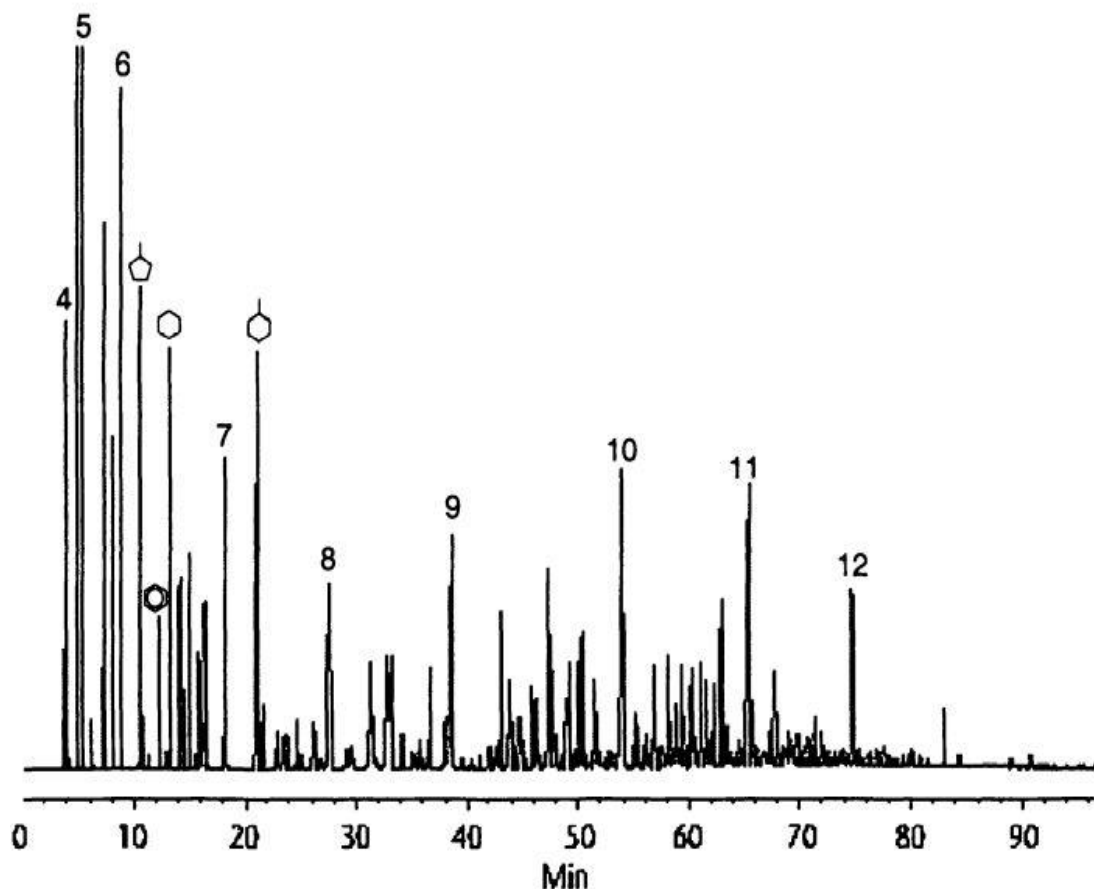
Figure 3. 4: Using ASTM 05134-98, typical crude oil chromatographic separation of C2-C9+ hydrocarbons. Normal alkanes are recognized, but their structure indicates carbon number, chosen cycloalkanes, and benzene.

The low injector temperature and high oven temperature in ASTM 05134-98 limit crude oil analysis to C10 hydrocarbons. Enhancing temperatures between 200°C to 325°C is a straightforward method change that allows separation up to -n-C35. Separations up to -n-C60 can be achieved employing on-column injection, pressure programming, and capillary columns capable of maintaining light hydrocarbon separation at temperatures as low as -400°C (Figure 3.2.2). Other non-specific, element-selective which are flame photometric and atomic emission, and specific as Fourier Transform IR and mass spectrometers replacement detectors were utilized, however flame ionization detectors are practically common in maximum methodologies.
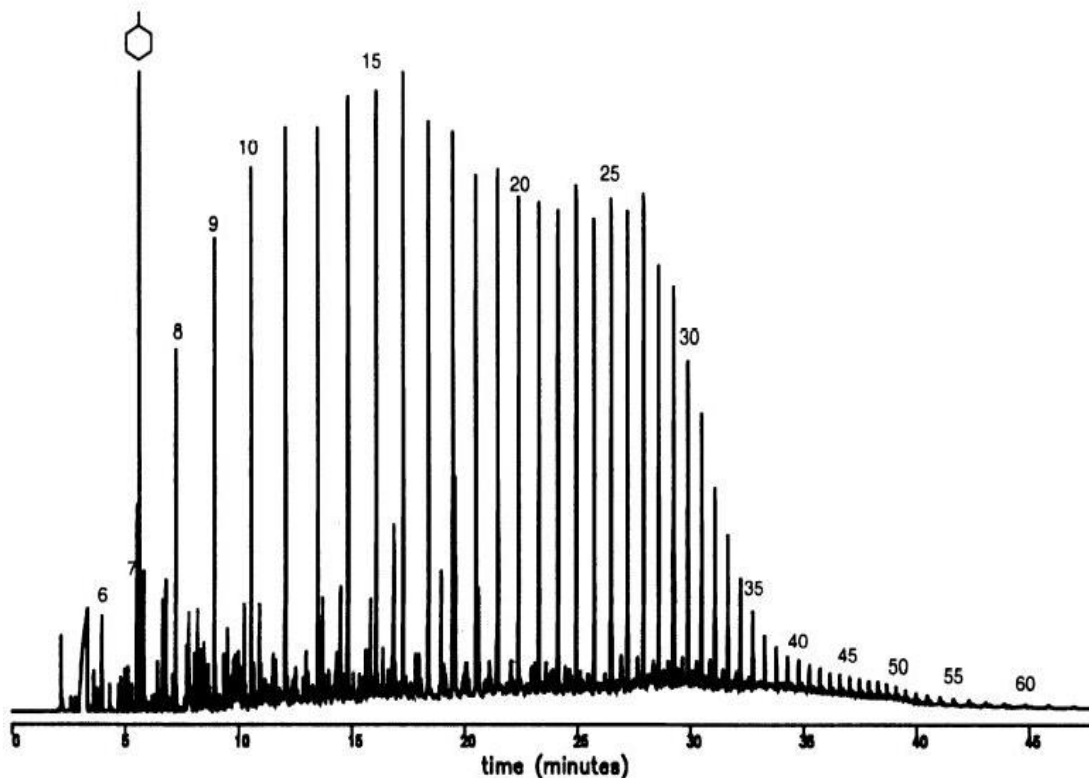
Figure 3. 5: Extended whole-oil analysis using a proprietary chromatographic technique. Separations from n-C3 to -n-C60 can be achieved by the help of on-column injection, pressure programming, and a high-temperature capillary column.

Column degradation is a key drawback of spreading chromatographic investigation to higher temperatures. The loss of immobile phase, the growth of dynamic sites, and the preservation of non-volatile molecules all contribute to the formation of active sites. Column polarity varies fast, making it difficult to maintain the ASTM 05134-98 strict requirements.

a) **C6-C7 Chromatographic Separations**

The bulk of light hydrocarbon molecular characteristics employed by upstream geochemists use isomers of C6 and C7 hydrocarbons. Apart from the fact that they are great enough to contain all hydrocarbon classes, these molecules are unremarkable (n- , iso-, and cyclo-paraffins, as well as aromatics), and that gas chromatographic technologies can separate and quantify all geological isomers. It's unlikely to resolve all of the Cs+ hydrocarbon isomers. Even partly fixed peaks can be related using larger light hydrocarbons distribution, which are frequently utilized in correlation studies. All non-olefinic hydrocarbon isomers (seventeen) can be determined at a carbon number of 23• 24 C7. Commercially accessible capillary

columns with chemically bound immobile phases and standard gas chromatographic methods cannot accomplish baseline parting of all seventeen C7 isomers, as well as possibly co-eluting C6 and Cs hydrocarbons. 1-trans-3-dimethylcyclopentane can only separate 3-ethylpentane partially by using 100 percent methyl silicone column, and methylcyclohexane has a shoulder of 1-cis-2-dimethylcyclopentane. The latter compounds' resolution can be enhanced by utilizing conditions tailored for their separation, but this comes at the expense of other compounds' resolution. The American Society for Testing Materials and the Gas Processors Association's standard procedures for analyzing petroleum light hydrocarbons (e.g., ASTM D 5134-98 and GPA 2186-95) decide even smaller number of the C7 isomers. Highly polar immobile phases, such as squalene or hexadecane-hexadecane, can be used to separate all C7 isomers; however, As chemically connected capillary columns, these phases are not available. As a result, they can only be employed at low temperatures (below 100°C), and just volatile hydrocarbon portion of the mixture must be placed on the column. If done carefully, the distillation and collection of the range of gasoline by not harming C7 hydrocarbons is possible. To ensure only light hydrocarbons being injected into temperature-sensitive columns, another way involves utilizing a pre-column or temperature-programmed injector.

Figure 3. 6: Optimized gas chromatographic separation of C7 hydrocarbons on a single-column gas chromatographic system.

For C7 hydrocarbon analysis, we designed a multi-dimensional gas chromatographic technique that attains baseline determination for all isomers." The process relies on commercially offered capillary columns and small volumes of cryogenic cooling liquids to produce rapid and consistent quantitative results with minimal sample preparation aside from the addition of an internal standard (Figure 3.7).
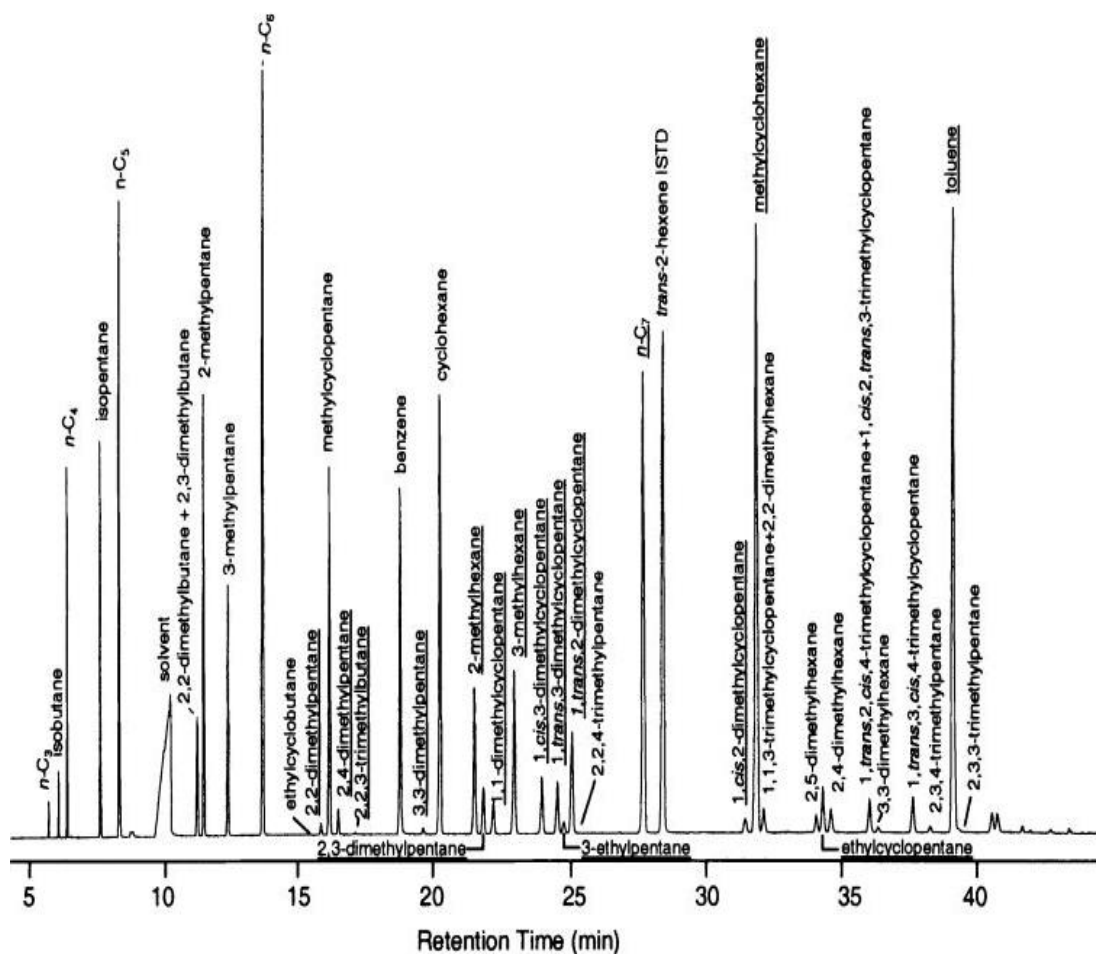
Figure 3. 7: The baseline resolution of multi-dimensional gas chromatographic separation of C7 hydrocarbons (underlined) is provided.

3.2 Geochemical characterization:

Geochemical characterization of the Oil samples is carried out using following parameters.

3.2.1 Thompson's (1983) Parameters:

a) Aromaticity

Aromaticity =Toluene/nC7   (Eq.1)

b) Paraffinicity

Paraffinicity=nC7/Methylcyclohexane   (Eq.2)

c) Heptane Ratio

Heptane ratio = (nC7/Σ CH through not includes MCH-1,2DMCP) *100(Eq.3)

d) C7 maturity Parameter

C7 Maturity Parameter =2,4-DMC5/2,3-DMC5 (Eq.4)

3.2.2   Mango's (1994) parameters Invariant Ratios (K1, K2):

a) K1= (2MH + 2,3DMP) / (3MH + 2,4DMP) (Eq.5)

b) K2 = P3 / (P2 + N2) (Eq.6)

c) P2 =2-methylhexane+3-methylhexane (Second parent) (Eq.7)

d) P3 =2,2-dimethylpentane+2,4-dimethylpentane+2,3-dimethylpentane+3,3-dimethylpentane+3-ethylpentane (daughter products of second parent) (Eq.8)

e) N2 =1,1-dimethylcyclopentane+cis-1,3-dimethylcyclopentane +trans-1,3-dimethylcyclopentane (cyclopentane daughter products of P2) (Eq.9)

3.2.3   Halpern Star correlation Diagrams:

Reservoir samples of oil and water show chemical composition using multivariate plots in polar coordinates. For oil samples the chromatographic data has been displayed on star diagrams (e.g., Slenttz, 1981; Kaufmen et al., 1987, 1990; Hweng et al., 1994). These graphs are constructed out of chromatographic peak ratios that represent unknown substances. Normal alkanes (e.g., pristane and phytane) & acyclic isoprenoids (e.g., pristane and phytane) are generally evaded. By graphing numerous oils, changes and resemblances across samples can be clearly identified. Light-hydrocarbon (C4–C7) gas chromatographic (GC) examination is performed using star diagram method. GC testing is performed on oil and condensate samples. The study resolves and calculates the relative areas of the majority of hydrocarbons between C4 and C7. The C7 compounds are less prone to evaporation than lighter

hydrocarbons due to their relatively high boiling temperatures, and as there are 17 hydrocarbons by seven carbon atoms, a wide range of possibly valuable ratios can be created. Thompson (1983, 1987, 1988) used light hydrocarbons to deduce crude oil transformation pathways. Mango (1987, 1990a, b, 1991) studied the C7 hydrocarbons in depth and concluded that source of light hydrocarbons is a kinetically regulated development that occurs in the parental kerogen. Because properties of the various C7 compounds differ so greatly (e.g., hot temperatures, water solubilities, and susceptibility to bacterial outbreak), numerous metrics for assessing the degree of transformation of petroleum have been developed on their C7 chemistry. (Transformation denotes to any procedure that causes petroleum to alter later it has been discharged from its source rock.) Some cases include water washing, biodegradation, thermal change, and evaporation.) Because of the multivariate methodology characteristic in star diagrams, they're a good way to summarize the plethora of parameters available with C7 molecules over two panels.

C7 star diagrams are classified into two categories:

Two Star diagrams are developed to study the correlation. The diagrams are built on an investigation of C7 HCs extracted from crude oils using gas chromatography (GC).

1:   C7 Oil Transformation Correlation Star Diagram (C7OTCSD)

One of the C7 diagrams is used to differentiate deviations in oils produced by transformations such water washing, biodegradation, or evaporation. Eight transformation fractions are shown in this graphic, in direction of falling biodegradation warmth. Tr1 through Tr8 are the ratios, and the figure is known as the C7 oil transformation star diagram (C7OTSD) (Fig 3.8).

Position On Star Diagram	Parameter Name	Ratio	Boiling Point (°C)	Solubility†† (ppm, dist. water)
1	Tr1	Toluene/1,1-dimethylcyclopentane	110.6/87.8	520/24
2	Tr2	n-C7/1,1-dimethylcyclopentane	98.4/87.8	2.2/24
3	Tr3	3MH/1,1-dimethylcyclopentane	91.8/87.8	2.6/24
4	Tr4	2MH/1,1-dimethylcyclopentane	90.0/87.8	2.5/24
5	Tr5	P2/1,1-dimethylcyclopentane*	91/87.8	2.6/24
6	Tr6**	1-cis-2-dimethylcyclopentane/1,1-dimethylcyclopentane	99.5/87.8	13/24
7	Tr7	1-trans-3-dimethylcyclopentane/1,1-dimethylcyclopentane	90.8/87.8	20/24
8	Tr8	P2/P3†	91/85	2.6/5.0

*P2 = 2-methylhexane + 3-methylhexane.
**The large boiling point difference in the compounds comprising Tr6 make it useful as a light-end loss (evaporation) parameter (it increases with light-end loss).
†P3 = 2,2-dimethylpentane + 2,3-dimethylpentane + 2,4-dimethylpentane + 3,3-dimethylpentane + 3-ethylpentane.
††Some values are approximate.

Figure 3. 8: C7 oil transformation correlation star diagram parameters

2:   C7 Oil Correlation Star Diagram (C7OCSD)

Second C7 light hydrocarbon based diagram comprises 5 fractions contained of mixtures which are highly resistive to transformational impacts and hence helpful for relationship. These proportions, labelled C1 through C5, are shown on the C7 oil correlation star diagram (C7OCSD) Fig (3.9). Built on source-related chemical changes, the C7OCSD Diagram can be taken to correlate converted and prime oils, a process that is difficult to execute with most traditional geochemical methods.

Position On Star Diagram	Parameter Name	Ratio	Boiling Point (°C)	Solubility† (ppm, dist. water)
1	C1	2,2-dimethylpentane/P3**	79.2/85	4.4/5
2	C2	2,3-dimethylpentane/P3	89.8/85	5.3/5
3	C3	2,4-dimethylpentane/P3	80.5/85	4.4/5
4	C4	3,3-dimethylpentane/P3	86.1/85	5.9/5
5	C5*	3-ethylpentane/P3	93.5/85	3.0/5

*The large boiling point difference in the compounds comprising C_5 make it useful as a light-end loss (evaporation) parameter (it increases with light-end loss).
**P3 = 2,2-dimethylpentane + 2,3-dimethylpentane + 2,4-dimethylpentane + 3,3-dimethylpentane + 3-ethylpentane.
†Some values are approximate.

Figure 3. 9: C7 oil correlation star diagram parameters (Henry I. Halpern2).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Chromatograms of studied Oil samples Adhi Oil Field Potwar Sub Basin Pakistan:

Five oil samples of Light Hydrocarbons from different wells of Adhi Oil Field Potwar Sub Basin were studied to analyze the geochemical characterization for transformations and correlation using Gas Chromatography (GC). The abbreviations and chemical names of analyzed C7 hydrocarbons are revealed in (Table 4.1).

Table 4. 1: Abbreviations and Chemical names of LHs Adhi Oil Field Potwar Sub Basin Pakistan.

Sr.	ABBREVIATION	CHEMICAL NAME
1	nC_3	n-propane
2	iC_4	i-butane
3	nC_4	n-butane
4	iC_5	i-pentane
5	nC_5	n-pentane
6	2,2-DMC4	2,2-dimethylbutane
7	CyC_5	Cyclopentane
8	2,3-DMC4	2,3-dimethylbutane
9	2-MCP	2-methylcyclopentane
10	3-MCP	3-methylcyclopentane
11	nC_6	n-hexane
12	2,2-DMP	2,2-di-methylpentane
13	MCP	Methylcyclopentane
14	2,4-DMP	2,4-dimethylpentane
15	Benz	Benzene

16	CyH	Cyclohexane
17	2-MH	2-methylhexane
18	1,1-DMCP	1,1-dimethylcyclopentane
19	3-MH	3-methylhexane
20	c-1,3-DMCP	Cis-1,3-dimethylcyclopentane
21	t-1,3-DMCP	Trans-1,3-dimethylcyclopentane
22	t-1,2-DMCP+3EP	Trans-1,2-dimethylcyclopentane
23	nC_7	n-heptane
24	c-1,2-DMCP	cis-1,2-dimethylcyclopentane
25	MCH	Methylcycloheptane
26	1,1,3-t-MCP+2,2-DMH	1,1,3-trans-methylcyclopentane + 2,2-dimethylheptane
27	2,5-DMH	2,5-dimethylheptane
28	1,2,4-t-MCP	1,2,4-trans--methylcyclopentane
29	1,2,3-t-MCP	1,2,3-trans--methylcyclopentane
30	TOL	Toluene
31	2,3-DMCH	2,3-dimethylcycloheptane
32	$2-MC_7$	2-methylheptane
33	$4-MC_7$	4-methylheptane
34	$3-MC_7$	3-methylheptane
35	1,3-DMCH	1,3-dimethylcycloheptane
36	t-1,4-DMCH	trans-1,4-dimethylcycloheptane
37	1,1-DMCH	1,1-dimethylcycloheptane
38	t-1,2-DMCH	trans-1,2-dimethylcycloheptane
39	nC_8	n-octane
40	t-1,3-DMH	trans-1,3-dimethylheptane
41	2,4-DMH	2,4-dimethylheptane

4.1.1 Chromatograms of Oil samples Adhi Oil Field Potwar Sub Basin Pakistan:
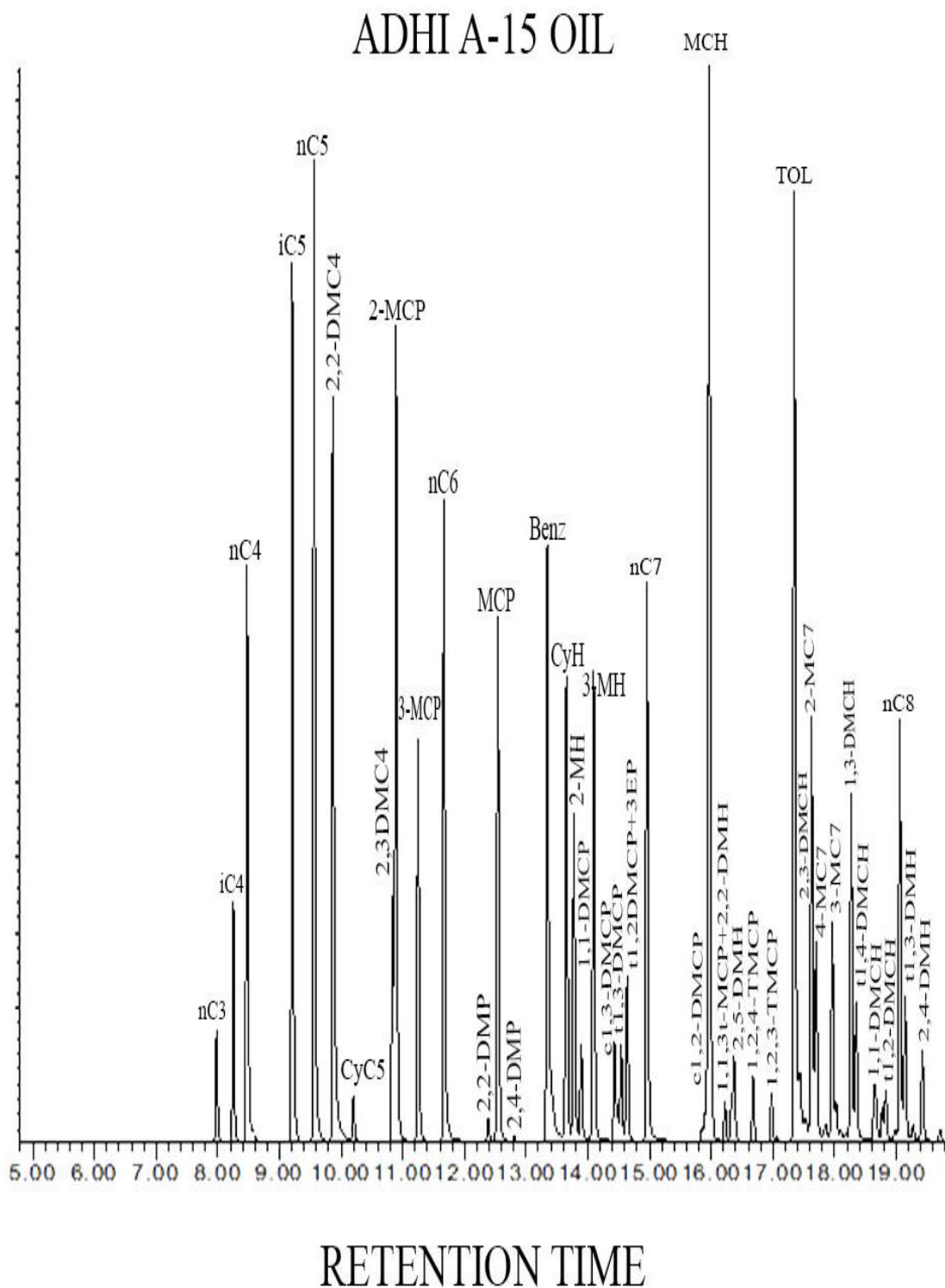
Figure 4. 1: Whole oil chromatogram showing the distribution of Light Hydrocarbons A-15 Oil, Adhi Oil Field Potwar Sub Basin Pakistan.

ADHI A-17 OIL

RETENTION TIME
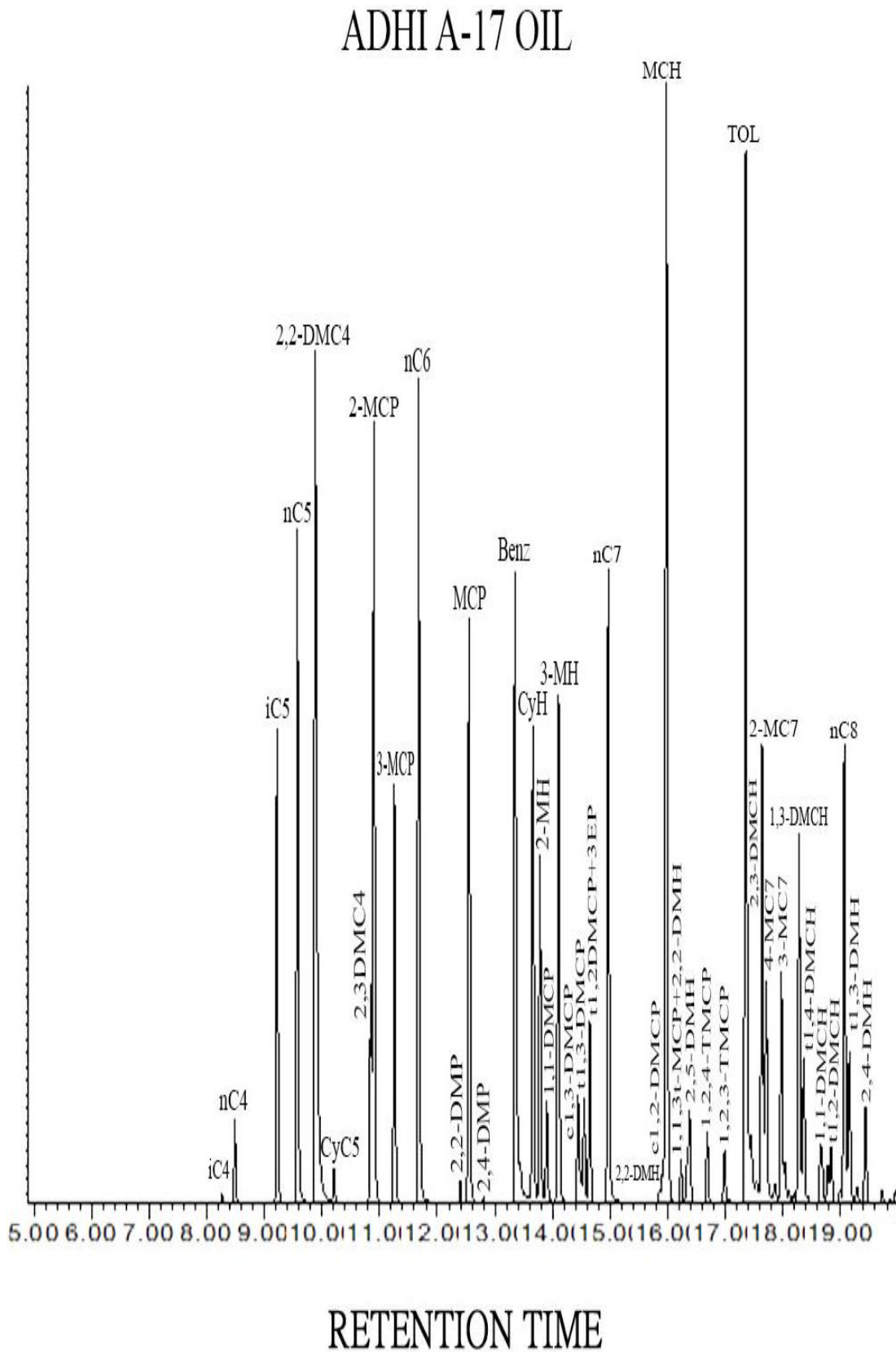
Figure 4. 2: Whole oil chromatogram showing the distribution of Light Hydrocarbons A-17 Oil, Adhi Oil Field Potwar Sub Basin Pakistan.
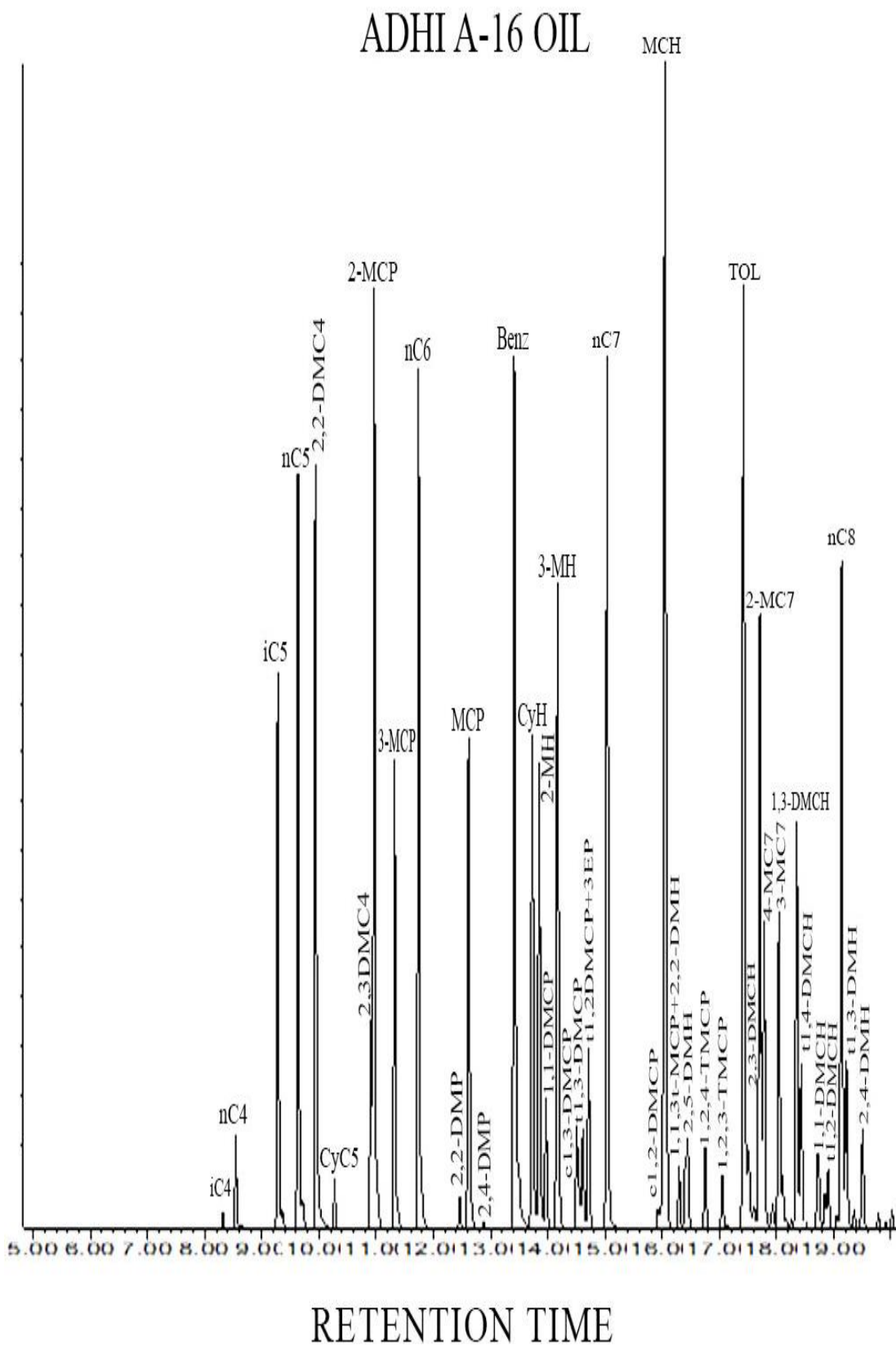
Figure 4. 3: Whole oil chromatogram showing the distribution of Light Hydrocarbons A-16 Oil, Adhi Oil Field Potwar Sub Basin Pakistan.
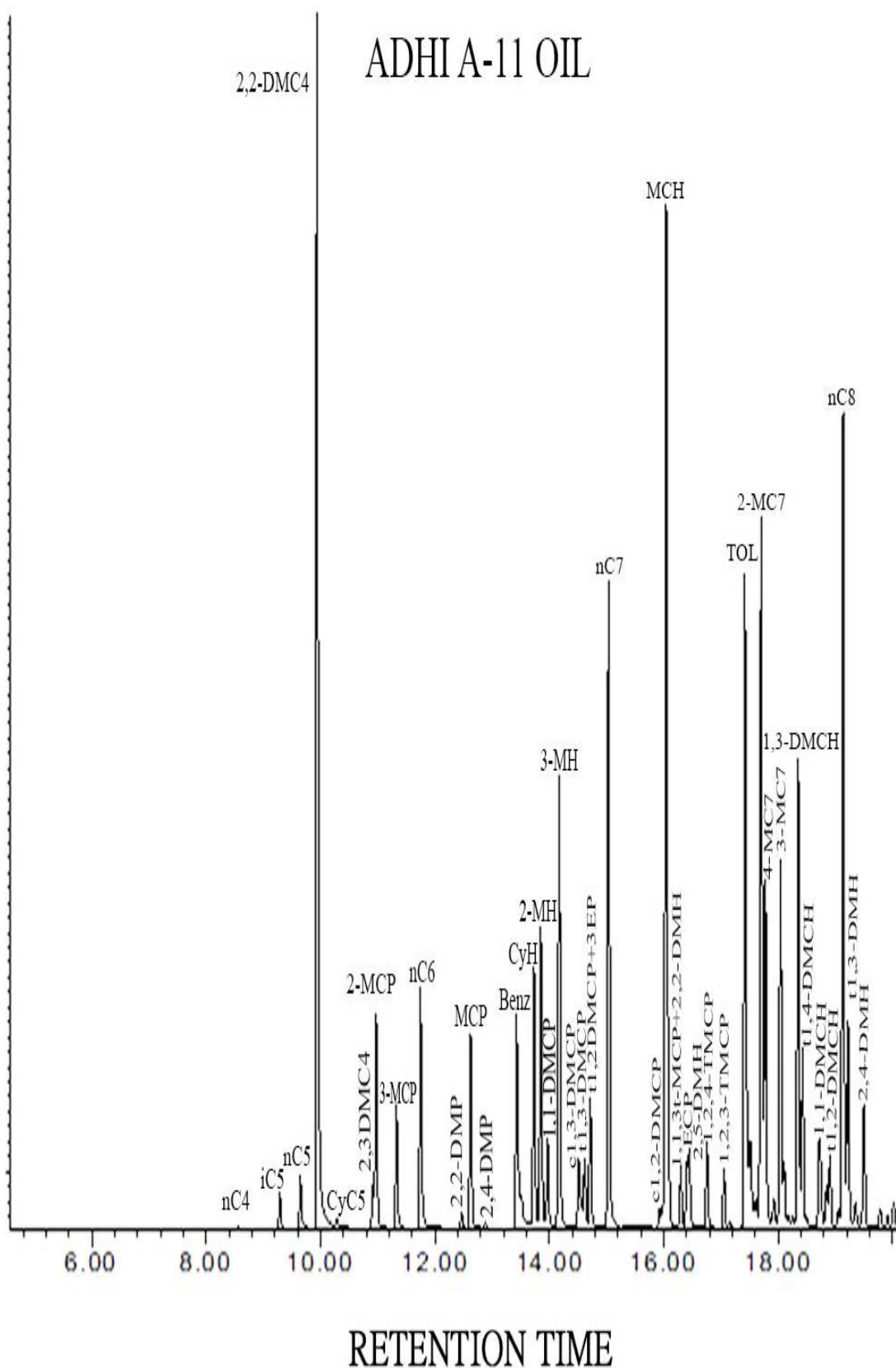
Figure 4. 4: Whole oil chromatogram showing the distribution of Light Hydrocarbons A-11 Oil, Adhi Oil Field Potwar Sub Basin Pakistan.
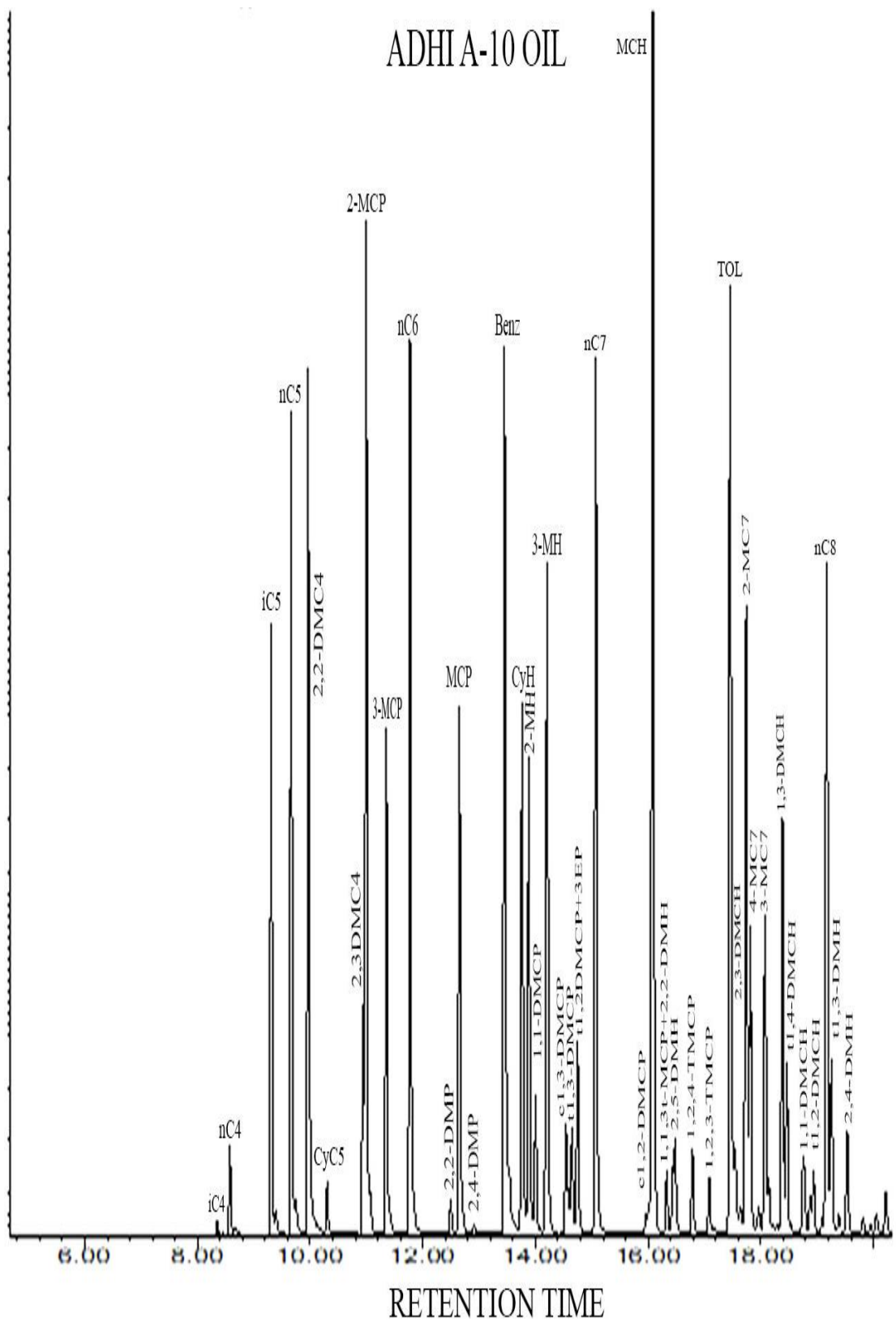
Figure 4. 5: Whole oil chromatogram showing the distribution of Light Hydrocarbons A-10 Oil, Adhi Oil Field Potwar Sub Basin Pakistan.

4.2   Parameters used to analyze the C₇ distribution of Light Hydrocarbons:

Geochemical characterization of Adhi Oil Field Potwar Sub Basin Pakistan oils is carried out using the following parameters.

i.   Thompson's 1983 Parameters

ii.   Mango's 1994 Parameters

4.2.1   Thompson's 1983 Parameters:

In this study, five samples (A-15, A-17, A-11, A-16, and A-10) from different wells were collected from the Adhi Oil Field Potwar Sub Basin and analyzed by gas chromatography (GC). Comparative investigation was used to regulate the degree of correlation between five oil samples.

Following ratios/parameters are proposed by Thompson were used to analyze the GC experimental data:

1) Heptane ratio

2) Invariance ratio

3) C7 maturity parameters

4) Aromaticity

5) Paraffinicity

The objective of correlation of geochemical parameters based on composition of light hydrocarbons was to provide a tool for evaluation of its reservoir connectivity, secondary alterations, and transformations/correlation to deliver a fast and cheap method of understanding.

Thompson (1994) parameters were calculated using (Eq.1 to Eq.4) and the results are revealed in the Table 4.2.

Table 4. 2: Calculated Values of Thompson's (1994) parameters from chromatographic peaks obtained by Gas chromatography (GC).

Sr.	SAMPLE	C_7 MATURITY	AROMATICITY	PARAFINICITY	HEPTANE RATIO
1.	A-15	0.93	1.85	0.47	18.16
2.	A-17	0.93	1.77	0.51	19.41
3.	A-11	0.93	1.10	0.56	27.26
4.	A-16	0.93	1.19	0.65	21.45
5.	A-10	0.93	1.18	0.62	20.88

i.   Aromaticity =Toluene/n-heptane (nC_7) (Eq.1)

ii. Paraffinicity = n-heptane (nC_7) / Methylcyclohexane (MCH) (Eq.2)

iii. Heptane ratio = (nC_7/Σ CH through not includes MCH, 1,2-DMCP) *100 (Eq.3)

iv. C_7 Maturity Parameter = 2,4-dimethyl pentane (2,4-DMC5) / 2,3-dimethyl pentane (2,3-DMC5) (Eq.4)

4.2.2 Mango's 1994 Parameters:

Mango (1994) showed a remarkable invariance in the fractions of the totality of concentrations of various C7 Light Hydrocarbons in crude oils. He found that relative richness of the Isoheptane is different by briefings of magnitude, the fraction of various compound particularly K1 (Eq.5) was constant. Also, oils from the identical source showed strangely constant K1 values. K2 is the fraction of the three-ring closure products (P3) to the totality of the methyl hexane parents (P2) and the five ring closure products (N2). The invariance of K2 inside homologous oil sets couples the C7 isoalkanes and dimethylcylcopentanes in a manner consistent with a kinetic steady-state model. Among oils from the same source, these invariant ratios (K1 and K2) are almost constant throughout hydrocarbon generation, regardless of their absolute concentration.

Five oil samples (Table 4.1) were analyzed, and the values calculated for the Mango's (1994) parameters are presented in the Table 4.3 using equations (5,6,7,8 and 10).

Table 4. 3: Calculated Values of Mango's (1994) parameters from chromatographic peaks obtained by Gas chromatography (GC).

Sr.	SAMPLE	K1	K2	P2	P3	N2
1.	A-15	1.02	0.76	27.9	53.6	42.9
2.	A-17	1.02	0.76	27.9	53.7	42.9
3.	A-11	1.02	0.76	28.1	53.9	43.1
4.	A-16	1.02	0.76	27.9	53.9	43.1
5.	A-10	1.02	0.76	28.1	54.1	43.2

i.   K1= [(2-methylhexane(2MH) + 2,3-dimethylpentane(2,3DMP)]/ [(3-methylhexane (3MH) + 2,4-dimethylpentane(2,4DMP)] (Eq.5)

ii. K2 = P3/ [(P2 + N2)] (Eq.6)

iii. P2 =2-methylhexane+3-methylhexane (Second parent) (Eq.7)

iv. P3 =2,2-dimethylpentane+2,4-dimethylpentane+2,3-dimethylpentane+3,3-dimethylpentane+3-ethylpentane (daughter products of second parent) (Eq.8)

v.   N2 =1,1-dimethylcyclopentane+cis-1,3-dimethylcyclopentane +trans-1,3-dimethylcyclopentane (cyclopentane daughter products of P2) (Eq.9)

4.2.3 Thermal Maturity

Thermal Maturity of the Oil samples is determined using following parameters.

I. Heptane Ratio:

Thompson (1983) announced the heptane ratio as a development parameter, which is designed by the fraction of n-heptane to the summation of various heptane isomers. Thomson described phases for maturity valuation of oils built on heptane fraction as follows. The Heptane fraction less than 18 is biodegraded oil and 18 to 22 is normal uncracked oil, 22 to 30 is classified as mature oil, and heptane fraction > 30 is defined as super mature (Table 4.4) (Keshmirizadeh1et, al.).

Table 4. 4: Showing the Thompson maturity parameters using Heptane ratios

Sr.	HEPTANE RATIO	THERMAL MATURITY
1	<18	Biodegraded
2	18-22	Normal
3	22-30	Mature
4	>30	Super Mature

Heptane ratio = (nC$_7$/Σ CH through not includes MCH-1,2DMCP) *100 (Eq.3)

According to Thompson (1983) heptane ratios maturity parameters the sample A-15, A-16, A-17, and A-10 has Heptane Ratio values (18.16, 21.45 19.5) and 20.88 which shows the oil samples are normal, however, the oil sample A-11 has heptane ratio 27.26 that indicates the sample is Mature (Table 4.2).

II. Heptane Ratio Versus Iso Heptane Ratio:

Thompson's (1983) parameters for thermal maturity are based on Heptane Value versus Iso heptane value (Table 4.5).

Table 4. 5: Light Hydrocarbons values for Heptane Ratio and Isoheptane Ratio.

Sr.	SAMPLE	HEPTANE RATIO (H)	ISO HEPTANE RATIO (I)
1.	A-15	18.16	0.66
2.	A-17	19.41	0.64
3.	A-11	27.26	0.64
4.	A-16	21.45	0.64
5.	A-10	20.88	0.64

i.   Heptane Ratio = (nC$_7$/Σ CH through not includes MCH, 1,2-DMCP) *100 (Eq.3)

ii. Iso-heptane Ratio(I)=[(2-MH+3-MH)/(c1,3-DMCP+t-1,3-DMCP+t-1,2-DMCP)]   (Eq.11)

Heptane Ratio is planned as the ratio of n-heptane (nC$_7$) and 2-Methylhexane (2-MH) + 3-Methylheptane (3-MH) + Dimethylbutane (DMC4) + cis-1,3-Dimethylcyclopentane (1-c3-DMCP) + trans-1,3- Dimethylcyclopentane (t-3-DMCP) + trans-1,2- Dimethylcyclopentane (1-t,2-DMCP) + n-heptane (nC$_7$).

Iso Heptane Ratio is calculated as the ratio of 2-Methylhexane (2-MH) + 3-Methylheptane (3MH) and cis-1,3-Dimethylcyclopentane (1-c3-DMCP) + trans-1,2-Dimethylcyclopentane (1-t,2-DMCP).
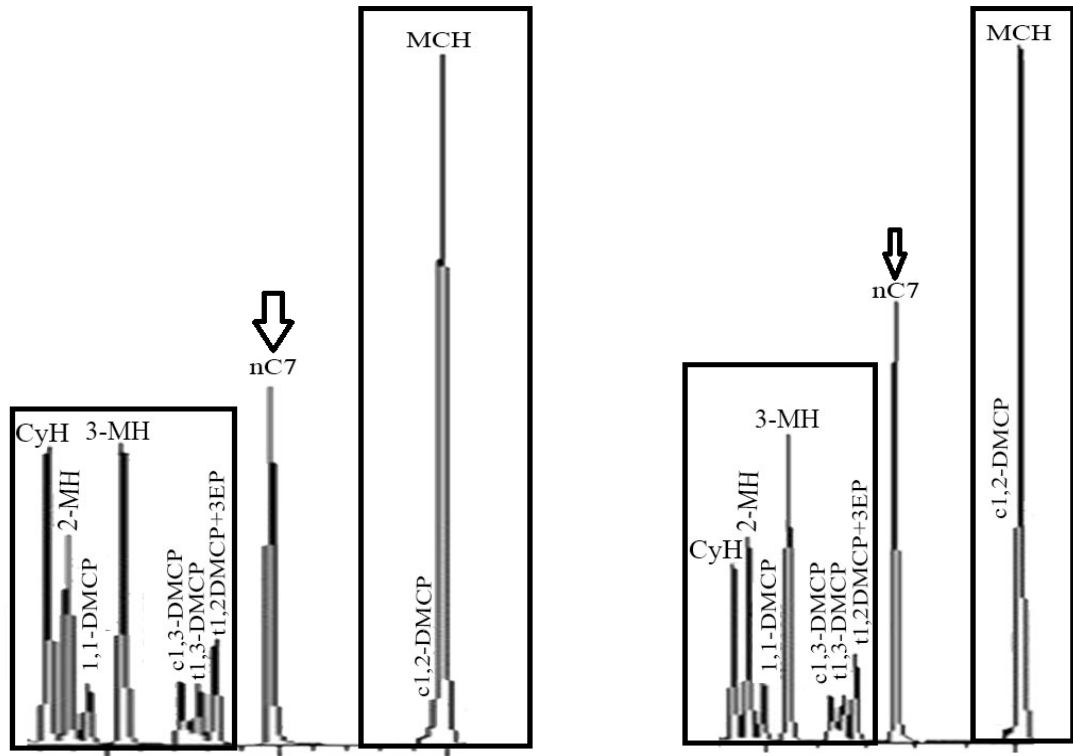
Adhi A-15 oil Heptane Ratio = 18.16   Adhi A-11 oil Heptane Ratio = 27.26

Figure 4. 7: Heptane Ratio[(100*nC$_7$)/(CyH+2-MH+3-MH+DMC4+1-c3-DMCP+1,t,3-DMCP+1-t,2-DMCP+nC$_7$+MCH] of A-15 and A-11 oil samples of Adhi Oil Field.
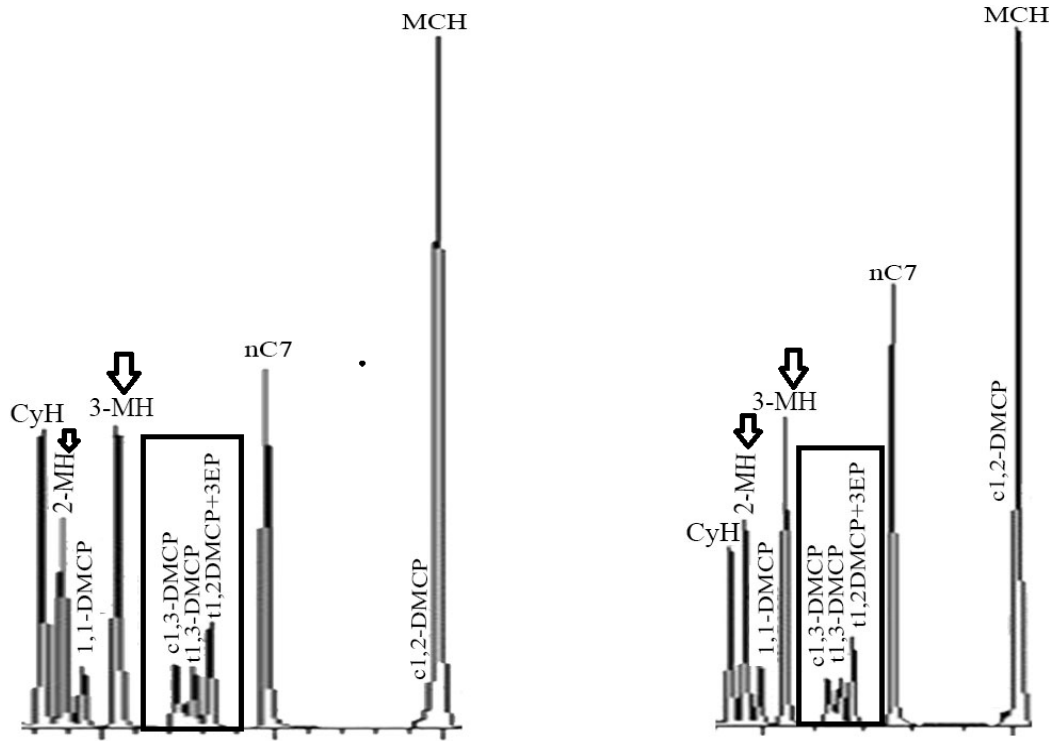
Adhi A-15 oil Iso-heptane Value=0.66   Adhi A-11 oil Iso-heptane Value=0.64

Figure 4. 6: Iso-heptane values [(2-MH+3-MH)/(c1,3-DMCP+t-1,3-DMCP+t-1,2-DMCP)] of A-15 and A-11 oil samples of Adhi Oil Field.

Figure 4.6 and Figure 4.7 representing the chromatographic peaks picked to calculate the Heptane ratio and Iso-heptane ratios of A-15 and A-11 oil samples of Adhi Oil field Potwar Sub Basin.
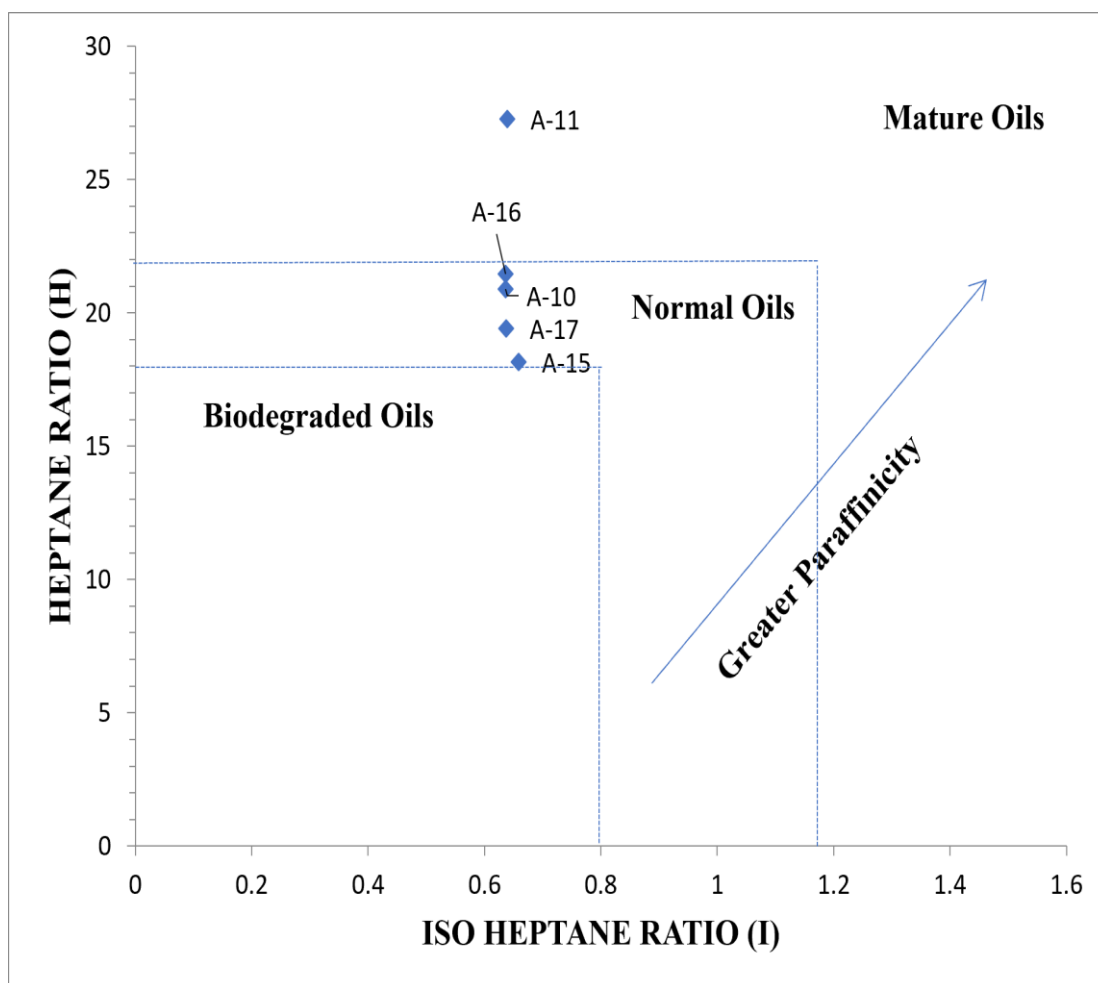
Figure 4. 8: Thompson's (1983) Graph of Iso Heptane Ratio (I) versus Heptane Ratio (H) for Adhi Oil Field oils.

The plot of Isoheptane Value (I) versus Heptane Value (H) (Thompson; 1983) for Adhi Oil Field Potwar Sub Basin Pakistan oils is presented in the Figure 4.8. The oil sample A-11 falls in the Mature Oils; however, all the remaining oil samples (A-15, A-17, A-16, and A-10) are fall in the Normal Oils category according to Thompson's (1983) classification (Table 4.6).

The difference in thermal maturity of A-11 oil sample from the other samples occurred due to the later generation of hydrocarbons from the source.

Table 4. 6: Thompson's (1983) classification for thermal maturity using heptane and iso-heptane values

CATEGORY	HEPTANE VALUE	ISO-HEPTANE VALUE
Biodegraded oil	0-18	0-0.8
Normal oil	18-22	0.8-1.2
Mature oil	22-30	1.2-2.0

III. C_7 Maturity Parameter

Thompson's C_7 maturity values given in (Table 4.2) were calculated using following equation.

C_7 Maturity Parameter = 2,4-DMC5/2,3-DMC5   (Eq.4).

The calculated C_7 maturity values for all oil samples (A-10, A-15, A-11, A-16, A-17) have constant C_7 Maturity value 0.93 (BeMent et al. 1994).

4.2.4 Source Related Parameters:

Source of Light hydrocarbons in Adhi Oil Field Potwar Sub Basin Pakistan is analyzed based on the Thompson's 1983 and Mango's 1990 parameters.

I.   Source of organic matter

Invariance fraction of isoheptanes and dimethylcyclopentanes, K2, is a consistent pointer of source organic matter. Zheng (2005) described that marine oils are characterized by low K2 values (average 0.23) and terrigenous oils by high K2 standards (average 0.35) respectively (Table 4.7).

Table 4. 7: Parameters to identify source of organic matter (Zhang, 2005).

K2 VALUE	SOURCE	AVERAGE
Low	Marine	0.23
High	Terrigenous	0.35

The K2 values of Adhi Oil Field oils are same (Table 4.3). The samples A-10 (0.76), A-16 (0.76), A-17 (0.76) A-15 (0.76), and A-11 (0.76), all the samples have same K2 values. The K2 value of oil samples are high which shows the samples have more of terrigenous organic matter input.

II.   Heptane Ratio

Thompson (1983) took heptane ratio as pointer of basis of crude oil. Heptane fractions of Adhi oils ranged from 18.41 to 27.26 (Table 4.2). Though, the heptane fractions of oils A-15 (18.16), A-10 (20.88), A-16 (21.45) and A-17 (19.41) are close, and A-11 (27.26) values showed a slight difference.

The Heptane ratios of all the oil samples have no prominent separation, a minor difference in A-11 oil sample is because of the thermal maturity factor. Heptane Ratio showed that crude oils from the Adhi Oil Field have the same source rock for the Hydrocarbon generation.

III.   KI versus K2:

The invariance of isoheptane (K1 and K2) is highly valuable in oil correlation studies (Mengo, 1990) as their fraction relics remarkably constant all over hydrocarbon generation, irrespective of their complete concentration, for a set of oils from the similar source (Mark O. Oniyema and Patiance N. Menilla).

The graphical representation of invariance ratios K1 versus K2 of five oil samples of Adhi oil field Potwar sub–Basin Pakistan is shown in (Fig. 4.9). The graph clearly shows the same sources of oil generation for all the samples in the field area.
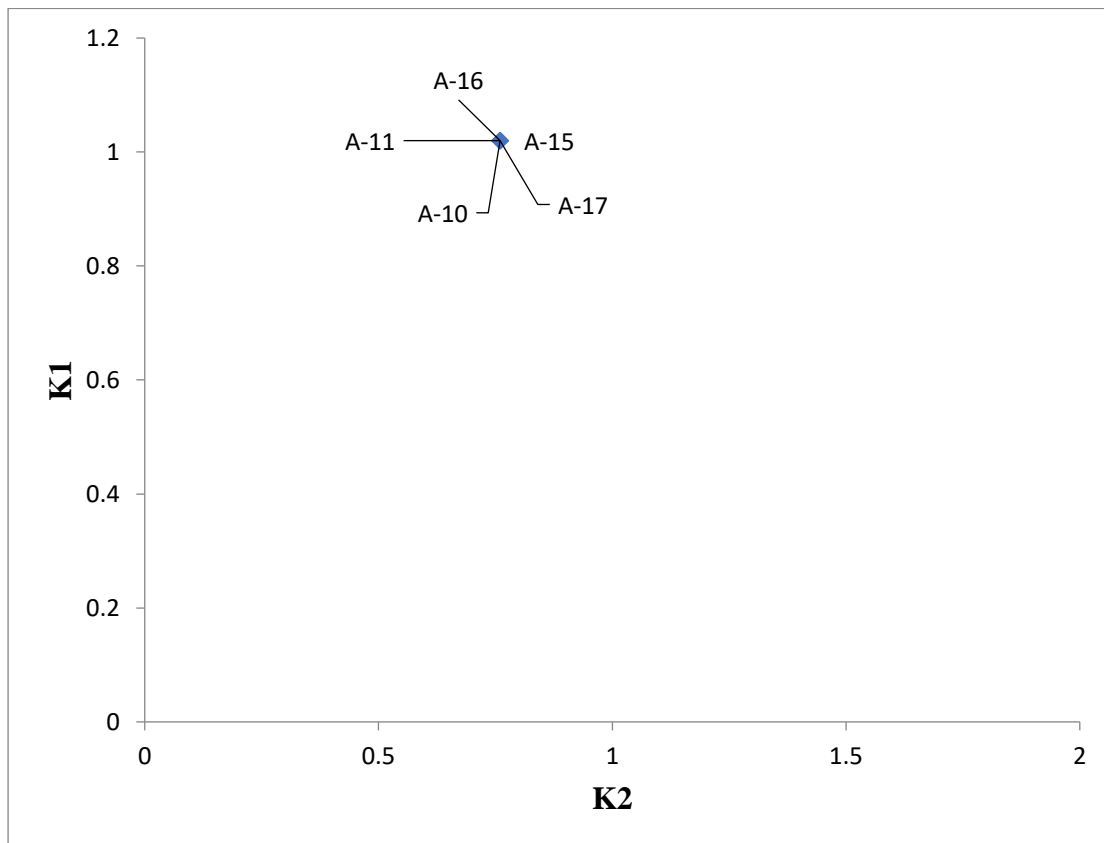
Figure 4. 9: An invariance plot of K1 versus K2 values showing the same source of oils for Adhi Oil Field Potwar Sub Basin Pakistan.

K1= [(2-methylhexane(2-MH) + 2,3-dimethylpentane(2,3-DMP)]/ [(3-methylhexane

(3-MH) + 2,4-dimethylpentane(2,4-DMP)]; K2 = P3/ [(P2 + N2)]

K2 = P3/ [(P2 + N2)]

The K1 values of Adhi Oil Field oils are same for all the samples (Table 4.3). The value of K1 for sample A-15 (1.02), A-10 (1.02), A-16 (1.02), A-17 (1.02), A-11 (1.02) respectively. The values for A-15, A-10, A-16, A-17, and A-11 showed similarity in K1 values.

The K2 values of analyzed hydrocarbons are below 1 (Table 4.3). The K2 values for oil samples are also same, A-10 (0.76), A-11 (0.76), A-15 (0.76), A-16 (0.76) and A-17 (0.76) respectively. The K2 values for oil samples A-10, A-11, A-16, A-17, and A-15 showed similar values.

The K1 versus K2 plot clearly suggests that all the samples have same source for the Hydrocarbons generation.

IV.   Aromaticity vs Paraffinicity

The graphical representation of invariance ratios Aromaticity versus Paraffinicity of five oil samples of Adhi oil field Potwar sub–Basin Pakistan is shown in Figure 4.10.
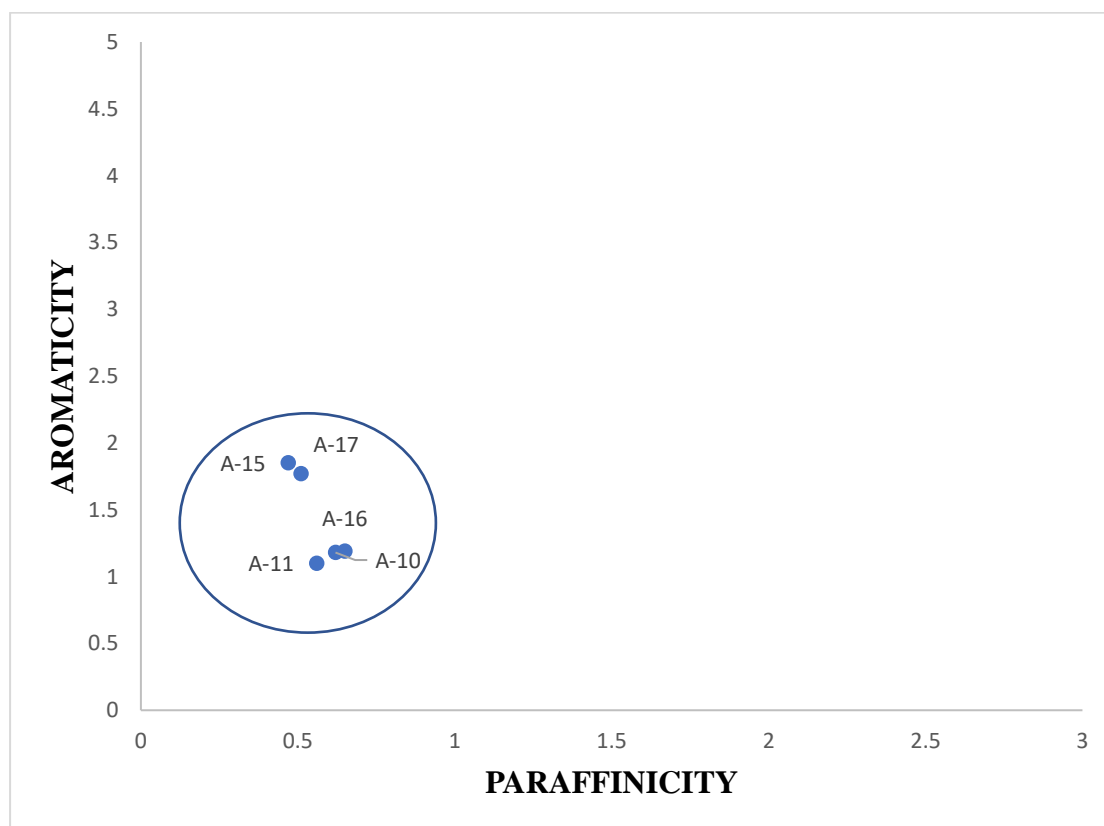
Figure 4. 10: Cross plot of Aromaticity versus Paraffinicity values shows the different oil sets of Adhi Oil Field Potwar Sub Basin Pakistan.

Aromaticity and Paraffinicity are valuable concepts in the assessment of light hydrocarbon compositional records. All LHC fractions are established based on comparative concentrations, relative to peak areas.

The Aromaticity versus Paraffinicity graph clearly showing the same source of oil generation in the Adhi field. The oil samples A-15 (1.85, 0.47), A-17 (1.77,0.51) A-11(1.10, 0.56), A-10 (1.18, 0.62) and A-16 (1.19, 0.65) oils have close Aromaticity

and Paraffinicity values (Table 4.2). The graphical representation clearly suggests that no prominent difference is observed in Aromaticity and Paraffinicity values. The Adhi Oil Field oils have the same source rock for hydrocarbon generation.

4.2.5   Light hydrocarbons based Star Diagrams:

Star diagrams are multivariate designs in polar coordinates that are frequently taken to describe chemical configurations of oil and water samples from reservoirs. Chromatographic information for oil samples have been added on star diagrams (Slantz, 1981; Kaufmen et al., 1987, 1990; Hweng et al., 1994).

Small-scale correlation method using gas chromatographic examination of light hydrocarbons was taken for the determination of correlation and or variation among the oils. This is used to correlate the oils by relating fractions of compounds. These assessments are put in graphic form of a star plot diagram to create correlation and or variation of the Adhi oil field oils easier. Star plots have been used to denote chemical configurations of oil samples from reservoirs, as well as association and or variation (Helpern, 1995; Ali et al, 2002; Valk et al; 2005).

I. C_7 Oil Correlation Star Diagram (C_7OCSD)

The C_7 oil correlation star diagrams containing of a sequence of fractions of chromatographic peaks, have been used to associate primary oils built on source associated hydrocarbon compounds. This variation is in line with changes in source rock between the oils.

Comparisons of the Adhi Oil Field oils using gas chromatographic analysis of C_7 Light Hydrocarbons utilized a star diagram to make correlation of the fluids easier. The selected ratios of chromatographic peaks on five axes are represented in (Table 4.8).

This phase comprises selecting fractions of compounds that are constant to transformation for the C7 oil association star diagram (C7OCSD). This phase is very hard for two motives:

(1) Compounds unaffected to biodegradation are hard to find between the light hydrocarbons, and

(2) The fractions determined using these compounds must be source associated. This means that they must be nearly invariant inside a family of oils (oils resulting from the similar source rock) but have to display enough change between oils from

dissimilar families to mark them useful for correlation determinations.

These compounds showed to be the multi-branched heptanes, which together are recognized as P3 (Mango, 1990b).

Table 4. 8: Selected ratios of light hydrocarbons selected for C_7 oil correlation star diagram(C7OCSD).

Sr.	SAMPLE	C1	C2	C3	C4	C5
1.	A-15	0.24	0.47	0.66	0.56	0.00058
2.	A-17	0.23	0.51	0.66	0.56	0.00672
3.	A-11	0.17	0.56	0.66	0.56	0.00073
4.	A-16	0.18	0.65	0.66	0.56	0.00088
5.	A-10	0.18	0.62	0.66	0.56	0.00099

    i.   C1= t-1,2-DMCP / t-1,2-DMCP + nC_7

   ii.   C2= nC_7/ MCC6

  iii.   C3= P3/P3+P2

  iv.   C4= P3/P3+N2

   v.   C5= 2,4-DMCP/2,4-DMP+TOL
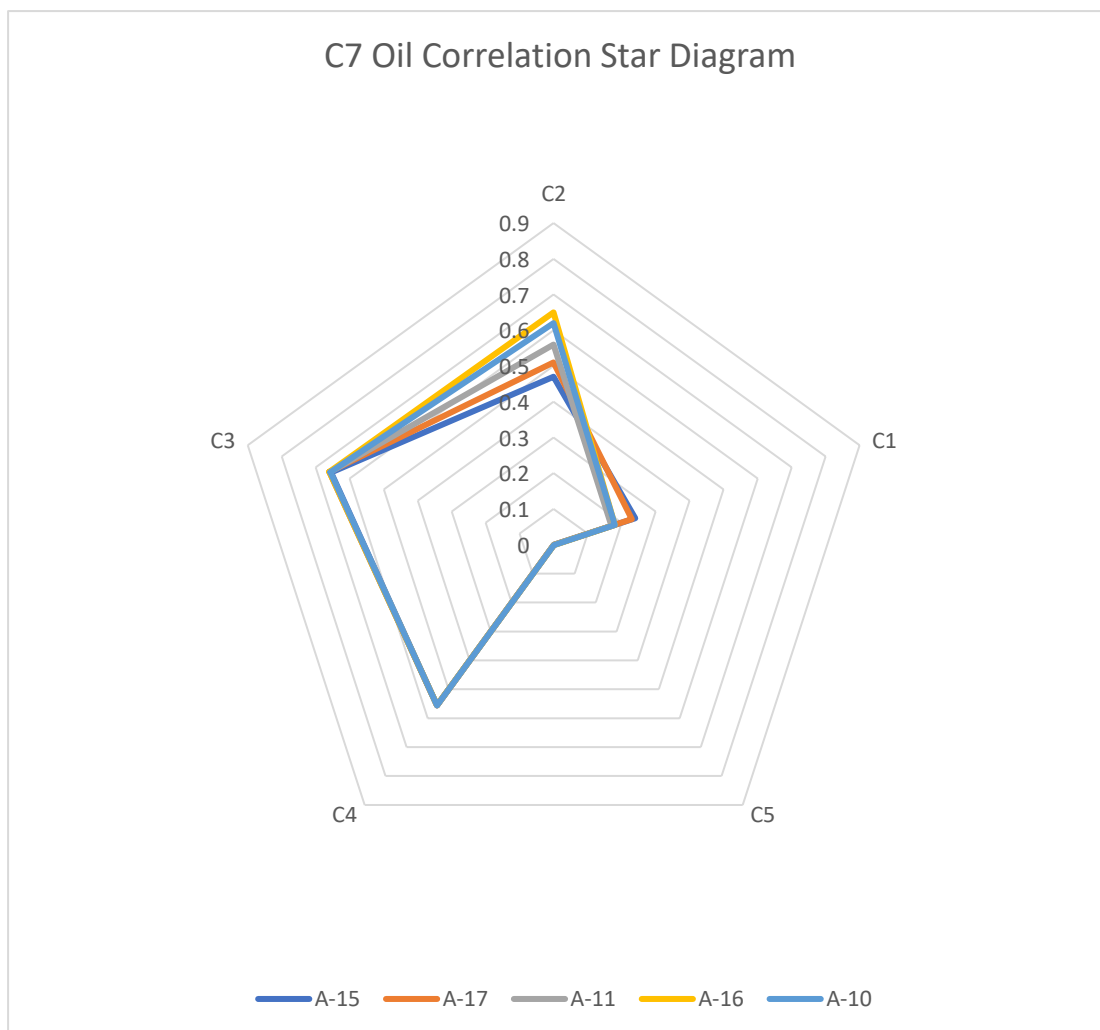
Figure 4. 11: Selected ratios of chromatographic peaks on five axes in a star diagram (C7OCSD).

Fractions C1 and C5 may be valuable for observing evaporation (or migration fractionation) between samples related to a particular family. Fraction C1 has a boiling-point variance of about $-6°C$ among numerator & denominator and should decline upon evaporation, whereas fraction C5 has a boiling-point variance of about $+8°C$ and should rise. Note that the variances in boiling points are estimated in the instance of the correlation constraints because the denominator denotes a set of mixtures whose individual richness differ from family to family, causing in slightly dissimilar average boiling points for the P3 group of any known oil family. (Hanry I. Helpern2, 1995).

The graphical representation of C_7 Star Correlation Diagram (C_7OCSD) (Fig. 4.11) showing that the Adhi oils have slightly variated C1 and C2 values, however the C5

values are minimum in this graphical representation. The C_7 Oil Correlation Star Diagram (C7OCSD) shows that oil samples A-15, A-17, A-11, A-16 and A-10 followed similar pattern, suggesting a close grouping among the oils and is reflective of oil generation from the same terrigenous source rock in Adhi Oil Field Potwar Sub Basin Pakistan. The variations in C1 and C2 values depict the alterations in oil samples by evaporative fractionation. (Hanry I. Helpern2, 1995)

II. C_7 Oil Transformation Correlation Star Diagram (C7OTCSD):

Light hydrocarbons have been taken by Thompson (1983, 1987, 1988) to conclude transformation procedures in crude oils. The C7 hydrocarbons have been examined in detail by Mango (1987, 1990a, b, 1991) who described that the source of the light hydrocarbons is a kinetically organized method taking place in the parent kerogen.

The dissimilar C_7 compounds have ominously dissimilar properties (e.g., boiling points, water solubilities, susceptibilities to bacterial outbreak) that directed to the growth of numerous parameters for assessing the degree of transformation of petroleum's established on their C7 chemistry. Transformation denotes to any procedure causing petroleum alteration later it has been excluded from its source rock. Some examples comprise water washing, biodegradation, thermal alteration, and evaporation (Hanry I. Helpern2, 1995).

The selected compounds and their ratios for the C_7 Oil Transformation Correlation Star Diagram are in (Table. 4.9 & Table. 4.10).

Table 4. 9: Ratios and selected values of light hydrocarbons by GC for C_7 Oil Transformation Correlation Star Diagram (C7OTCSD).

C7 OTCSD	A-15	A-17	A-11	A-16	A-10
Tol	17.4	17.4	17.5	17.5	17.5

nC7	14.2	15	15.1	15.1	16.1
3MH	14.1	14.1	14.2	14.2	14.1
2MH	13.8	13.8	13.9	13.8	14
1-c-2-DMCP	15.9	16	15.9	15.9	16
1-t-3-DMCP	14.6	14.6	14.7	14.7	14.7
1,1-DMCP	13.9	13.9	14	14	14.1
P2	27.9	27.9	28.1	27.9	28.1
P3	53.6	53.7	54	53.9	54.1

Table 4. 10: Calculated ratios of light hydrocarbons for C$_7$ Oil Transformation Correlation Star Diagram (C7OTCSD).

Sr.	C7OTCSD RAIOS	A-15	A-17	A11	A16	A10
1	Tr1	1.25	1.25	1.25	1.25	1.25
2	Tr2	1.08	1.08	1.08	1.08	1.15
3	Tr3	1.01	1.01	1.01	1.01	1.01
4	Tr4	1	1	1	1	1
5	Tr5	2	2	2	2	2
6	Tr6	1.14	1.14	1.14	1.14	1.14
7	Tr7	1.05	1.05	1.05	1.05	1.05
8	Tr8	0.52	0.52	0.52	0.52	0.52

i.   Tr1= Toluene / 1,1-dimethylcyclopentane

ii.   Tr2= n-heptane/ 1,1-dimethylcyclopentane

iii. Tr3= 3-methylhexane / 1,1-dimethylcyclopentane

iv.   Tr4= 2-methylhexane / 1,1-dimethylcyclopentane

v.   Tr5= P2 / 1,1-dimethylcyclopentane

vi.   Tr6= 1-cis-dimethylcyclopentane / 1,1-dimethylcyclopentane

vii.   Tr7= 1-trans-3-dimethylcyclopentane / 1,1-dimethylcyclopentane

viii.   Tr8= P2/P3
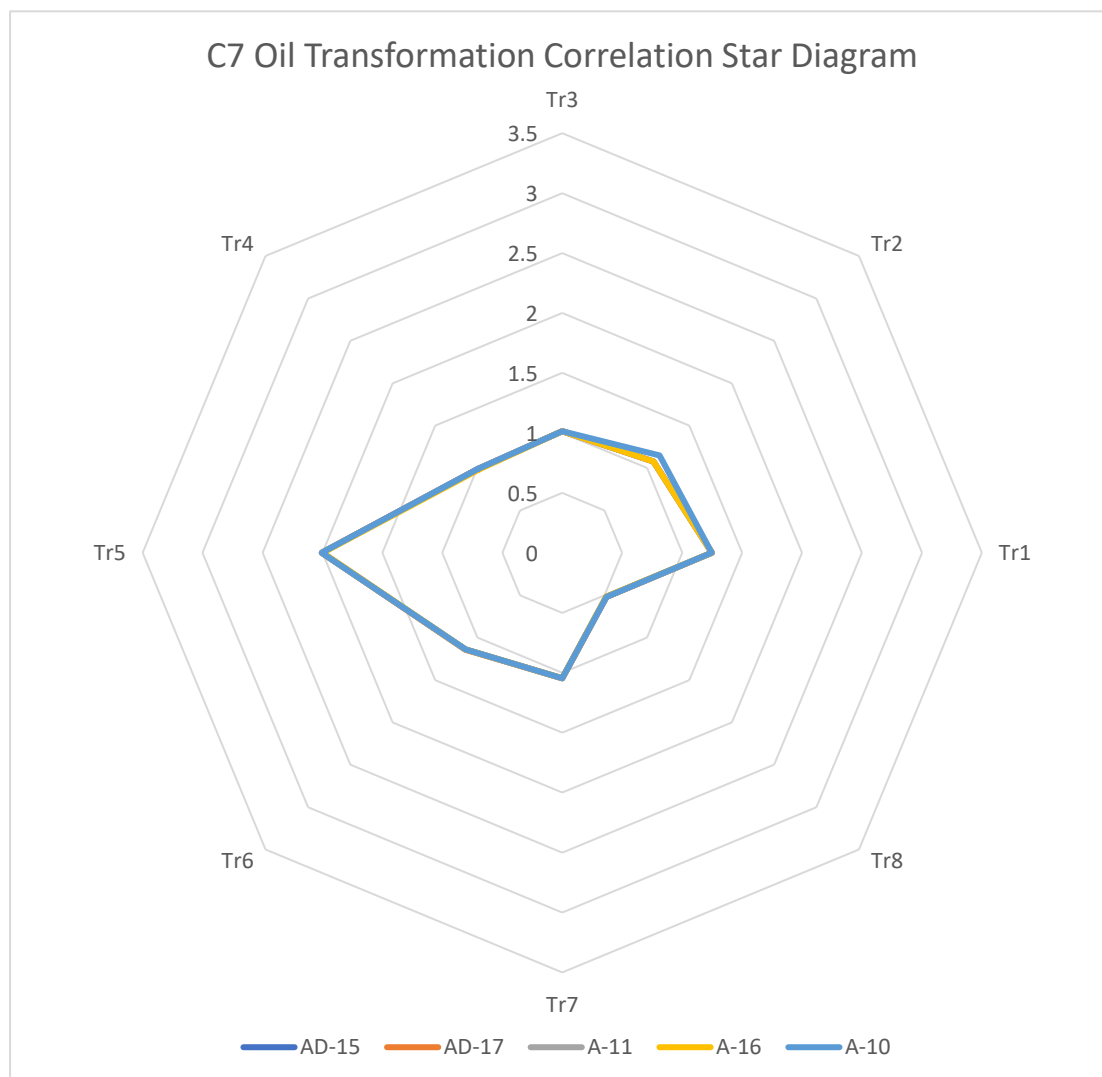
Figure 4. 12: Selected ratios of chromatographic peaks on eight axes in a star diagram (C$_7$OTCSD).

Tr1 calculates the reduction in toluene, which is by far the greatest water-soluble C$_7$ compound. Water washing usually is a precursor to biodegradation, but can sometimes happen without biodegradation (Palmar, 1984). The lasting fractions calculate biodegradation, with Tr6 also valuable for evaluating evaporation. Fractions Tr1 through Tr7 all comprise the similar denominator 1,1-dimethylcyclopentane (1,1-DMCP). By experimental studies, this compound has been found to be the utmost resistant of all the C7 hydrocarbons to biodegradation (Helparn, unpublished results). The numerator compounds in Tr2 through Tr7 are all liable to biodegradation in

declining degrees. Hence, the fraction of labile compounds to a constant compound effect in variances interpreted as being due to biodegradation.

The graphical representation of C7 oil transformation correlation star diagram (C$_7$OTCSD) (Figure 4.12) clearly shows that all the ratios have similar pattern from Tr1 to Tr8 in a C$_7$ Oil Transformation Correlation Star Diagram.

The C$_7$ Oil Transformation Correlation Star Diagram (C$_7$OTCSD) shows that all the oil samples are following the same pattern, the pictorial representation of all the oil samples (A-15, A-17, A-11, A-16, A-10) showing that none of the Adhi Oil Field Potwar Sub Basin oil is biodegraded.

4.2.6   Secondary Alterations:

1- Biodegradation

2- Water Washing

3- Evaporative Fractionation

I.   2MH/3MH versus 2MCP/3MCP

The ratio of 2MH/3MH versus 2MCP/3MCP for Adhi Oil field oil samples was calculated to graphically represented the biodegradation in all the light hydrocarbons samples. The calculated values of oil samples are in Table 4.11.

Table 4. 11: Calculated ratios of 2MH/3MH versus 2MCP/3MCP for Adhi Oil Field oils.

Sr.	SAMPLE	2MH/3MH	2MCP/3MCP
1.	A-15	1.02	0.48
2.	A-17	1.09	0.53
3.	A-11	1.69	0.58
4.	A-16	1.32	0.50
5.	A-10	1.26	0.56

   i.   2MH= 2-Methylhexane
  ii.   3MH= 3-Methylhexane
 iii.   2MCP= 2-Methylcyclopentane

iv.   3MCP= 3-Methylcyclopentane
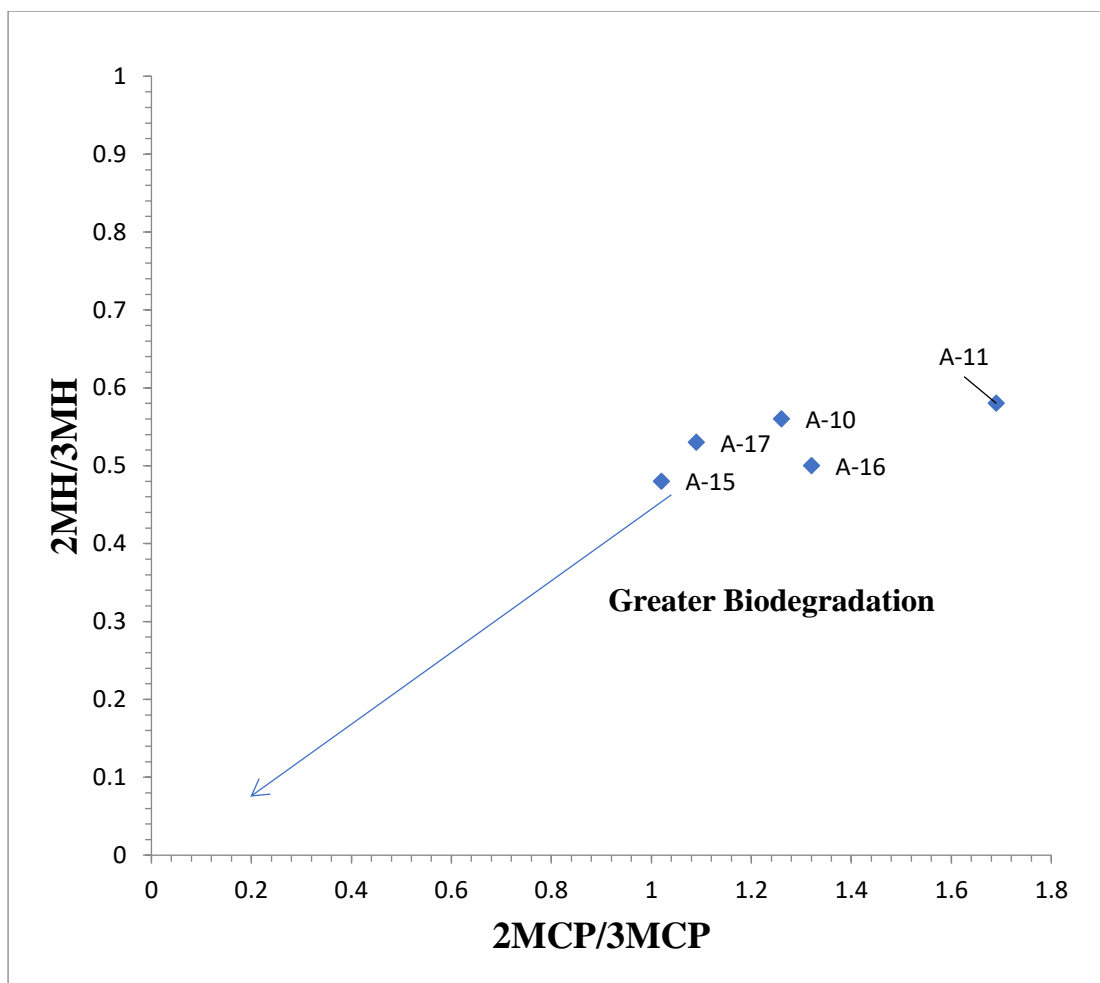
Figure 4. 13: Graphical representation of 2MH/3MH versus 2MCP/3MCP for Adhi Oil Field Oil samples.

There is a tough linear style among 2-methylcyclopentane/3-methylcyclopentane and 2-methylhexane/3-methylhexane. Though this plot is of basically invariant fractions, as proposed by Mengo (2000), and therefore the high association is to be expected, in this sample set the main control is extent of biodegradation. (Fig. 4.12) shows that 2-methylcyclopentane and 2-methylhexane are more susceptible to biodegradation than 3-methylcyclopentane and 3-methylhexane (Simon C. George et. al; 2002).

The graphical representation of the Adhi oil field samples for biodegradation based on 2MH/3MH versus 2MCP/3MCP ratios is shown in the (Fig. 4.13). The direction of arrow in the graph indicates towards the increasing degree of biodegradation. The ratios of 2-methylcyclopentane/ 3-methylcyclopentane and 2-

methylhexane/ 3-methylhexane indicating that Adhi Oil Field oil samples are not altered by biodegradation.

II. Aromaticity versus Paraffinicity

The graph of Aromaticity versus Paraffinicity for Adhi oil field (Fig. 4.13) shows the secondary alterations in oil samples.
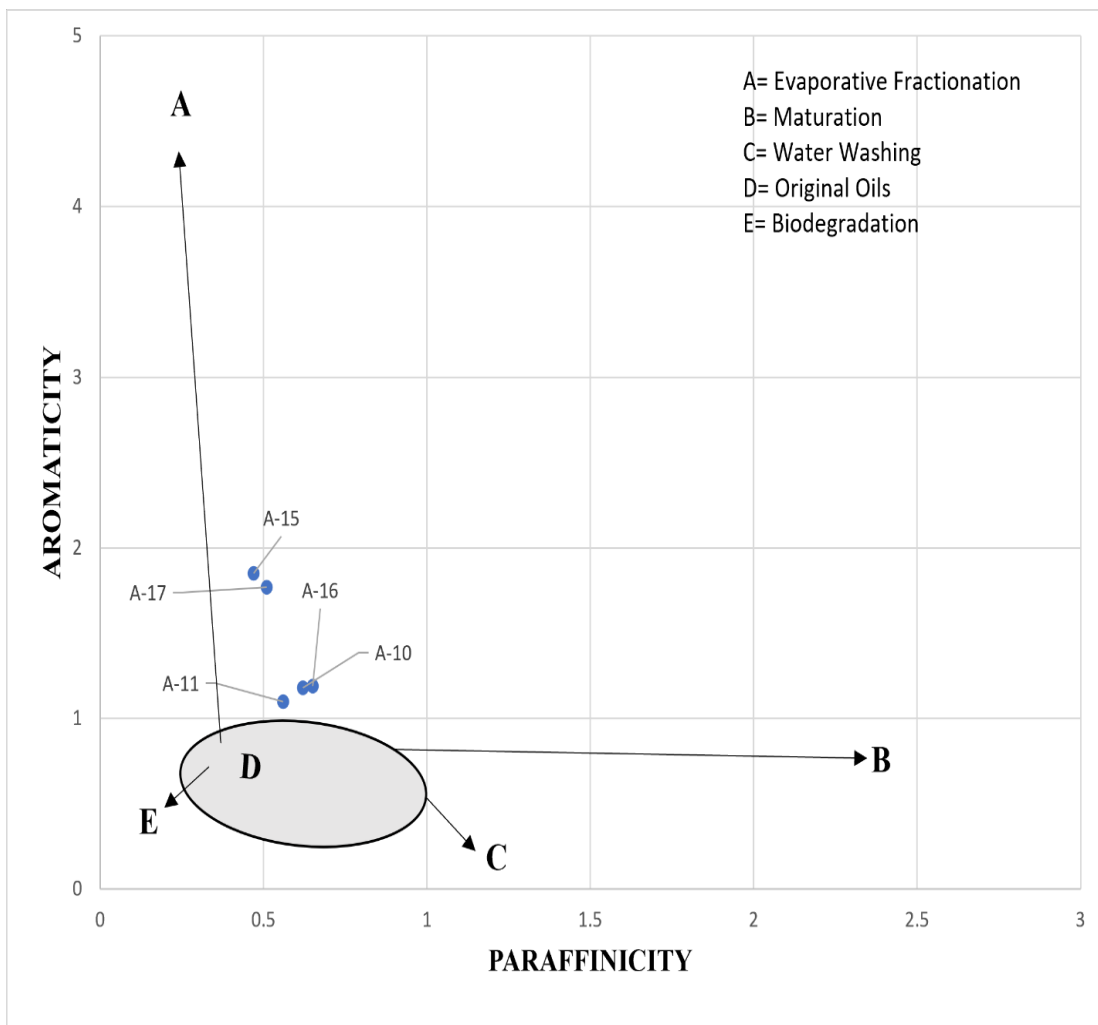
Figure 4. 14: Graphical representation of Aromaticity versus Paraffinicity to identify secondary alterations in Adhi Oil Field oil samples.

i.   A= Evaporative Fractionation

ii. B= Maturation

iii. C= Water Washing

iv. D= Original Oils

v. E= Biodegradation

Paraffinicity refers to n-alkane (paraffin) versus naphthene ratios. Rise in Paraffinicity in sediment extracts is related with growing yield and the advanced domination of n-

alkanes is related with growing stages of maturity. Decline in Paraffinicity in oils is diagnostic of change, mainly of biodegradation.

Aromaticity is based on the relative concentrations of aromatic hydrocarbons and n-alkanes of alike carbon number, thus: Benzene/ n-hexane, Toluene/ n-heptane.

The graphical representation of the Aromaticity versus Paraffinicity for Adhi Oil field samples clearly suggests that the oil samples A-15 and A-17 have more alterations comparative to A-10, A-11, and A-16 oils (Fig 4.14). The oil sample A-11, A-16 and A-10 are closely associated to each other.

The Toluene is by far the greatest water-soluble C_7 compound, all the samples are showing progressive Aromaticity. The graph shows that the alterations in oils are by Evaporative Fractionation.

III.   Molecular compound ratios as indicator of secondary alterations:

Concentrations of specific gasoline range components have been used as possible indicators of biodegradation and other reservoir alteration processes (Thompson, 1987; Osadetz et al.,1992; Rooney et al.,1998) (Table 4.12). The ratio of n-alkanes to their methylcyclic counterparts (nC6/MCYC5, nC7/MCYC6) as a Maturity indicator (a) (Fig. 4.15). The straight chain and branched alkanes ratios (iC5/nC5, 3MC5/nC6) indicate the Biodegradation (b) (Fig. 4.16). Water-washing is often indicated by the ratio between cyclic- or iso-alkanes and aromatic compounds of the same carbon number (3MC5/Benzene, MYC6/Toluene, CYC6/Benzene), given the large differences in solubility for each compound type (c) (Fig. 4.17). The low concentration of Benzene in these oils can sometimes be a product of the original source rock composition that generated the oils, rather than evidence of secondary alteration (Scott A. Harris; Michael J. Whiticar; Martin G. Fowler, 2003).

Table 4. 12: Calculated ratios of 3MCP/nC6, iC5/nC5, nC7/MCH, nC6/MCP Adhi oil field

Sr.	SAMPLE	3MCP/nC$_6$	iC5/nC$_5$	nC$_7$/MCH	nC$_6$/MCP	3MCP/Ben	MCH/Tol	CyC6/Ben
1.	A-15	0.61	0.87	0.47	1.16	0.85	0.92	1
2.	A-17	0.50	0.67	0.51	1.33	0.85	0.92	1
3.	A-11	0.51	0.62	0.56	1.17	0.85	0.92	1
4.	A-16	0.54	0.72	0.65	1.61	0.85	0.92	1
5.	A-10	0.56	0.73	0.62	1.56	0.85	0.92	1

i.   3MCP/nC6= 3-methylcyclopentane / n-hexane

ii. iC5/nC5= i-pentane / n-pentane

iii. nC7/MCH= n-alkane / methylcycloheptane

iv. nC6/MCP= n-hexane / methylcyclopentane

v.   3MCP/Ben= 3-methylcyclopentane / Benzene

vi.   MCH/Tol= Methylcyclohexane / Toluene

vii.   CyC6/Ben= Cyclohexane / Benzene
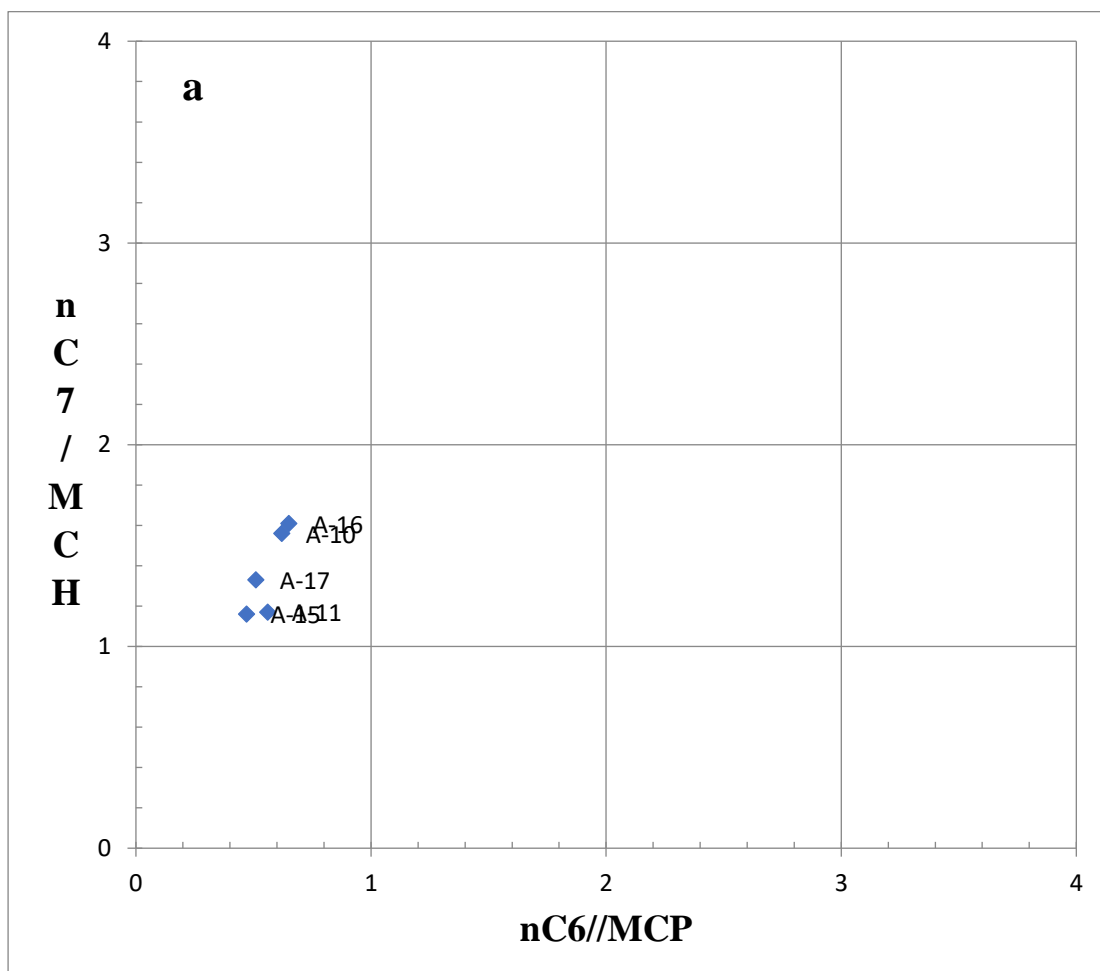
Figure 4. 15: Molecular compound ratios as indicator of maturity and secondary alteration processes for Adhi oil field oils.

All the samples are close to each other, no prominent separation in (nC_6/MCP, nC_7/MCH) ratios is noticeable. The ratios of n-alkanes to their methylcyclic counter parts (nC6/MCP, nC7/MCH) values as a maturity indicator shows that these oils are homogenous in composition.
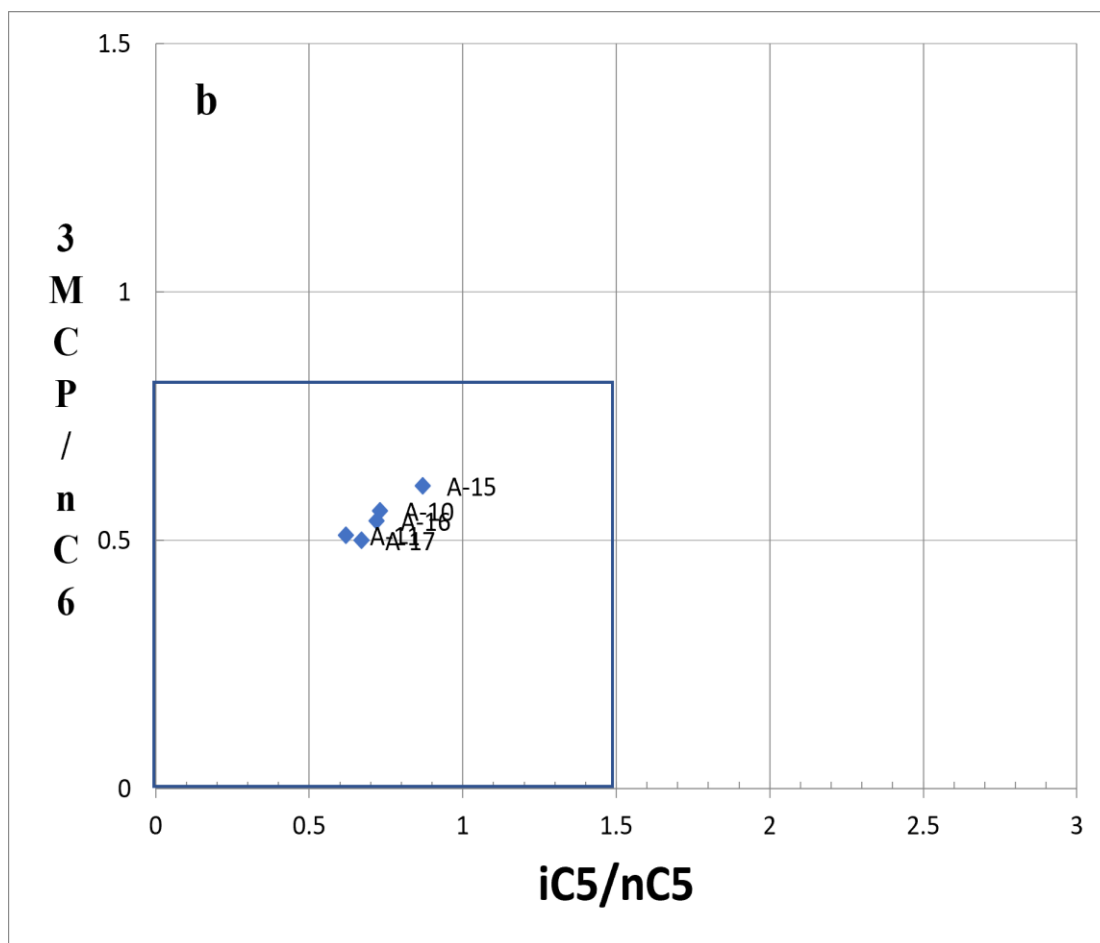
Figure 4. 16: Molecular compound ratios as indicator of biodegradation for Adhi oil field oils using 3-methylcyclopentane/n-hexane versus i-pentane/n-pentane. The square indicates the range of unaltered samples.

Biodegradation ratios between straight chain and branched alkanes (iC_5/nC_5, $3MC_5/nC_6$) indicate that no oil sample is biodegraded. All the oil samples A-10 to A-17 fall in unaltered zone. The rectangle represents the unaltered zone (Fig: 4.16).
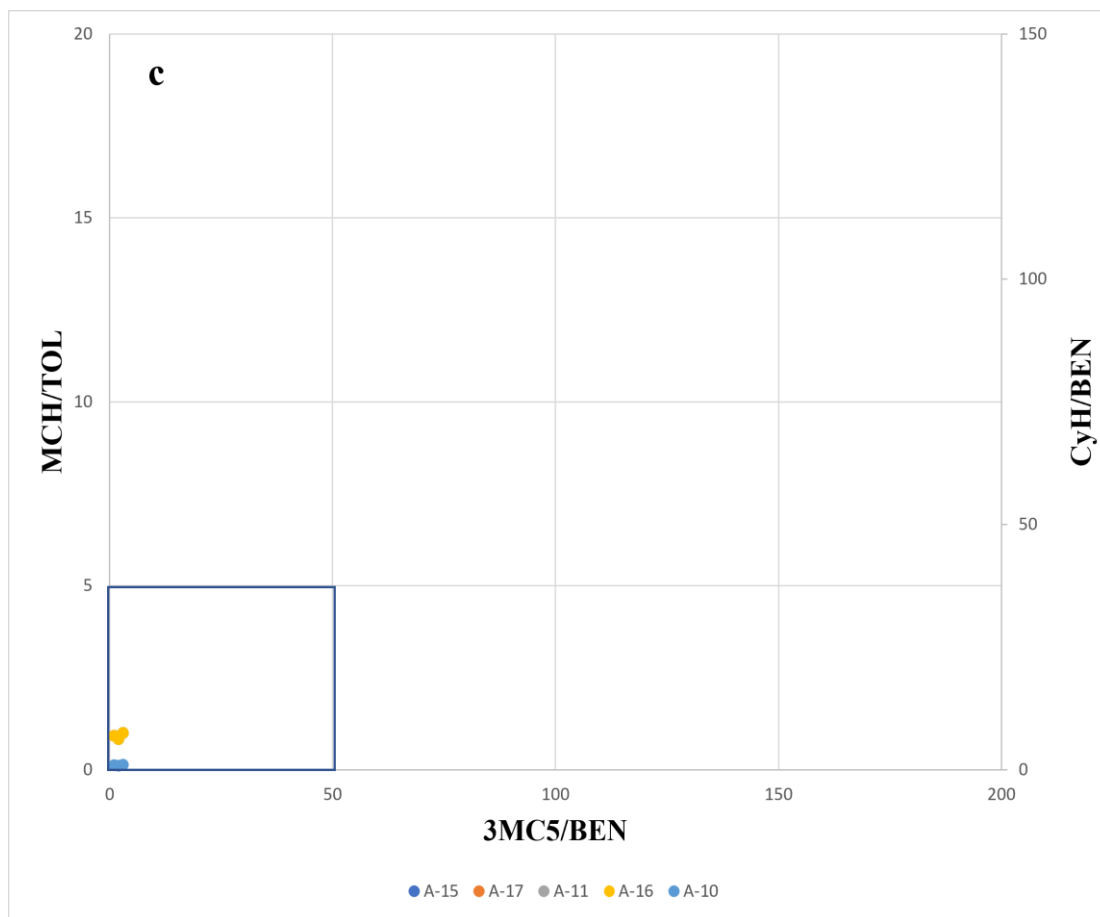
Figure 4. 17: Molecular compound ratios (3MC5/Benzene, MYC6/Toluene, CYC6/Benzene) as indicator of water washing. The square indicates the range of unaltered samples.

i.   3MCP/Ben= 3-methylcyclopentane / Benzene

ii.   MCH/Tol= Methylcyclohexane / Toluene

iii. CyC6/Ben= Cyclohexane / Benzene

The ratio between cyclic- or iso-alkanes and aromatic compounds of the same carbon number (3MC5/Benzene, MYC6/Toluene, CYC6/Benzene) for oil samples of Adhi oil field Potwar Sub Basin Pakistan indicates that none of the sample is affected by water washing.

CONCLUSION

The research work includes the geochemical characterization of different oil samples of Adhi Oil Field Potwar Sub Basin. The main conclusion derived from this research work includes:

1. Thermal Maturity of oil samples is analyzed using Heptane ratio and Heptane ratio versus Iso Heptane ratios plot which indicate that all oil samples are Normal except the A-11 oil sample which is Mature.

2. The Mango's invariance ratio K2 is a reliable indicator of source of organic matter input. The oil samples have same K2 value (0.76) showing that organic matter input is terrigenous. K1 and K2 ratios are very useful in source identification oil correlation studies as their ratio remains remarkably constant throughout hydrocarbon generation. All the oil samples have same K1 and K2 values (1.02,0.76), clearly indicating the same source rock for oil generation. The Aromaticity versus Paraffinicity plot and C_7 Oil Correlation Star Diagram (C_7OCSD) also depicting the same source for oil samples.

3. The Secondary Alterations assessment is carried out using 2MH/3MH versus 2MCP/3MCP, Aromaticity versus Paraffinicity, C_7 Oil Correlation Star Diagram (C_7OCSD), C_7 Oil Transformation Correlation Star Diagram (C_7OTCSD), and molecular compound ratios. All the parameters showed that none of the oil sample is biodegraded or affected by water washing, however the Aromaticity versus Paraffinicity and C_7OCSD represent that the oil samples are altered by Evaporative Fractionation.

REFERENCE

Ahmed, W., Alam, S., 2007. Organic geochemistry and source rock characteristics of salt range formation, Potwar Basin, Pakistan. Pak. J. Hydrocarb. Res. 17, 37–59.

Ali, F.M., Al-Khadrawi, R.M, Perzanowski, H. and Halpern, H.J. Central Saudi Arabia Crude Oil: A Geochemical Investigation. Petroleum Science and Technology 2002; 20(5&6):633-654.

Asif, M., Fazeelat, T., 2006. Characterization of aromatic hydrocarbons in Dhurnal oil from Northern Indus Basin. J. Chem. Soc. Pakistan 28, 169–175.

Asif, M., Grice, K., Fazeelat, T., Dawson, D., 2008. Oil–il correlation in the Upper Indus Basin (Pakistan) based on biomarker distributions and compound-specific d13C and dD. 15th Australian Organic Geochemistry Conf., National Wine Centre, Adelaide, SA, Australia.

Asif, M., Grice, K., Fazeelat, T., 2009. Assessment of petroleum biodegradation using stable hydrogen isotopes of individual saturated hydrocarbon and polycyclic aromatic hydrocarbon distributions in oils from the Upper Indus Basin, Pakistan. Org. Geochem. 40, 301–311.

Asif, M., Fazeelat, T., Grice, K., 2011. Petroleum geochemistry of the Potwar Basin, Pakistan: 1-Oil–oil correlation from biomarkers and d13C/dD. Org. Geochem. 42, 1226–1240.

Asif,M., T. Fazeelat / Applied Geochemistry 27 (2012) 1655–1665.

Buller, A. T., Bjørkum, P. A., Nadeau, P., & Walderhaug, O., 2005. Distribution of hydrocarbons in sedimentary basins - the importance of temperature.

Coward, M.P., Windley, B.F., Broughton, R.D., Luff, I.W., Peterson, M.G., Pudsey, C.J., Rex, D.C., Khan, M.A. 1986. Collision tectonics in the NW Himalaya. In: Collision Tectonics. Geological Society Special Publication 19, 201-219.

Dai J (1993a) Identification of coal formed gas and oil type gas by light hydrocarbons. Petroleum Exploration and Development 20(5): 26–32.

Davis, A. M., 1992. Shallow gas: an overview. Elsevier - Continental Shelf Research, 1077-1079.

E. Keshmirizadeh et al. (2012) Characterization and Evaluation of Light Hydrocarbon in Northwestern Iranian Crude Oil by Detailed Hydrocarbon Analysis (D.H.A)Gas Chromatography. J. Appl. Chem. Res., 6, 2, 38-47.

Fazeelat, T., Asif, M., Saleem, A., Nazir, A., Zulfiqar, M.A., Naseer, S., Nadeem, S., 2009. Geochemical investigation of Crude oils from different oil fields of the Potwar Basin. J. Chem. Soc. Pakistan 31, 863–870.

Fazeelat T, Jalees M I and Bianchi T S 2010 Source rock potential of Eocene, Paleocene and Jurassic deposits in the subsurface of the Potwar Basin, northern Pakistan; J. Pet. Geol. 33(1) 87–96.

Fazeelat, T., Asif, M., Jalees, M.I., Saleem, A., Nazir, A., Saleem, H., Nasir, S., Nadeem, S., 2011. Source correlation between biodegraded oil seeps and a commercial crude oil from the Punjab Basin, Pakistan. J. Petrol. Sci. Engin. 77, 1–9.

Floodgate, G. D., & Judd, A. G., 1992. The origins of shallow gas. Continental Shelf Research, 1145-1156.

Ganser, A., 1964. Geology of the Himalayas. Interscience Publishers London etc. (J.Wiley & Sons), 1-289.

Guo R, Li Y, Wang T, et al. (2009) Application of light hydrocarbon parameters in geochemical analysis of hydrocarbon accumulation. Special Oil and Gas Reservoirs 16(5): 5-9.

Halpern, H. I. Development and Applications of Light -Hydrocarbon-Based Star Diagrams. American Association of Petroleum Geologists Bulletin 1995; 76(6):801–815.

Harris, S. (2003). Classification of Duvernay sourced oils from central and southern Alberta using Compound Specific Isotope Correlation (CSIC). Bulletin Of Canadian Petroleum Geology, 51(2), 99-125.

Hwang, R. J., A. S. Ahmed, and J. M. Moldowan, 1994, Oil composition variation and reservoir continuity: Unity field, Sudan: Organic Geochemistry, v. 21, p. 171–188.

Iqbal, M, W, A., and Shah, S, M, I., 1980 A guide to the stratigrphy of Pakistan. Quetta, Geological Survey of Pakistan Records, v, 53, 34p.

Jaswal, T.M., Lillie, R.J., and Lawrence, R.D., 1997, Structure and evolution of the northern Potwar deformed zone, Pakistan: American Association of Petroleum Geologists Bulletin, v. 81, no. 2, p. 308–328.

Johnsone, G. D., Powall, C., Mac, A., Veevers, J.J., 1976. Spreading history of the eastern Indian Ocean, and greater India's northwards flight from Antarctica and Australia. Geological Society of America Bulletin, 87, 1560-1566.

Kadri, I, B., 1995. Petroleum Geology of Pakistan. Pakistan Petroleum Ltd, Karachi, 30, 275p.

Kaufman, R. L., A. S. Ahmed, and W. B. Hempkins, 1987, A new technique for the analysis of commingled oils and its application to production allocation calculations: Proceedings of the Sixteenth Annual Convention of the Indonesian Petroleum Association, Indonesian Petroleum Association, p. 247–268.

Kaufman, R. L., A. S. Ahmed, and R. L. Elsinger, 1990, Gas chromatography as a development and production tool for fingerprinting oils from individual reservoirs: application in the Gulf of Mexico: Gulf Coast Section of the Society of Economic Paleontologists and Mineralogists Foundation Ninth Annual Research Conference Proceedings, p. 263–282.

Kazmi, A.H., and Rana, R.A., 1982. Tectonic map of Pakistan: Geological Survey of Pakistan, scale: 1:2,000,000.

Kazmi, A.H. and M.Q. Jan, 1997. Geology and Tectonics of Pakistan. Graphic Publishers Karachi. Pakistan, pp 1-554.

Khan, M.A., Ahmed, R., Raza, H.A., and Kemal, A., 1986. Geology of petroleum in Kohat-Potwar Depression, Pakistan: American Association of Petroleum Geologists Bulletin, v. 70, no. 4, p. 396– 414.

Kimble B., 1972. The geochemistry of triterpenoid hydrocarbons. Ph.d Thesis, University of Britol, 302p.

MANCXI F. D. (1987) An invariance in the isoheptanes of petroleum. Science 273, 5 14-5 17.

Mango, F. D. An Invariance in the Isoheptanes of Petroleum. Science 1987; 237:514-517.

Mango, F. D., 1991, The stability of hydrocarbons under the time temperature conditions of petroleum genesis: Nature, v. 352, p. 146–148.

Mango F.D. (1990a) The origin of light cycloalkanes in petroleum. Geochim. Cosmochim. Acta. 54, 23-27.

Mango F.D. (1990b) The origin of light hydrocarbons in petroleum: A kinetic test of steady-state catalytic hypothesis. Geochim. Cosmochim. Acta. 54, 1315-1323.

Mango F.D. (1994) The origin of light hydmcarbans in petroleum: Ring preference in the closure of carbocyclic rings. Geochim. Cosmochim. Acta. 58, 895-901.

Mango F (1997) The light hydrocarbons in petroleum review. Organic Geochemistry 26(7):417–440.

Odden W (1999) A study of natural and artificially generated light hydrocarbons (C4–C13) in source rocks and petroleum fluids from offshore Mid-Norway and the southernmost Norwegian and Danish sectors. Marine and Petroleum Geology 16(8): 747–770.

Oil and Gas Development Corporation limited (OGDC), 1996, Pakistan petroleum prospect- An overview: Islamabad, Oil and Gas Development Corporation, 22p.

Osadetz, K.G., Brooks, P.W. and Snowdon, L.R. 1992. Oil families and their sources in Canadian Williston Basin (southeastern Saskatchewan and southwestern Manitoba). Bulletin of Canadian Petroleum Geology, v. 40, p. 254-273.

Palmer, S. E., 1984, Effect of water washing on C15+ hydrocarbon fraction of crude oils from northwest Palawan, Philippines: AAPG Bulletin, v. 68, p. 137–149.

Paracha, W., Kemal, A., Abbasi, F., 2000: Kohat Duplex in Northern Potwar Deformed Zone,Pakistan. Geol. Survey. Of Pakistan, Geological, vol.5. pp. 99-107.

Perrodon, A., 1983. Dynamics of oil and gas accumulations (Vol. 5): Editions TECHNIP.

Peterson, M.G., Windley, B.F., 1985. Rb-Sr dating of the Kohistan arc Batholith in the Trans Himalaya of North Pakistan and tectonic implications. Earth and Planetary Science Letters 74, 54-75.

Petroconsultant, 1996, Petroleum exploration and production digital database: Petro-consultants, Inc., [P.O. Box 740619, 6600 Sands Point Drive, Houston TX 77274-0619, U.S.A. or Petro-consultants, Inc., P.O. Box 152, 24 Chemin de la Mairie, 1258 Perly, Geneva, Switzerland.

Philip, R. P., 2003. Formation and geochemistry of oil and gas. University of Oklahoma, Norman, OK, USA. Treatise on geochemistry, v, 7, 223-256.

Powall, C. McA., 1979. A speculative tectonic history of Pakistan and surroundings: some constraints from the Indian Ocean, In: Farah, A., DeJong, K. A. (Eds.) Geodynamics of Pakistan. Geological Survey of Pakistan, Quetta, 5-24.

Quadrei, Viqar-un-Nisa, and Quadrei, S.M.G.J., 1996, Exploration anatomy of success in oil and gas exploration in Pakistan, 1915–94, Oil and Gas Journal, v. 94, i. 20.

Quadri, V.N., Quadri, S.M.J.G., 1997. Indus Basin of Pakistan contains few wells. Oil and Gas Journal Archives 95, i. 24.

Rice, D. D., & Claypool, G. E., 1981. Generation, accumulation, and resource potential of biogenic gas. AAPG bulletin, 65(1), 5-25.

Rooney, M.A. 1995. Carbon isotope ratios of light hydrocarbons as indicators of thermochemical sulfate reduction. In: Organic Geochemistry: Developments and Applications to Energy, Climate, Environment and Human History, Selected Papers from the 17th International Meeting on Organic Geochemistry. J.O. Grimalt and C. Dorronsoro (eds.). p. 523-525.

Searle, M. P., 1991. Geology and Tectonics of the Karakorum mountains. John Wiley and Sons, New York, 358.

Shah, S.M.I., Ahmed, R., Cheema, M.R., Fatmi, A.N., Iqbal, M.W.A., Raza, H.A., and Raza, S.M., 1977, Stratigraphy of Pakistan: Geological Survey of Pakistan, Memoirs, v. 12, 137 p.

Shen Z, Wang P, Liu S, et al. (2011) Geochemical characteristics of light hydrocarbon in natural gas in the middle member of the west Sichuan Depression, China. Journal of Chengdu University of Technology: Science and Technology Edition 38(5): 500–506.

Slentz, L. W., 1981, Geochemistry of reservoir fluids as a unique approach to optimum reservoir management: Society of Petroleum Engineers paper 9582, Proceedings of the Society of Petroleum Engineers Middle East Technical Conference, Manama, Bahrain, p. 37–50.

Thompson K. F. M. (1983) Classification and thermal history of petroleum based on light hydrocarbons. Geochim. Cosmochim. Acta 47, 303-316.

Thompson, K. F. M., 1987, Fractionated aromatic petroleums and the generation of gas-condensates: Organic Geochemistry, v. 11, p. 573–590.

Tissot, B.P and welte, D.H., 1984. Petroleun formation and occurrence. Second revised and enlarged edition, Berlin Heidelberg New York Tokyo, springer-verlag, 20, 30, 73, 94, 198, 242, 699, 53-53.

Tobin, R.C., and Claxton, B.L., 2000, Multidisciplinary thermal maturity studies using vitrinite reflectance and fluid inclusion microthermometry; A new calibration of old techniques: American Association of Petroleum Geologists Bulletin, v. 84, no. 10, p. 1647–1665.

Traloar, P. J., Izzat, C. N., 1993. Tectonics of the Himalayan collision between the Indian Plate and the Afghan block: A synthesis in: Traloar, P. J., Searle, M. P. (Eds.), Himalayan Tectonics. Geological Society of London (Special publication) 74, 69-87.

Volk, H., George, S.C., Middleton, H. and Schofield, S. Geochemical Comparison of Fluid Inclusion and Present-Day Oil Accumulations in the Papuan Foreland –

Evidence for Previously Unrecognized Petroleum Source Rocks. Organic Geochemistry 2005; 36(1):29-51.

Wandrey, C. J., Law, B.E and Shah, H. A., 2004. Patala- Nammal composite total petroleum system, Kohat-Potwar geological province, Pakistan, United States Geological Survey Bulletin Open File Report 2208-B, 1-18.

Yu C, Gong DY, Huang SP, et al. (2014) Characteristics of light hydrocarbons of tight gases   and its application in the Sulige gas field, Ordos basin, China. Energy Exploration and Exploitation 32(1): 211–226.

Zhang, M., 2005. Compositional characteristics and geochemical significance of light hydrocarbons for crude oils in Tarim Basin, China. Chinese Journal of Geochemistry, 24(3), pp.228-231.

GEOCHEMICAL CHARACTERIZATION OF RESERVOIR FLUIDS FOR CONNECTIVITY AND ALTERATIONS, ADHI OIL FIELD, POTWAR SUB BASIN, PAKISTAN

by Syed Abdul Quddus

GEOCHEMICAL CHARACTERIZATION OF RESERVOIR FLUIDS FOR CONNECTIVITY AND ALTERATIONS, ADHI OIL FIELD, POTWAR SUB BASIN, PAKISTAN

ORIGINALITY REPORT

18% SIMILARITY INDEX	5% INTERNET SOURCES	16% PUBLICATIONS	2% STUDENT PAPERS

PRIMARY SOURCES

1   Henry I. Halpern (2). "Development and Applications of Light-Hydrocarbon-Based Star Diagrams", AAPG Bulletin, 1995
Publication   5%

2   Clifford C. Walters, Gary H. Isaksen, Kenneth E. Peters. "Chapter 10 Applications of Light Hydrocarbon Molecular and Isotopic Compositions in Oil and Gas Exploration", Springer Science and Business Media LLC, 2003
Publication   1%

3   www.sciencepub.net
Internet Source   1%

4   Asif, Muhammad, and Tahira Fazeelat. "Petroleum geochemistry of the Potwar Basin, Pakistan: II â€" Oil classification based on heterocyclic and polycyclic aromatic hydrocarbons", Applied Geochemistry, 2012.
Publication   1%