

**DISTILLATION BEHAVIOR OF VARIOUS PARENT AND  
CHEMICALLY DISPERSED CRUDE OILS: COMPARISON OF  
YIELDS, CHEMICAL COMPOSITIONS AND FUEL QUALITY OF  
DISTILLATE FRACTIONS**



**Submitted By  
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**(Ph. D. Scholar)**

**INSTITUTE OF CHEMICAL SCIENCES  
UNIVERSITY OF PESHAWAR  
(SESSION, 2009-2010)**

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**SYED MOHAMMAD SOHAIL**

*A dissertation submitted to the University of Peshawar in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry*

**INSTITUTE OF CHEMICAL SCIENCES  
UNIVERSITY OF PESHAWAR  
(SESSION, 2009-2010)**

## DECLARATION

I, S. Mohammad Sohail, Ph.D. scholar, Institute of Chemical Sciences, University of Peshawar declare that the present dissertation titled **“Distillation Behavior of Various Parent and Chemically Dispersed Crude Oils: Comparison of Yields, Chemical Composition and Fuel Quality of Distillate Fractions”** is based on the results of a study carried out as partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry. All previous research has been properly cited. The thesis is in accordance with the University regulations and has not been accepted for any degree and not concurrently submitted in candidature of any other degree. Further, disclosing, copying, distributing or taking any action in reliance on the contents of this dissertation is strictly prohibited.

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## Certificate of Approval

This is to certify that the research work presented in this thesis entitled “Distillation Behavior of Various Parent and Chemically Dispersed Crude Oils: Comparison of Yields, Chemical Composition and Fuel Quality of Distillate Fractions” was conducted by Mr. Syed Muhammad Sohail, Ph.D. scholar (Enrolment #002/Fuel/ICS/2009-10-16) under the supervision of Prof. Dr. Imtiaz Ahmad. No part of this thesis has been submitted anywhere else for any other degree. This thesis is submitted to the Institute of Chemical Sciences, University of Peshawar, Pakistan in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the field of Chemistry.

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**In the Name of Almighty**

**ALLAH**

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## LIST OF ABBREVIATIONS AND NOTATIONS

<b>Abbreviation</b>	<b>Explanation</b>
ASTM	American Society for Testing and Materials
API	American Petroleum Institute
EOR	Enhanced Oil Recovery
H/C	Hydrogen to Carbon ratio
RFCC	Refinery Fluid Cracking Cracking
PAHs	Poly Aromatic Hydrocarbons
SARA	Saturates, Aromatics, Resins and Asphaltenes
VPO	Vapor Pressure Osmometry
SANS	Small Angle Neutron Scattering
SDS	Solid Detection System
CMC	Critical Micelle Concentration
CNAC	Critical Nano-Aggregate Concentration
DMNS	Decyl Methyl-naphthalene Sulfonate
DOR	Dispersant-to-Oil Ratio
IL	Ionic Liquids
MCOs	Mexican Crude Oils
WDT	Wax Dissolution Temperature
DSC	Differential Scanning Calorimetry
TGA	Thermo-Gravimetric Analysis
DMV	Diameter of Mean Volume
IFT	Interfacial Tension
SDBS	Sodium Dodecyl Benzene Sulfonate

BFT	Baffled Flask Test
SFT	Swirling Flask Test
DPD	Dissipative Particle Dynamics
GPUs	Graphics Processing Units
ASB	Alkyl Sulfo Betaine
XSB	Xylyl substituted alkyl Sulfobetaine
AR	Analytical Reagents
CTAB	Hexadecyl Trimethyl Ammonium Bromide
SDS	Sodium Dodecyl Sulfate
TBP	True Boiling Point

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## ABSTRACT

Crude oil after preliminary treatments is subjected to refining so as to get marketable products like naphtha, gasoline, kerosene, diesel fuel, lubricating oil feed stock, furnace oil, etc. A large amount of asphalt/bitumen is left over as residue. Owing to its high viscosity, density and contamination by sediments as well as high asphaltene and resin contents, the residue cannot be directly used as a boiler fuel and instead used for non-fuel purposes. The global demand for energy continues and will increase over the next few decades as the world's energy consumption will increase phenomenally in the next few decades. Alternative energy sources like nuclear and renewable energy have attracted much attention in the recent years, however, the main role of these sources, will be to supplant, rather than to substitute the fossil fuels. Therefore, major breakthroughs in the oil industry's core science and engineering are needed so as to meet with the World's growing energy demand for petro-fuels. The high yields of residue/residuum is an ongoing challenge at a refinery and economic & strategic reasons demands the exploitation of residual streams. Accordingly, the selection of proper processes may play a key role so as to cope with the challenge.

The objective of the present thesis was to employ atmospheric distillation process using three crude oils dispersed with chemical surfactants in order to get lighter fuel fractions in high yields in comparison with the plain crudes (control). The thesis summarizes the characterization of the crude oils with respect to their key physico-chemical properties including density ( $\text{kg/m}^3$ ), viscosity ( $\text{mPa}\cdot\text{s}$ ), API gravity, total acid number ( $\text{mg KOH/g}$ ), and asphaltene contents ( $\text{wt } \%$ ). Chemical dispersants i.e. sodium dodecyl sulfate (SDS); a anionic surfactant, hexa decyltrimethylammonium bromide as cationic surfactant, and Triton-X as neutral surfactant were used. The crude oils investigated included paraffinic (denoted as RCP-I), naphthenic (denoted as RCN-II)



and aromatic (denoted as RCA-III) Pakistani crudes. Each crude oil was spiked with the varying dispersant –to-oil ratios (5:100, 10:100, 15:100, 20:100, 25:100 and 30:100) and then subjected to atmospheric distillation. The distillation of each surfactant-dispersed crude oil was carried out in comparative experiments with the plain crude oil so as to investigate the effect of each dispersant on the yield, chemical composition and fuel properties of the derived distillate fractions (F1, F2 and F3). The Gas Chromatographic-Mass Spectrometric analysis (GC-MS) was carried out in order to ascertain compositional stability of the distillate fractions. The desired fuel properties of the light fractions were also determined as per ASTM standards and compared with the generic gasoline and diesel fuel samples.

Looking at the results, we conclude that using chemically dispersed crudes enabled to obtain better yields of the light distillate fractions in comparison with the control without disturbing the key fuel properties. Among the three crudes used, the SDS-dispersed RCA-III, CTAB-dispersed RCN-II and Triton-X-100-dispersed RCN-II crudes were more effective which gave significant increase in the yields of light distillate fractions and reduced the residues without disturbing the fuel quality criteria.

# **CHAPTER # 1**

# **INTRODUCTION**

# CHAPTER- 1

## INTRODUCTION

### 1.1. PROBLEM STATEMENT/SCOPE OF THE THESIS

Crude oil after preliminary treatments is subjected to refining so as to get a number of valuable products including, gasoline, kerosene, diesel fuel, lubricating oil feed stock, furnace oil, etc. During refining, a large amount of asphalt/bitumen is obtained as residue (10-35%) [1]. Owing to undesired properties and contamination by inorganic sediments as well as by high asphaltene and resin contents, the residue cannot be directly used as a boiler fuel and used for non-fuel purposes [2, 3].

The global demand for energy resources continues and increases day by day as the energy consumption has increased considerably. A number of alternative sources including nuclear and renewable energy (biomass) which have drawn much attention of the energy sector recently, however, the role of these sources, is just to supplant, rather than to substitute the generic fossil fuels. Therefore, there is a dire need of major breakthroughs in the oil industry's core science and engineering as to cope with the situation. Most of the recent research is focused on the plausible solutions of the problems being faced during oil refining [4-6] which include the high yields of residue/residuum.

Ample research is underway on upgrading crude oil and processing of heavy residues so as to get high yields of low molecular weight fraction (s) through several options like delayed coking [2], thermal cracking [7], catalytic cracking [8], hydrocracking [9], steam cracking [10], dispersed catalytic upgradation [11], etc. However, several issues like the changes in the chemical composition of the derived light fractions and the change in the physico-chemical properties have created

difficulties for the refiners to meet with the standard specifications. Further, most of the afore mentioned methods are costly owing to requirement of severe reaction conditions and expensive catalysts. In order to avoid these problems, new oil refining approaches like hydrogen addition and carbon rejection, deasphalting, gasification, delayed coking, residue fluid catalytic cracking (RFCC), ebullated-bed hydrocracking, slurry-phase hydrocracking, fixed-bed hydro-treating, microwave extraction, treatment with ionic liquids, etc. [12-16] are researched so as to get aimed high yields of light distillate fractions [17-18]. However, further research is needed for integrated schemes focusing on product yields, composition, quality of products, elimination of low-value by-products, reduction in impurities/coking, and removal of obnoxious sulfur and nitrogen. Thus, there is an urgent need to search for new and novel cost effective methods so as to get last drop of distillable oils.

The main factors responsible for high amount of residual fractions during atmospheric distillation of petroleum crudes are the heavy molecular weight components of the crude oil like asphaltenes and resins [19]. Under ordinary atmospheric pressure distillation, the giant asphaltic and resinous molecules are not suffered from thermal scissions, remain intact and thereby concentrate in residues. Further, these constituents tend to form stable aggregate, hence keep some hydrocarbons including sterane biomarkers, polyaromatic hydrocarbons, C<sub>27</sub>–C<sub>31</sub> hopanes, and resins caged/occluded with in asphaltenes via strong intermolecular forces. Modifications in the conventional atmospheric distillation to increase the yields without reducing the quality of the derived premium fuels could be a better solution.

Asphaltenes have island architecture, which provide space/rooms for the occluded hydrocarbons and protected them from thermal degradation during distillation and even during petroleum formation by diagenesis. The occluded components can be

released by heat treatment, just like the biomarkers which are released from the kerogen during crude oil formation. However, this is possible only, if the interaction between the adjoined asphaltene molecules is disrupted so as to open up caged hydrocarbons. Dispersion of crude oils with surfactants prior submitting to distillation would be an ideal solution in this regard.

The idea of the this thesis/work is to explore the efficacy of various chemical surfactants to keep the asphaltenes emulsified during the distillation and to release the oil caged with in the asphaltene framework not only to in increase the yield of light distillate fractions i.e. gasoline and diesel fuels from various Pakistani crudes without disturbing the chemical composition and desired fuel properties but also to combat with the collateral process problems associated with asphaltenes and resins.

## **1.2. CRUDE OIL**

### **1.2.1. Origin**

Crude oil (parent oil) commonly known as petroleum exists down the earth crust at greater depths in geo-pressurized areas of the world. Physically, it is black in color, viscous to flow and has a bad odor. Chemically, it is comprised mostly of hydrocarbons exist in the range of 50%-97%, other organic compounds exist in the range of 6%-10%, inorganic metals up to <1% and gases mostly in dissolved forms. The major precursors for formation of crude oil are the remains of animals and plants (called biomass) who after being settled at the bottom of an ocean or lake and combined with mud, silt and sand, which then undergo physico-chemical changes (via diagenesis and catagenesis) assisted by heat, pressure and microbes. These activities convert hydrocarbons into liquid oil which is eventually forced into porous rock strata called traps/reservoirs. The reservoir rocks are covered by an impervious rock (cap rocks) that prevents the passage of the hydrocarbon fluids to the surface.

There are a series of physico-chemical changes occur in the fossilized remains of animal and plants under submerged or anaerobic conditions. The organic matter accumulated in the sedimentary rocks first converted into kerogen; a precursor for the formation of hydrocarbons constituting the crude oil. The kerogen consists of a complex mixture of lipids, polymers, and biochemicals cross-linked into a very high molecular weight geopolymer that is insoluble in any organic solvent. Chemically, kerogen is composed of a number of aromatic, naphthenic, naphthoaromatic, heteroaromatic cores that are linked by aliphatic, ester, ether, or thioether chains, in addition to pendant groups present on the cores. Further changes undergo in the kerogen through catagenesis, or thermal cracking, thereby releasing petroleum which accumulate in geological formations called traps [20- 24].

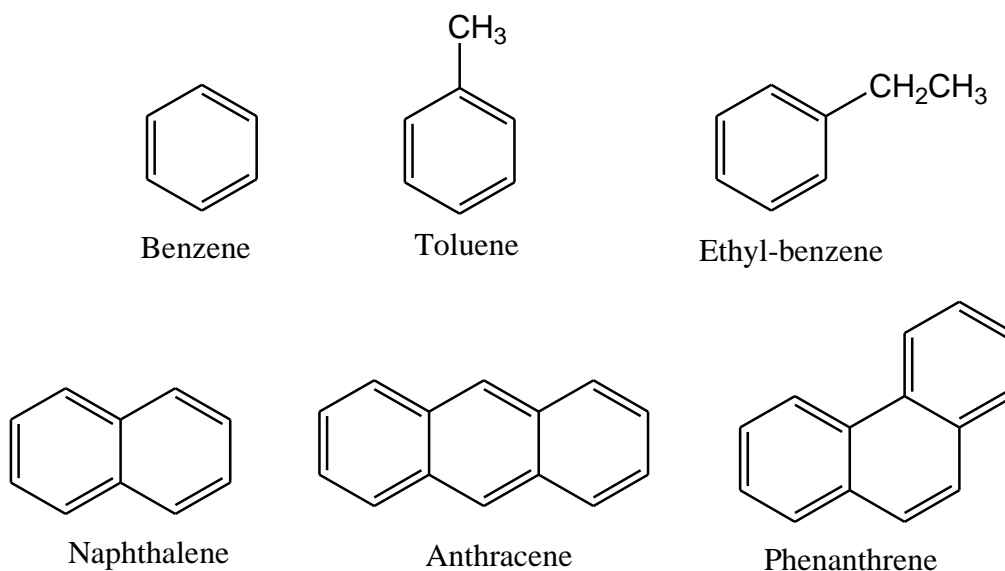
The crude oil after its detection is recovered by standard drilling methods (cable tool and rotary). The recovered oil accompanied by sediments and water (brine) is pumped/transmitted to an oil refinery where it is subjected to preliminary treatments (sludge removal and dewatering) followed by conversion to marketable products like gasoline, diesel fuel oil, kerosene, lubricating oil feed stocks, etc. [25, 26].

### **1.2.2. Constituents of Crude Oil**

The crude oil is a mixture of different hydrocarbons including paraffins, naphthenes, aromatics, and oxygenates. It is liquid at room temperature and pressure. In addition to carbonaceous matrix, it is also associated with non-hydrocarbons such as nitrogen, carbon dioxide, sulphur, hydrogen sulphide, metals and water. The hydrocarbons in crude oil include aliphatics, cycloaliphatics and aromatic compounds. Nitrogen, oxygen and sulfur containing hydrocarbons and trace quantities of metals include iron, nickel, copper and vanadium are also present.



mostly concentrate in the heavy oil fractions like resin or asphaltenes or residue. Most of the aromatic compounds contain substituents like alkyl chains and cycloalkane rings, along with additional aromatic rings. Examples of typical aromatic hydrocarbons found in petroleum are:



Low and high molecular weight impurities are present in crude oil including carbon dioxide (CO<sub>2</sub>), hydrogen sulphides (H<sub>2</sub>S), oxides of metals (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc.), salts (NaCl, CaCO<sub>3</sub>, etc.) and water. Thiophene, benzothiophene, aromatic sulphides, sulphones, asphaltenes, waxes, resins, etc. are present as high molecular weight impurities. In addition to these, miscellaneous impurities are also present which mainly added to the crude oil during production, transportation and processing. These include acids, alcohols, detergents and polymers. Some minor impurities also exist in crude petroleum. These are formed due to association of the above mentioned impurities with the hydrocarbon matrix. These are clathrates, colloids, crystalline solids, flocs, sludge and slug.

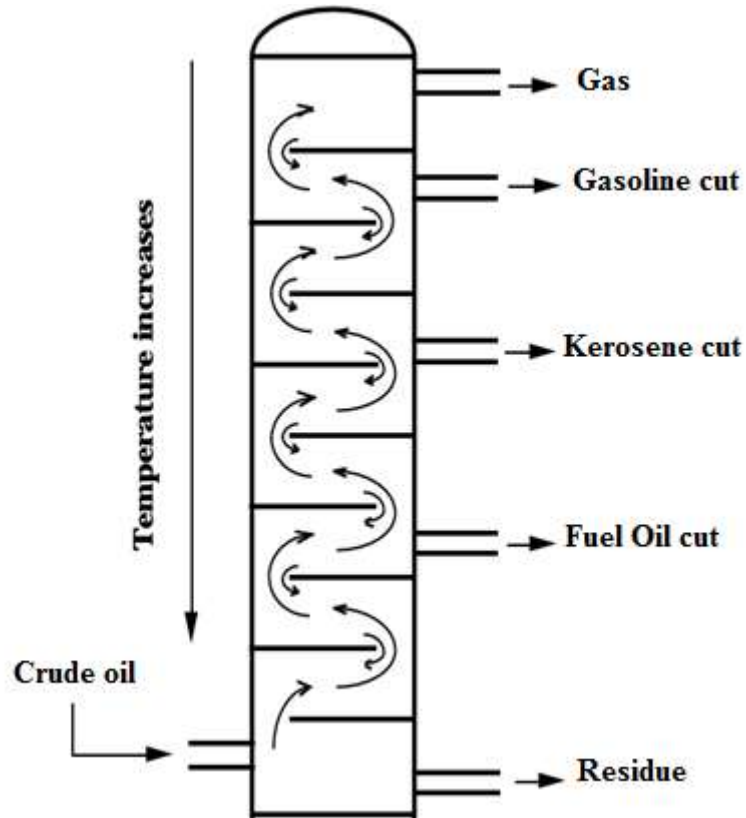


Additionally, some chemicals which may be needed during the transportation and logistical handling are added to the crude oil. These include drag reducing agents, pour point depressants, mercaptan scavengers, hydrogen sulfide scavengers, etc.

### **1.2.3. Refining of Crude Petroleum**

Refining of petroleum is a complex process which is carried out so as to get marketable products with the desired qualities and in the amounts required by the market. Distillation, sweetening, dewaxing, thermal cracking, catalytic cracking, thermal and catalytic reforming are the widely used refining steps. Refinery operations are aimed to produce products that meet specifications set by ASME (American Society of Mechanical Engineers), ASTM (American Society for Testing and Materials), and API (American Petroleum Institute).

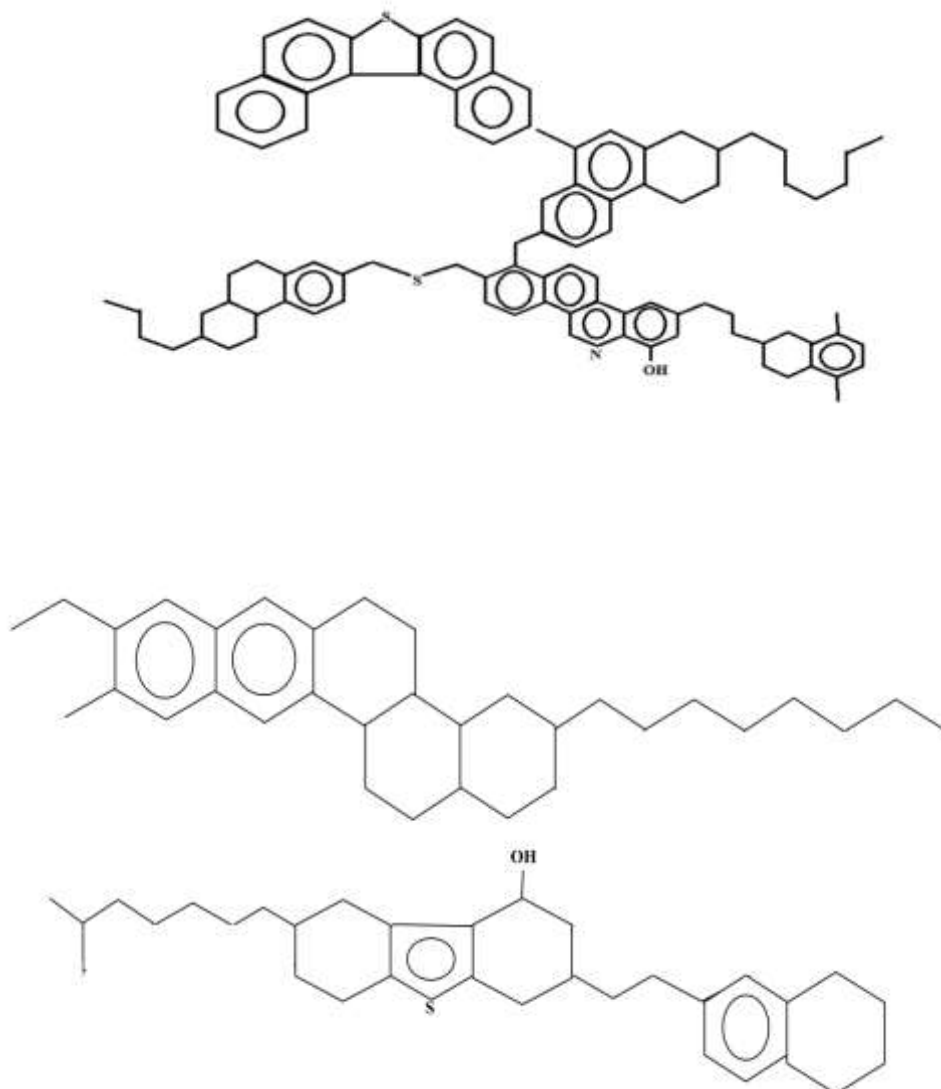
Even though distillation is the first step in crude oil refining, however, the as received crude oil is contaminated by salt water and sediments which should be removed owing to their detrimental effects on refinery operations. After the removal of salt and water, the crude petroleum is sent to the refinery where it is fractionally distilled in large stills and various fractions are separated after condensing them in towers erecting high in to sky. These stills or high towers are known as fractionating columns. The vapors, when raised up in the fractionating column are cooled and subsequently condensed in the shelves at various heights. The highest boiling fraction condenses at the bottom and the lowest boiling fraction at the top of the still. Uncondensed fractions are collected as still gasses at the head of column. Out let has been provided at various heights so as to collect the fractions [27-30]. A typical distillation column is provided in Fig. 1.1.



**Fig.1.1.** Schematic of a typical distillation unit

### 1.3. ASPHALTENES AND RESINS

**Asphaltenes:** The residual fractions mostly contain asphaltenes and resins which create several problem during oil refining operations. These are hydrocarbon compounds having higher than 20 carbon atoms in a single molecule which are often solids at ambient temperature. Therefore, the crude oils which contain excess of hydrocarbons with molecular size larger than  $C_{20}$  (particularly  $C_{40}$ ) lead to solid deposits and gave high residues. Most of these high molecular weight constituents are polycyclic aromatic or naphthenoaromatic compounds with heteroatoms (O, N, S) and side chain substituents. The distribution of molecular weight of apshaltenes is within 500-2000. Some hypothetical structures of typical asphaltenes are shown in Fig. 1.2.



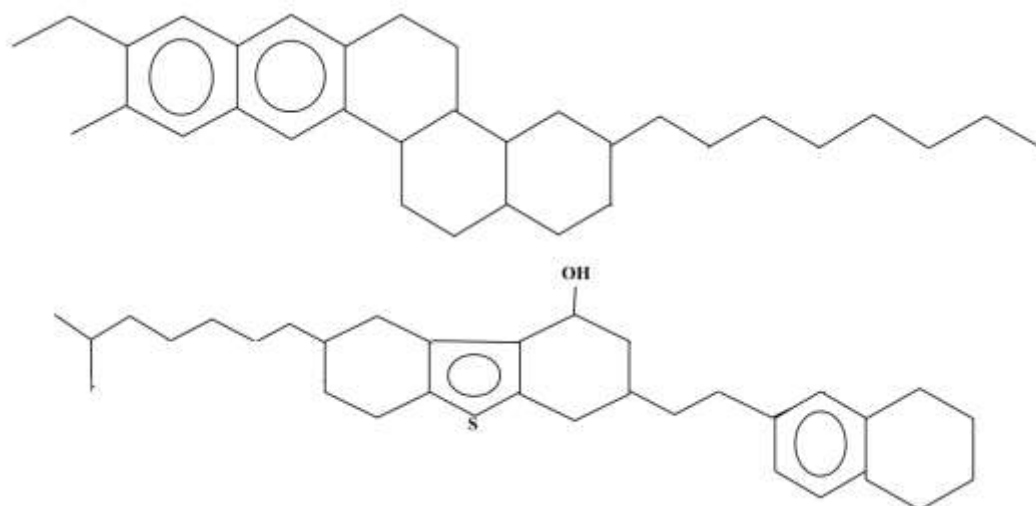
**Fig.1.2.** Hypothetical structure of a typical asphaltene

There are a number of problems associated during crude oil production, transportation and its subsequent processing due to asphaltenes. The most frequent problems encountered during upstream and downstream production operations include:

- a. Precipitation problems in surface facilities, pipelines, downhole tubulars, and within the reservoir
- b. The resultant deposits mainly due to high atomic ratio carbon/hydrogen, high aromaticity and high condensation of aromatic rings present in the asphaltenes cause loss in recovery of distillate fractions.

- c. Fouling, foaming, erosion, corrosion, etc.
- d. Formation of tar mats and sites for paraffin crystallization.
- e. Formation of waste during the thermal and thermo-chemical processing of heavy residues of oil as residue.
- f. Stabilization of emulsions which can cause several secondary problems.
- g. In the presence of acidic species, they create “salts”.
- h. The deposits also affect the efficiency of the refinery equipment
- i. Coat surface and interfere with heat and mass transfer processes.
- j. Cause sedimentation and plugging during crude oil storage.
- k. Act as precursors for coke formation and hence responsible for deactivation/poisoning of catalysts used in downstream processing which decline the process efficiency.
- l. The economic impact; the cost associated with the asphaltene deposition during production and refining operations is in billions of dollars a year.

**Resins:** Resins are lower molecular weight analogs of the asphaltene. The resins are polar molecules containing heteroatoms such as nitrogen, oxygen or sulphur. Resins are defined as the fraction soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane. They have a higher H/C ratio of 1.2-1.7 compared to 0.9-1.2 of asphaltenes. They are structurally similar to asphaltenes, but smaller in molecular weight (< 1000 g/mole). Naphthenic acids are commonly regarded as a part of the resin fraction. The distinct difference between the asphaltenes and resins is that the asphaltenes are insoluble in heptane or pentane, while resins are miscible/soluble. Some structures of petroleum resins are depicted in Fig.1.3.



**Fig.1.3.** Hypothetical structures of typical resins

#### 1.4. DISPERSANTS FOR ASPHALTENES

Asphaltenes are liable to self-aggregation, which creates the aforementioned problems. This is due to  $\pi$ - $\pi^*$  and dipole interactions. Various dispersants are used to avoid this aggregation during petroleum recovery, transportation and subsequent refining [31]. A variety of dispersants are available commercially, these include surface active agents like detergents, ionic liquids, etc.

Surfactants are primarily used as dispersants for asphaltenes which are chemical compounds like amphiphiles. They have found diverse applications in a variety of industries owing to the fact that they lower the surface or interfacial tension of the medium and are capable of associating to form micelles. Surfactants are also enjoying popularity in the petroleum industry due to their ability to disperse asphaltenes. The properties of surfactants can be ascribed to their chemical properties i.e. presence of a hydrophilic head and a hydrophobic tail in them. The polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated via dipole-dipole or ion-dipole interactions. Based on the nature of the polar head group

(hydrophilic), they are classified as anionic, cationic, neutral (nonionic) and Zwitterionic surfactants. A non-ionic surfactant has no charge groups, anionic has negatively charged groups while cationic has positively charged groups. Zwitterionic surfactant has a head with two oppositely charged groups. Some typical surfactants and details of hydrophilic and hydrophobic groups are given as under:

**Table 1.1. Various Polar and Non-polar Groups of Surfactant Molecules**

Group type	Example	Structure
<b>A. Hydrophilic groups</b>		
Anionic surfactant	Sulfate	$-\text{SO}_4^{-2}$
	Sulfonate	$-\text{SO}_3^{-1}$
	Ether sulfate	$-(\text{OCH}_2\text{CH}_2)_n \text{SO}_3^{-1}$
	Ether phosphate	$-(\text{OCH}_2\text{CH}_2)_n \text{PO}_2^{-1}$
	Ether carboxylate	$-(\text{OCH}_2\text{CH}_2)_n \text{CO}_2^{-1}$
	carboxylate	$-\text{CO}_2^{-1}$
Cationic surfactant	Primary ammonium	$-\text{NH}_3^+$
	Secondary ammonium	$-\text{R}-\text{NH}_2^+$
	Tertiary ammonium	$-\text{R}_2\text{NH}^+$
	Quaternary ammonium	$-\text{R}_3\text{N}^+$
Amphoteric surfactant	Amine oxide	$-\text{N}^+(\text{R})_3\text{O}^-$
	Betain	$-\text{N}^+(\text{R})_3(\text{CH}_2)_n\text{C}(\text{O})\text{O}^-$
	Aminocarboxylates	$-\text{N}^+\text{H}(\text{R})_2(\text{CH}_2)_n\text{C}(\text{O})\text{O}^-$
Non-ionic surfactant	Ethoxylate	$-(\text{OCH}_2\text{CH}_2)_n\text{OH}$
	Acetylenic	$-\text{CH}(\text{OH})\text{C}=\text{CH}(\text{OH})-$
	Monoethanolamine	$-\text{NHCH}_2\text{CH}_2\text{OH}$
	Diethanolamine	$-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$
<b>B. Lipophilic groups</b>		
Alkylbenzene	Linear dodecyl benzene	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{C}_6\text{H}_4)(\text{CH}_2)_5\text{CH}_3$
Linear alkyl (saturated)	n-dodecyl	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2-$
Saturated alkyl (unsaturated)	2-ethyl hexyl	$\text{CH}_3(\text{CH}_2)_3\text{CH}-\text{CH}_2(\text{C}_2\text{H}_5)$
Linear alkyl (unsaturated)	Oleyl	$(\text{Cis})-\text{CH}_3(\text{CH}_2)_7=\text{CH}(\text{CH}_2) \text{CH}_2-$

## 1.5. LITERATURE REVIEW

Substantial work in the literature has been devoted to the crude oil and the petroleum literature is quite rich in data regarding the use of surface active agents and their role to lower the interfacial tension between asphaltenes and to avoid their aggregates during recovery, transportation and processing to get distillate fuels in high yields. Ample literature has also been documented on the solid crystal aggregation, colloidal micellar solutions, aggregation, flocculation, non-crystalline solid formation and separation in petroleum fluids. However, in the past few years, the focus was on the increase in distillate products by overcoming problems encountered due to complexity present in the oil refinery supply chain. In view of the complexity of the petroleum crudes in terms of polydispersity of hydrocarbons and other organic and inorganic constituents, understanding their phase behavior in production, transportation and refining is still a challenging task. We represent a literature review on existing approaches that address the problem of optimization in the petroleum industry. We are documenting recent literature carried out on the issue in the proceeding section.

**Canevari *et al.***, studied the oil viscosity; one of the major factors affecting the dispersibility of the oil. They were of the view that oils having high viscosity (20,000 centistokes, cs) or more may offer resistance to disperseability in a solvent, however, it is not the case for all oils. They used ExxonMobil Research facilities in New Jersey. They further added that other properties of the viscous oil, can influence its dispersibility. The dispersibility measurements were carried out using a COREXIT dispersant. They did not detect any correlation among some chemical characteristics i.e. sulfur, aromatics, paraffins, resins, vanadium, nickel content, etc., with dispersibility. They, however, identified a statistically important relationship between

the studied parameters, which may help to explain anomalies like viscous oils which do not disperse [32].

**Wiehe & Jermansen** used some synthetic dispersants to enhance the solubility of asphaltenes in the oils under study particularly when used in small quantities. They concluded that those dispersant which having more head and tail groups can complex with the polynuclear aromatic structures in asphaltenes and long paraffinic which can promote solubility in the rest of the oil, could be more effective than the natural dispersants, Neutral surfactants (resins) are always present in crude oils already present in the oil. When used in high quantities, they can solubilize the asphaltenes in n-heptane which convert asphaltenes into resins. They found that the  $\text{SO}_3$  was determined to be the most effective head group attached to a two ring aromatic structure [33].

**Gawrys *et al.***, fractionated asphaltenes they obtained from four different crude oils. They used mixtures prepared from heptane and toluene and confirmed their results by small angle neutron scattering (SANS). The elemental analysis showed that the fractionation appeared to have concentrated in case of the most polar species into the least soluble sub-fraction. The results indicated a wide range of asphaltene aggregate sizes and molecular weights; however, they observed that the less soluble (more polar) fraction have contributed a lot in the majority of the species responsible for asphaltene aggregation in solution. They further reported that the resins effectively solvated the asphaltene aggregates as determined by an increase in the asphaltene solubility, reduction in aggregate size and molecular weight [34].

**Hiwale *et al.***, studied the use of reactive distillation (RD) process as an emerging technique. They reviewed and furnished the information on the current research. They also elaborated newly introduced applications of RD such as



manufacture of phenol, linear alkyl benzene, carbonates, chlorosilane derivatives and chiral chemicals. The review also covered the multiple reactions occurring in RD, failure of the RD in some cases and new RD configurations so as to increase the overall yields [35].

**Gharfeh *et al.***, performed a study. They reported that the transport of heavy oils from the wellbore to the refinery is a tedious and costly process may be due to high viscosity which results in higher energy requirements to pump such oils. The intensity of the problem, however, can be minimized by using reagents like diluents. However, the addition of diluents may create problems like asphaltene precipitation from the heavy oil which may cause plugging and fouling problems. The asphaltene flocculation is often used to predict about the asphaltene precipitation tendency of a crude/diluent mixture. A heavy crude (Venezuelan) was used in this investigation using a solvent dilution method. The flocculation point measurements under high pressure utilizing a high-pressure cell with the solid detection system (SDS) were performed. The obtained results showed a good correlation among the high-pressure titration experiments and solvent dilution method using dead crude oils [36].

**Sirota** reported about the colloidal models of asphaltene which can be extremely beneficial in understanding the asphaltene behavior. The asphaltene are found to be comprised of particles having several nanometers in size which were studied by small-angle neutron and X-ray scattering (SANS and SAXS). Using other techniques, they found that the giant molecules of asphaltene can also form micelles of colloidal nature. Its colloidal appearance at micrometer to millimeter lengths may not be confused with or be used to imply such colloidal structure for solvated asphaltene at nanometer length scales. From the results they showed that the scattering often attributed to asphaltene colloidal aggregates may be the result of ephemeral

dynamically fluctuating compositional inhomogeneities similar to those observed in one-phase liquid mixture of unlike molecules [37].

**Andreatta *et al.***, have shown that the asphaltenes are interracially active in many instances particularly at interfaces of toluene & water. They further added that the term micelle is helpful so as describes the primary aggregation of asphaltenes in solvent (toluene). However, the more appropriate terminology of critical micelle concentration (CMC) of asphaltenes can be used. They used the nomenclature of critical nanoaggregate concentration (CNAC) for asphaltenes instead of CMC. They also studied the dissolution/dispersion of asphaltenes with some AR grade surfactants through a high-Q, ultrasonic spectroscopy. The results showed a sharp break in sonic velocity as expected concentration at known CMCs. They further measured the known surfactants with CMCs. They obtained micelle compressibilities consistent with the early studies. They inferred from the compiled results that the asphaltenes behaved similar to that of ultrasonic velocity versus concentration used as standard surfactants; asphaltene CNACs in toluene occurred at roughly 0.1 g/L [38].

**Bruno** reported on the distillation behaviour of a complex fluid through the distillation curve. It can also be used in certain applications as a guide for blending virgin stock with reclaimed oil, guiding the formulation of product that will be suitable in various applications. Keeping in view its diverse applications, in the work under reporting, the authors presented several modifications to the measurement of distillation curves so as to provide information on the temperature and volume measurements, and its relation to composition-explicit data [39].

**Zhao *et al.***, studied the effects of surfactant concentration and salinity of the oil on interfacial behavior in detail. The obtained results which indicated that DMNS surfactant had great capability and efficiency of lowering the solution surface tension

and the critical micelle concentration (CMC) i.e. 0.02 mass% and the surface tension of  $31.61 \text{ mN m}^{-1}$  at this concentration. They further noticed that the DMNS surfactant played a significant role in reducing the interfacial tensions and the tension of crude oil–water interface to ultra-low at very low concentration, 0.002 mass%, without alkali and the other additives. The addition of salt like sodium chloride resulted beneficial effect to surfactant in reducing the interfacial tension. It was concluded that the surfactant can reduce the interfacial tension to ultra-low only at a certain sodium chloride concentration range [40].

**Hernández-Trujillo *et al.***, studied the interaction between a series of p-alkyl phenols with the solvent n-heptane (n-C<sub>7</sub>) by means of theoretical methods. The solvation energies were estimated by using quantum mechanical methods where in the solvent acted as a dielectric medium. The dispersion, and repulsion contributed to great deal to the solvation energies analyzed as a function of the alkyl chain length. The constraints on the role of the studied surfactants as asphaltene dispersants determined at the microscopic level, has been discussed. The solubility was correlated with their experimental results. The observations were in conformance with the earlier hypothesis that the relative ability of a series of p-alkyl phenols to dissolve a given asphaltene in n-C<sub>7</sub> is due to the amphiphile-solvent interactions [41].

**Khelifa *et al.***, studied the effect of chemical dispersants (Corexit 9500 and Corexit 9527) on the physical properties and dispersion of oil. They optimized the dispersant-to-oil ratio (DOR) using various crude oils. The obtained results showed a linear increase in oil viscosity with the increase in DOR. The increase was higher with the less viscous oils compared to the more viscous oils. They noticed that with the increase in DOR from 0 to 1:5, oil-dispersant mixture viscosity of approximately 20, 30 and 40 % greater than the pure crude oils for Arabian Medium, Alaska North Slope,

and South Louisiana crude oils, respectively were achieved. Similar results were obtained with the other chemical dispersants. The application of chemical dispersants reduced the interfacial tension significantly for all values of DOR examined in the current study even at 1:200. The interfacial tension of Arabian Medium crude decreased from 20 mN/m to less than 3.6 mN/m at DOR=1:200. The results also showed that an optimum DOR at which the IFT reduction reached a maximum value. At this optimum value, the effectiveness of the chemical dispersant was at a maximum. The consequent effects of the observed IFT reductions on the resulting size distribution of oil droplets was studied using existing theories and size measurements using UV Epifluorescence microscopy [42].

**Nordgård & Sjöblom** synthesized three model compounds for asphaltenes and two model compounds for the C<sub>80</sub> isoprenoid tetra acids. They studied their interfacial and solubility properties and all compounds exhibited high interfacial activities. The asphaltene models lowered the interfacial tension between toluene and pH 9 to around 5 mN/m at 12.5–35 µM and the tetraacid models gave a significant drop in the interfacial tension between chloroform and pH 9 to 13 mN/m at only 5 µM. The results were consistent with the previous findings carried out on natural occurring C<sub>80</sub> tetraacids. For two of three asphaltene models, a sudden drop in the IFT over a very narrow concentration range was observed. The NIR spectroscopy results indicated an aggregation most probably due to polar and hydrogen bond interactions. The results also confirmed the different behavior with only small changes in the chemical structure. The tetraacid models have similar interfacial behavior as the C<sub>80</sub> tetraacids and are thus reported to be suitable model compounds owing to their highly UV active and fluorescent properties [43].

**Mostowf *et al.***, concluded from a study that the colloidal structure of asphaltenes may impact the various physical properties. In their previous studies carried out in both laboratory as well as oilfield studies, they inferred that asphaltenes usually form nanoaggregates. Further, asphaltenes can exhibit a critical nanoaggregate concentration (CNAC) in toluene in the range of 50-150 mg/L. In this study, centrifugation was used to prove a major change in asphaltene aggregation at the CNAC concentration. They collected the aggregates by centrifugation. The nanoaggregate size was found to be ~2.5 nm, which was compatible with corresponding previous determinations from gravitational gradients. Asphaltene monomers were observed to be small [44].

**Boukherissa *et al.***, investigated the mechanism involved in the inhibition of asphaltenes aggregation. They used new ionic liquids like 1-propylboronicacid-3-alkylimidazoliumbromides and 1-propenyl-3-alkylimidazolium bromides due to strong electron-donor-acceptor properties. The length of the side alkyl chain of the ionic liquid was reported to be an important parameter. The minimum length of eight carbons was found to be essential so as to obtain steric stabilization of the resultant IL-asphaltene complexes [45].

**Castro & Vazquez** studied a series of typical Mexican Crude Oils (MCOs) with different physico-chemical properties. The oils were characterized through different physical, spectroscopic, and thermal methods. The oils were duly fractionated into saturates (S), aromatics (A), resin (R), and asphaltenes (A) by using chromatography method i.e. HPLC. The resultant fractions were characterized by physico-chemical techniques. Fourier transform infrared (FTIR) spectroscopy, vapor pressure osmometry (VPO), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were used. The VPO enabled to determine the average molar mass of each MCO

fraction. It was observed that the molar mass of the resin and asphaltene fractions increased when the nature of crude oil. The thermal stability of the oils MCOs results indicated that the decomposition temperature increased with the average molecular mass of the crude oil. The results inferred that the heat effects were associated to phase transitions monitored for each fraction. It was concluded that the behaviours of crude oils may be correlated to the average molar mass of different constituents present in the oil [46].

**Deng *et al.***, reported about the effects of different surfactants on the hydrocracking of oil investigated in a magnetically stirred reactor. They observed some obvious changes in coke-formation when a mixture of anionic and cationic surfactants was added to the reactants. To further study its influence, they changed the mixing ratios of the surfactants, and observed the coke formation behavior. They noticed that the coke-formation rate decreased first and then increased. On contrary, the average relative molecular mass of the asphaltene increased first and then decreased [47].

**Mukherjee & Wrenn** carried out a study that explored the impacts of oil type and mixing energy on the efficiency of some chemical dispersants using a specially designed reactor. They used “Corexit 9500” as dispersant and investigated the effect of process variables like viscosity and interfacial tension. Three crude oils were used at two dispersant-to-oil ratios (DOR; 1:100 and 1:25) and three energy dissipation rates. The effectiveness of dispersion (DE) i.e., fraction entrained as droplets in the water column of all three oils was found to be maximum at a mixing energy of 0.016 W/kg. In case of some crudes, the DE was influenced by DOR only at the lowest mixing energy, but it was proportional to DOR at all mixing energies for the more viscous oil. The droplet-size distributions were multimodal for all oil–dispersant combinations that were tested, indicated the involvement of multiple droplet-formation mechanisms [48].

**Trabelsi *et al.***, has undertaken a study so as to get an insight to the interactions between the oil recovery and the surfactants in heavy oil recovery from the well. The measured the IFT and found that the dynamic IFT between the diluted heavy oil and the alkaline solution (pH 11) in plain sample increased sharply with time, which was attributed to the transfer of the *in situ* surfactant across the oil/water interface. They used sodium dodecyl benzene sulfonate (SDBS) above the CMC, and found change in IFT behavior of the oil which strongly decreased and finally reached a plateau, at a concentration of only 0.02%. They further attributed this behavior to a synergistic effect among the *in situ* surfactant and the added surfactant due to decreased IFT to ultra-low values [49].

**Lago *et al.***, studied the enhanced oil recovery (EOR) assisted by ionic liquids as surfactants. The study was aimed at evaluating the suitability of several ionic liquids as substitute for conventional surfactants. The reservoir fluid was modelled as a ternary system of water (pure water or aqueous solution of NaCl) plus the ionic liquid trihexyl (tetradecyl) phosphonium chloride plus dodecane. The interfacial tensions in the system exhibited the ability of the ionic liquid to act as a surface active agent. Viscosity and density were experimentally measured for the equilibrium phases [50].

**Venosa & Holder** recently conducted a laboratory study in order to measure the dispersion effectiveness of eight dispersants. The results were found to be useful in determining how many commercial dispersant products would have been effective for use on South Louisiana crude oil. The test used was a modification in the Baffled Flask Test (BFT). The used one oil and increased the runs from m 4 runs to 6 at two different temperatures. The results indicated that the effect of temperature was not as pronounced

suggested in the literature may be due to the low viscosity and light weight of the SLC. Of the eight dispersants studied, only three gave good results at both temperatures [51].

**Yang *et al.***, studied the effects DBSA and LA on the viscosity of three heavy oils having different resin/asphaltene (R/A) mass ratios. They used DSC analysis, rheological test and electrical conductivity measurements. The wax formation temperatures were found to be  $<40$  °C. The viscosity determined at temperature range of  $50\sim70$  °C increased with the increase in DBSA concentration but decreased in case of LA. The addition of DBSA also increased the electrical conductivity, which established its activity as asphaltene dispersants. The electrical conductivity decreased when LA was added, which established that the LA as asphaltene flocculants. Further, the addition of DBSA decreased the size of asphaltene particles and generated new solvation layers, which favored an increase in the viscosity of the oil. The addition of LA increased the size of asphaltene particles and helped to release liquid oils caged with in the asphaltenes, which favored a decrease in oil viscosity. With the increase in R/A mass ratio, the stability of heavy oils increased while the ability of DBSA/LA to increase the viscosity decreased [52].

**Wang *et al.***, studied the aggregation and diffusion of asphaltenes in a crude oil. In this study, the DPD integrated with the quaternion method was implemented on graphics processing units (GPUs). They inferred that using multiple GPUs can provide faster computation speed and more storage space for simulations of significant large systems. They added that by using large systems, simulations of the asphaltene–toluene system at extremely dilute concentrations can be performed. They reported that the diffusion coefficients of asphaltenes determined in simulation studies were similar to that of experimentally determined values and the aggregation behavior of the



asphaltenes in heptane and the simulation results agreed with the modified Yen model [53].

**Kumar *et al.***, studied the rheological properties of heavy crude oil in the absence and presence surfactant derived from a tropical plant namely *Madhuca longifolia* (Mahua) and the nonionic surfactant Brij-30. The influence temperature, concentration, and shear rate was studied and reported. They observed that at 25°C, 2000 ppm addition of these surfactants caused a significant reduction in viscosity of oil. The complexity of the crude oil also decreased significantly. The FTIR analysis showed remarkable decrease in the concentration of viscosity promoting groups (alkanes, alcoholic, and acidic groups) which indicated the effectiveness of the surfactants under study. They inferred that the naturally extracted surfactant may be used as substitute to commercial surfactants in reducing the hurdles in flow of heavy crude oil [54].

**Banrjee** reported the use of natural surfactant so as to enhance rheological properties. They studied the pour point, viscosity, thixotropic behavior, yield stress, and interfacial tension using an Indian heavy crude oil. The surfactant was prepared in the laboratory from the extracts derived from a plant i.e. *Sapindus mukorossi* (soapnut). They observed a significant reduction in viscosity which reduced by 80%. The thixotropy was reduced by 94.64%, and yield stress by 98%. The interfacial tension was also reduced by 97%. They studied the possible mechanism in improvement of the rheological properties through FTIR. The results showed reduced concentration of C=O and C=C groups in surfactant-crude mixture which indicated the effectiveness of the surfactant [55]

**Karambeigi *et al.***, conducted a study on the asphaltene precipitation which always creates problems in the petroleum industry. They reported asphaltene

precipitation can be achieved via several procedures, but the use of some inhibitors like salicylic acid, phthalic acid, nonylphenol, phenanthrene, benzoic acid and IR95 can be more effective in handling and overcoming the deposits. They concluded that the hydroxyl group in inhibitors play a vital role by creating a compact planar phenol structure through a stable  $\pi$ - $\pi$  interaction with the asphaltenes. The results revealed that the adsorption of the anionic chemicals in carbonate reservoirs is expected to be high because of the expected positive surface charge possessed by the carbonate minerals. They also related the adsorption of anionic chemicals on minerals with the surface charge of the mineral. The salicylic acid they used has an extra hydroxyl group on benzoic ring. On the other hand, the high capability of IR95 was correlated with the adsorption on the porous media which prevented asphaltene particles from being precipitated on the pore surface [56].

**Zhou *et al.***, two novel zwitterionic surfactants with different hydrophobic groups i.e. alkyl sulfobetaine (ASB), and xylyl substituted alkyl sulfobetaine (XSB). The oil sample used included kerosene, crude oil, and model oils containing crude oil fractions, such as resins, asphaltenes, saturates, aromatics, and acidic fractions. The plain and surfactant added sample were investigated by a spinning drop interfacial tensiometer. The obtained results showed that XSB solutions showed good results due to higher interfacial activity (because of the larger size of the hydrophobic part) than ASB in case of kerosene. The resins, aromatics, and acidic fractions showed strong effects on IFTs of betaine solutions. On the other hand, the asphaltenes and the saturates have little effect on the interfacial properties. They concluded that the hydrophilic part of the betaine molecule at the interface may vary its orientation from vertical to flat with aging time. The dynamic IFT curves of the ASB solutions against model oils showed a V shape in case of resins, aromatics, and acidic fractions [57].

**Guzmán *et al.***, performed different tests and predicted about the asphaltene stability in some crude oils. They used certain tests including Bureau of Mines correlation index–toluene equivalence, Stankiewicz plot, colloidal instability index, colloidal stability index, qualitative-quantitative analysis, stability cross plot, toluene equivalence, Heithaus parameter , and oil compatibility model. In addition, asphaltene flocculation point, SARA fractionation, stationary column stability test, S-value, P-value, separability number, compatibility test, and spot test were also carried out. Among the various tests carried out, it was found that the qualitative-quantitative analysis and stability cross plot behaved better than the colloidal instability index and Stankiewicz plot [58].

## **1.6. THE PRESENT WORK**

The results of most of the above mentioned studies unveiled the role of dispersants i.e. cationic, anionic, and neutral dispersants in avoiding asphaltens aggregation and preventing asphaltenes particles for precipitation.

The idea of the present work is to explore the efficacy of some synthetic chemical surfactants so as to keep the asphaltenes dispersed during the distillation and also to release the oil caged with in the asphaltene globules not only to increase the yields of light distillate fractions i.e. gasoline and diesel fuels from various Pakistani crudes without disturbing the chemical composition and desired fuel properties but also to combat with the collateral process problems associated with asphaltenes and resins like coking, and impairing heat and mass transfer activities in the refining reactors.

## **1.7. AIMS AND OBJECTIVES**

The aims and objectives of the present study include:

- a. To ascertain the effect of various surfactants on the recovery of light fractions including gasoline and kerosene during distillation
- b. To find out a safe and cost effective route for increasing the yield of gasoline and diesel fuels and decreasing the residue instead of going for tedious and costly advanced refining steps like thermal, catalytic and hydro cracking processes
- c. To optimize experimental conditions by carrying out a number of experiments so as to find a best surfactant(s) and its optimum ratio with the oil which give high yields of desired distillate fractions
- d. To perform compositional study and determine the key fuel properties of the light distillate fractions obtained from surfactant (s) dispersed/additized samples in comparison with the generic fuels.

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# **CHAPTER # 2**

# **EXPERIMENTAL**

## **CHAPTER- 2**

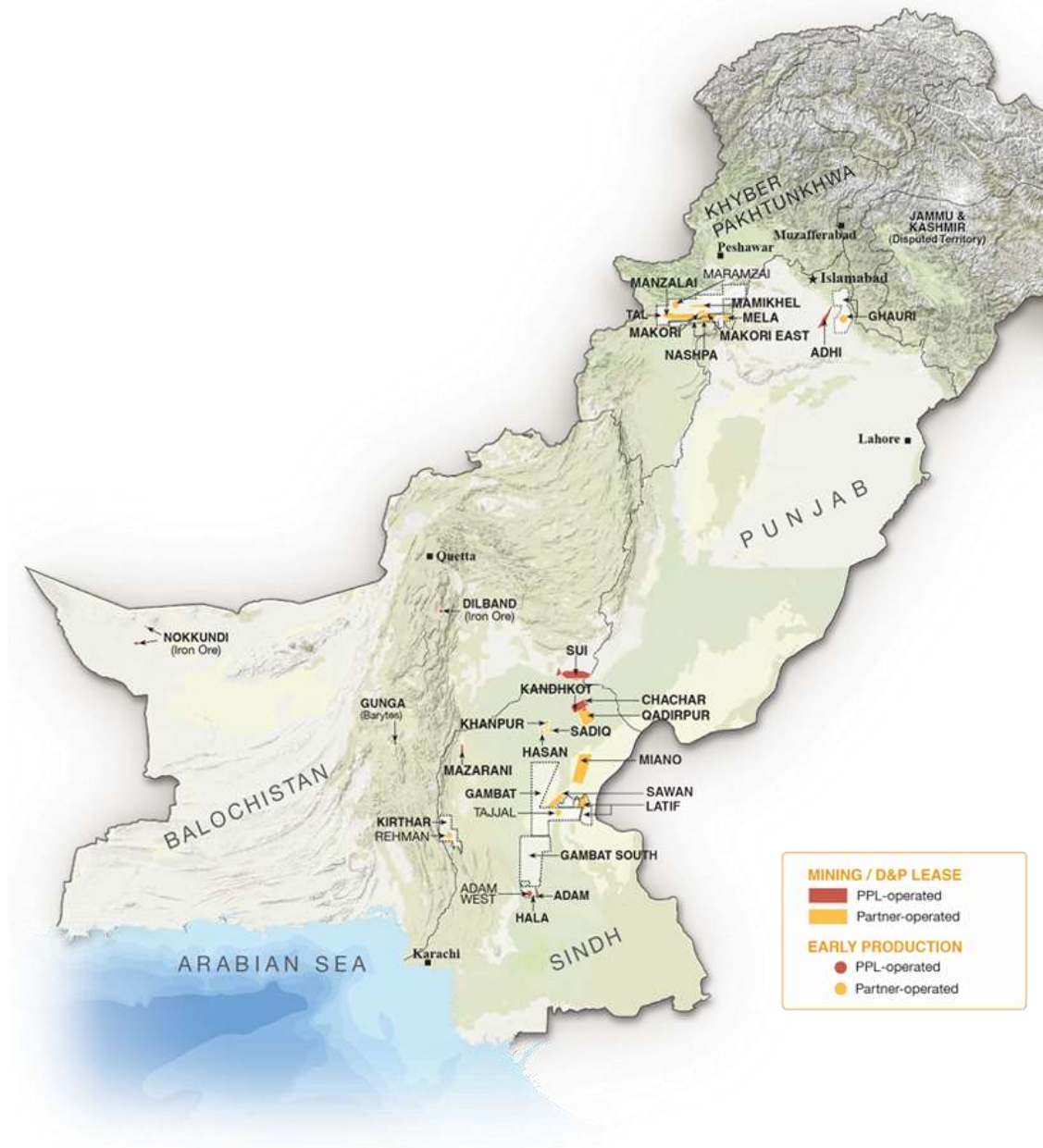
### **EXPERIMENTAL**

#### **2.1. CHEMICALS AND REAGENTS**

In the present work, in order to get maximum light fractions and to reduce the amount of residue, a number of Analytical Reagents (AR) grade chemicals/reagents were used. The as received crude oils were supplied by Hydrocarbon Development Institute, Peshawar in properly sealed metal made cans. The other chemicals used were surfactants and solvents. The surfactants employed were; anionic, cationic and nonionic nature. Anionic surfactant includes sodium dodecyl sulphonate (ACROSS Organics), cationic surfactant i.e., cetyl tri methyl ammonium bromide (CTBA/HDTM, BIO WORLD Chemical industry) and nonionic surfactant i.e. Titron-X 100 (BIO Basic Company, Canada). Different solvents i.e., methyl alcohol, ethyl alcohol and n-hexane were procured from Merck (Germany).

#### **2.2. CRUDE OILS AND THEIR PRELIMINARY CHARACTERIZATION**

Crude oil samples of different nature i.e. paraffin, naphthene and aromatic-base were kindly supplied by Hydrocarbon Development Institute of Pakistan from Naspha, Pariwali and Turkawali wells. The map showing the sites location is given in Fig. 2.1. Preliminary characterization of the samples was carried out by standard ASTM/IP methods for key basic properties. The physico-chemical properties like density ( $\text{kg/m}^3$ ), API gravity, viscosity ( $\text{mPa}\cdot\text{s}$ ), total acid number ( $\text{mg KOH/g}$ ), asphaltene contents (wt %), etc. were determined.



**Fig. 2.1.** Map showing the crude oil sites

### 2.3. SURFACE ACTIVE AGENTS AND THEIR CHARACTERIZATION

Three chemical surfactants were procured from reputed suppliers and evaluated for their fuel dispersant qualities for enhanced oil recovery. These were hexadecyltrimethylammonium bromide (CTAB, 98 %), sodium dodecyl sulfate (SDS,

99 %) and polyethylene glycol p-(1, 1, 3, 3-tetramethylbutyl)-phenyl ether, octyl phenol ethoxylate (Triton-X-100). The linear formula & molecular weight, and category; (cationic, ionic, neutral, etc.) of each surfactant were collected from the literature values. In addition, their thermal stabilities were determined in temperature range of interest by thermo-analytical methods i.e. thermogravimetry (TG) and differential thermal analysis (DTA).

#### **2.4. PREPARATION OF SURFACTANT SOLUTIONS**

**Preparation of Stock Solution:** The stock solution of the dispersant (30%) was prepared by weighing 30 g of the reagent and dissolving it in methanol (Merck), making total volume up to 100 mL in a volumetric flask. The solution was homogenized by constant stirring using a magnetic stirrer for 15 minutes.

**Working Solutions:** The different working solutions were prepared in the concentration range of 5-30 % by pipetting out adequate amount from the stock solution and consequently diluting with methanol. Each flask was then labelled and stored for further use.

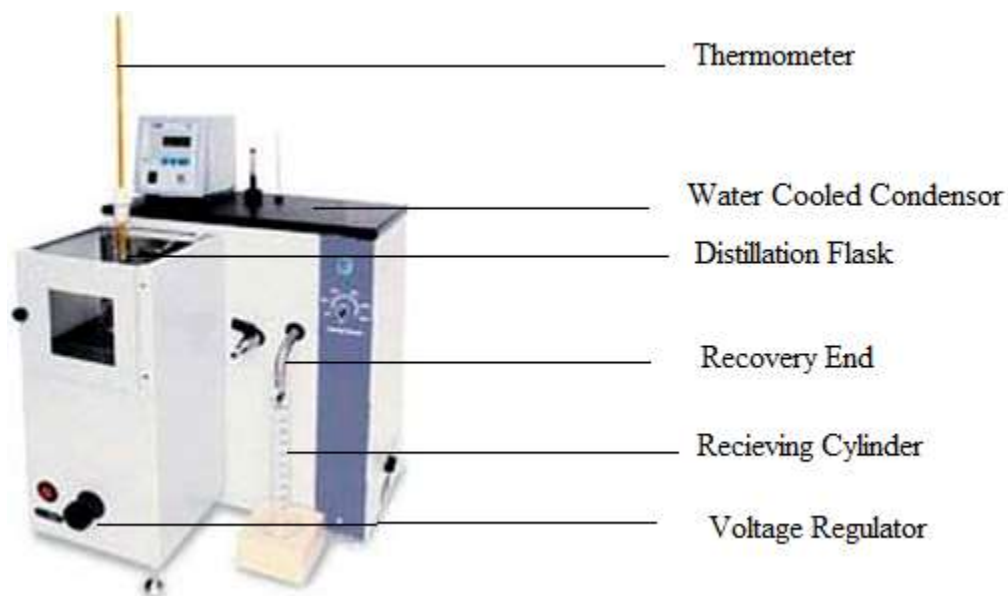
**Preparation of Different Dispersant-to-Oil Ratios:** The as received crude oils were homogenized by constant stirring using a magnetic stirrer provided with a magnetic bar for 20 minutes, separately. Oil-surfactant solutions (calculated amounts) were prepared in Dispersant-to-Oil Ratio of 5:100, 10:100, 15:100, 20:100, 25:100 and 30:100 (W/V). In total, 18 solutions were prepared, homogenized and subsequently subjected to atmospheric distillation.

#### **2.5. ATMOSPHERIC DISTILLATION**

The raw as well as the surfactant– dispersed crude oil samples were subjected to atmospheric distillation separately which was carried out with automatic distillation

apparatus (Stanhope-SETA) according to the American Society for Testing and Material (ASTM D86) standard method [1]. The sketch is provided in Fig. 2.1. The apparatus was calibrated before the measurements were performed. In a typical run, a 100 mL aliquot of a pre-warmed crude oil was trickled in a distillation flask (500 mL round bottom flask provided with a side arm), coupled to a temperature sensor (a thermometer inserted into the proper location, not submerged in to the fluid and positioned at the low point of distillate take-off). The assembly was mounted on temperature controlled heater. The flask was connected to a built-in condenser and heated so as to maintain a distillation rate between 4 and 5 mL min<sup>-1</sup>. The yield of each distillate fraction (volume %) was determined in comparison with the plain crude oil sample (control). The volume measurements were made in a level-stabilized receiver with an illuminated screen at the background. The distillation curves (the boiling temperature versus cumulative volume fraction distilled), at 10% (v/v) intervals, were obtained. ASTM distillation curves were drawn for each oil with the temperature on the vertical axis (Y-axis) and the volume percent distilled on the horizontal axis (X-axis).

Each crude oil was distilled into three fractions and residue: light fraction designated as F1 [initial boiling point (IBP)–160°C], medium fraction designated as F2 (160-250–380 °C), heavy fraction designated as F3 (250–340°C), and residue R (>340 °C).



**Fig.2.2.** Automatic batch distiller (distillation apparatus)

## 2.6. CHARACTERIZATION FOR FUEL PROPERTIES

Different instruments/ apparatus were employed in the characterization of the crude oils which include hydrometer/pycnometer, Conradson carbon residue apparatus, Ostwald viscometer, Pensky Marten tester, pour point apparatus, aniline point apparatus, bomb calorimeter, etc.

**Fuel Properties:** The crude oils as well as their distillate fractions were characterized by physico-chemical methods. The desired fuel properties of the fractions were determined in comparison with the petro-fuels i.e. gasoline and diesel fuel samples according to the ASTM test methods (referred in Table-2.1). The various key properties were determined as per given methods:

**Table 2.1.** ASTM and IP Standard Test Methods

<b>property</b>	<b>unit</b>	<b>test method</b>
density	g/cm <sup>3</sup>	ASTM D 1480
API gravity @ 60°F	-	ASTM D 4052
carbon residue	% wt	ASTM D 189 – 05
Ash	% wt	ASTM D 189 – 05
kinematic viscosity @ 40 °C	mm <sup>2</sup> /s	ASTM 445
pour point	°C	ASTM D 97 – 05
flash point	°C	ASTM D 93
aniline point	°C	ASTM-D 611-04
Distillation	-	ASTM D86
diesel index	-	-
octane number	-	ASTM D2699-16e1
cetane number	-	ASTM D613-16a

### 2.6.1. Density

The density was determined by pycnometer method (ASTM D1480) [2]. The density of the test oil sample was calculated from the difference in weight between the full and empty pycnometer and its known volume. As per standard procedure, the pycnometer of a specified volume (50 mL) was taken and thoroughly rinsed first with distilled water and then with petroleum spirit to remove previous impurities, dried in an oven at 105 °C. Then, its weight was determined using an analytical balance as  $m_1$ . The crude oil was then carefully poured in to the pycnometer till filling with the help



of a graduated cylinder. The stopper was properly capped to allow the air bubbles to escape. The pycnometer filled with the sample was weighed and its weight was determined as  $m_2$ . The density of the test oil was determined according to equation-1:

$$\rho = \frac{m}{v} \dots\dots\dots(1)$$

Where  $m$ = mass of the oil ( $m_2-m_1$ )

Specific gravity (SG) of the test oil was then calculated as equation-2:

$$SG = \frac{\rho_s}{\rho_w} \dots\dots\dots(2)$$

Where as

$\rho_s$  = density of the test oil

$\rho_w$  = density of the water

The density of petroleum oils is widely expressed all over the world as American Petroleum Institute (API) gravity. The units of API gravity are °API which was calculated as equation -3:

$$API\ gravity = \frac{141.5}{SG} - 131.5 \dots\dots\dots(3)$$

Where: SG is the sp.gr and determined as the weight of crude oil per unit volume compared to water at 60 °F (15.6 °C).

### 2.6.2. Carbon Residue

The ASTM method D 189 – 05 [3] was used for the determination of carbon residue. The method is used to cover the determination of the amount of carbon residue in a petroleum sample. The method provides relative coke-forming propensities. The unit quantity of sample (free of moisture and other suspended matter), was weighed in

to a clean and well dried tared porcelain crucible which was then placed in a Skidmore crucible. The Skidmore crucible was set in to the center of large sheet-iron crucible filled with sand. Covers were applied to both the Skidmore and the iron crucibles, the one on the latter fitting loosely to allow free exit to the vapors as formed. On a suitable stand or ring, placed the bare Nichrome wire triangle and on it the insulator. Next was centered the sheet-iron crucible in the insulator with its bottom resting on top of the triangle, and covered the whole with the sheet-iron hood in order to distribute the heat uniformly during the process. Heat was applied with a high, strong flame from the Meker type gas burner, so that to achieve the pre-ignition in 10 min. Allowed the flames to lit on, when the vapors ceased to burn and no further blue smoke observed, the burner was re adjusted and held the heat as at the beginning so as to have the bottom and lower part of the sheet-iron crucible a cherry red, maintained heating for exactly 7 min.

Removed the burner and allowed the apparatus to cool until no smoke, and then removed the cover of the Skidmore crucible (about 15 min). Removed the porcelain or silica crucible with heated tongs, placed in the desiccator, cool, and weighed. The percentage of carbon residue on the original sample was calculated as:

$$\text{Carbon residue (\%)}: [(A-B)/W] \times 100$$

Where: A = mass of sample holder, g + residue, g

B= mass of sample holder, g and W = mass of sample, g

### **2.6.3. Viscosity**

Viscosity was determined by ASTM 445 method [4]. A capillary viscometer was used for the purpose, and all determinations were made without changing the viscometer of proper viscometer constant. The selected viscometer was cleaned with petroleum spirit before analysis and stacked in the thermostate bath. The temperature

of the bath was maintained at 40 °C using paraffin oil as bath liquid and to avoid fogging. A definite amount of the oil sample was filtered in order to remove any impurity and then a small aliquot of the oil was pipetted out and poured in to the selected viscometer. The sample was allowed to flow under its own head. The time elapsed in the flow of sample from mark A to mark B on the viscometer was recorded with a timer in seconds. The kinematic viscosity was determined using equation -4 as:

$$v = Ct \dots \dots \dots (4)$$

Where v describes the kinematic viscosity, mm<sup>2</sup>/s, C the calibration constant of the viscometer, (mm<sup>2</sup>/s)/s, and t is the mean flow time, (s).

The dynamic viscosity (η) was determined using the equation-5 as:

$$\eta = v \rho \dots \dots \dots (5)$$

Where:

v = kinematic viscosity, mm<sup>2</sup>/s and ρ is the density (g/cm<sup>3</sup>) of the test oil

#### 2.6.4. Cloud and Pour Points

ASTM D 97-05 method was followed [5]. The apparatus used in cloud point determination comprised of a test jar, cork holding a thermometer, water bath with heater, cloud point chamber and crushed ice. The test jar was filled to the level mark with the sample under test, and closed tightly by the cork carrying the thermometer. The arrangement was placed into a bath containing crushed ice provided with salt. The test jar was removed momentarily from the jacket taking care not to disturb the sample and observed. Cloud point is the temperature of a liquid when the haziness was noted in the sample jacket upon cooling. The arrangement was again placed into a bath containing crushed ice and salt and further allowed to cool. It was removed from the cooling mixture and tilted. Upon tilting, the oil surface stayed in the vertical position

for a period of 5 seconds without sagging. The pour point is recorded 3°C higher than the thermometer reading as allowed under standard procedure.

#### **2.6.5. Flash and Fire Points**

The flash and fire points were determined by ASTM method [6]. The sample was filled in to the cup to the level mark. The cup was placed within the heater. The lids on the top was fixed through which inserted a thermometer and a stirrer. The heater was turned on and the sample was allowed to heat @ 1°C/min. A test flame adjusted to about 4 mm in diameter was momentarily (every 0.5 °C rise in temperature) applied at the top of the cup (into the oil vapor). The temperature read at the time the test flame application caused a distinct flash in the interior of the test cup was recorded as the observed flash point. Further the oil was heated at the rate of 1°C/ min. and continued applying the test flame as before. The temperature at which the vapors of the oil gave a clear and distinct blue flash for five seconds was recorded as the fire point of the oil.

#### **2.6.6. Aniline Point**

Aniline point was determined according to the standard designated method [7]. The 'U' tube was cleaned and rinsed to remove any previous impurity. Now 20 ml. of distilled aniline and 20 ml. of the given sample were taken in the 'U' tube. Two distinct phases separating the liquids were observed (two layers). The apparatus was provided with stirrers in such way so that the liquid in 'U' tube and the paraffin of the beaker stirred simultaneously. The heater was turned on to heat the paraffin bath containing the U tube at a controlled rate. The minimum temperature at which the two layers gave a single phase was recorded as the aniline point ( $T_1$ ). After that, the stirring of 'U' tube mixture was discontinued, and the mixture was allowed to cool. The temperature at which the two layers formed again was considered as aniline point ( $T_2$ ). The mean of  $T_1$  and  $T_2$  was recorded as the Aniline Point of the test sample.

### 2.6.7. Watson K index

Watson characterization index was determined according to the following expression [8]:

$$K = \frac{1.216 \sqrt[3]{T_b}}{SG}$$

Where  $T_b$  (K) denotes the average boiling point and SG, the specific gravity at 15.6/15.6 °C. Average boiling point is determined by distillation from the boiling points at which 10, 30, 50, 70 and 90 mL of distillates are recovered.

### 2.6.8. Correlation Index (C.I)

The Correlation Index (C.I) was also determined [9] as:

$$C.I = 87552/TB + 473.7 G - 456.8$$

Where TB denotes the average boiling point in Rankine (°R) and G, the specific gravity determined at 15.6/15.6 °C.

OR

$$CI = 473.7d - 456.8 + 48,640/TK$$

Where,  $T_K$  denotes average boiling point (K) and d, the specific gravity.

### 2.6.9. Acidity (mg KOH/g)

Acid-base titration method endorsed/ covered by ASTM standards was used [10]. ASTM D 974 Standard Test Method for Acid and Base Number by Color Indicator Titration was used for the purpose. The titrant used was KOH. Five (5g) of the test oil was weighed accurately and diluted in a beaker by dosing with 30 mL of solvent (benzene). The contents were mixed thoroughly. Then, the sample was further dosed

with pre-neutralized alcohol. The contents were mildly warmed using a water bath. A standard indicator (phenolphthalein) was added and the contents were subsequently titrated against alcoholic KOH solution (0.1N). The volume of KOH consumed was noted. A blank test was also carried out and volume of KOH consumed in blank was noted. Total Acid Number (TAN) was calculated as equation 6.

$$\text{TAN in mg KOH/g} = V_n \times C_t \times M[\text{KOH}]/W_s \dots \dots \dots (6)$$

$V_n$ :  $V_1 - V_2$  ( $V_1$ : volume of KOH consumed in case of sample,  $V_2$  is the volume of KOH consumed in case of blank)

$C_t$ : Concentration of titrant in mol/L

$M[\text{KOH}]$ : Formula mass of KOH i.e. 56.11 g/mol

$W_s$ : Sample weight in g.

#### **2.6.10. Asphaltene Contents (wt %)**

The ASTM D3279 is widely used method for determination of *n*-heptane insolubles [11]. The asphaltenes fraction was isolated from crude oil by adding an excess of the solvent (normal heptane). A definite amount of the crude oil (10 g) and 600 mL of the solvent were mixed and the contents were stirred for time duration of 20 min, cooled to room temperature. Then, the mixture was filtered using a Whatman filter paper. The non-filterables were washed with a fresh portion of *n*, heptane. The asphaltenes retained on filter paper were dried at 107 °C in a closed fume hood until the total mass of the filter did not change significantly (constant mass) and weighed for asphaltenes content.

### 2.6.11. Heat of Combustion

The calorific value is a measure of the amount of heat obtained by combustion of unit of mass (or volume) of fuel. Bomb combustion method designated by ASTM is used for the purpose [12]. The heat of combustion is the amount of heat (expressed in kJ / kg) released by complete combustion of unit mass of fuel in a bomb calorimeter, when the combustion products cool off to the initial fuel temperature (at constant volume), but assuming that water is not condensed. The experiment was performed inside a pressure calorimetric bomb under oxygen atmosphere (pressure ca. 30 bars). For this purpose, one g of the test sample was taken in the test cup, which was placed in the holder. An ignition wire was fastened to the two terminals (electrodes) and then a cotton thread fasted around the ignition wire and extended to the cup, aligned the cotton thread with a pair of tweezers in such a way so that it hung down into the crucible and immersed in the sample. Assemble the bomb by the screwing the cap. The bomb was then placed in the bucket in place in the hosing. After calibrating the temperature with in the bucket t and the jacket, the desired operating mode was set and “start” button was pressed and ignited under standard conditions. The rise in temperature was read from the thermometer and noted. The heat of combustion was calculated as:

$$Q = [-K \times \Delta T_{cal} - C_b - C_n] / m_s$$

where: K calorimetric constant (heat capacity of the calorimeter) and  $\Delta T_{cal}$  is increase of temperature calculated with corrections (heat of combustion of wire),  $C_b$ -correction for heat released during cotton thread combustion,  $C_n$ - correction for heat released during combustion of nitrogen to form  $HNO_3$  and  $m_s$ -mass of the sample.

## **2.7. COMPOSITIONAL ANALYSIS**

### **2.7.1. Elemental Analysis**

The elemental analysis of the raw crudes was carried out by elemental analyzer (CHNSO analyzer, ELEMENTAR Model VARIOELII).

### **2.7.2. Spectroscopic and Chromatographic Analyses**

The spectroscopic and chromatographic analyses including Fourier Transform Infra-Red spectroscopy (FT-IR) and Gas Chromatographic-Mass Spectrometry (GC-MS) were carried.

The FT-IR analysis was performed by using Fourier Transform Infra-Red spectrometer (Model FTIR Prestige-21 Shimadzu, Japan). The analysis was performed in the wave number range of 4000 to 400  $\text{cm}^{-1}$ .

The GC-MS analysis was carried with a gas chromatograph coupled with MS analyzer (GC-MSQP2010 Shimadzu). The experimental conditions were: Injector: ADC-201, column: DB-5MS column (25 m x 0.25 mm i. d., 0.25  $\mu\text{m}$ , carrier gas used: helium, flow rate of carrier gas (ml/min):1.3, split ratio : 50 , injector temperature ( $^{\circ}\text{C}$ ) : 300, sample injection volume ( $\mu\text{l}$ ) : 1, initial oven temperature ( $^{\circ}\text{C}$ ) : 35.

The peaks in the chromatogram were identified from the data of NIST MS library search [13].



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**CHAPTER # 3**  
**RESULTS AND DISCUSSION**

## CHAPTER- 3

### RESULTS AND DISCUSSION

The present work focuses on the use of different surfactants in the atmospheric distillation in order to get distillate fractions in high yields without disturbing their chemical compositions and fuel properties. The work was carried out in different steps/phases detailed as under:

#### **Phase: 1: Samples Collection and Their Preliminary Characterization**

The crude oil samples of different chemical nature i.e. paraffin, naphthenes and aromatic-base were collected from indigenous oil fields through Hydrocarbon Development Institute, Pakistan and preliminary characterized by standard ASTM/IP methods for key basic properties. The three different surfactants including hexadecyltrimethylammonium bromide as cationic surfactant, sodium dodecyl sulfate (SDS) as anionic surfactant, and Triton-X-100 as neutral surfactant were used owing to their dispersant qualities.

#### **Phase-II: Atmospheric Distillation Study**

The plain as well as the chemically dispersed crude oil samples were subjected to atmospheric distillation study and three main fractions i.e. light oil (F1), middle oil (F2) and heavy oil (F3) were collected. Each of these fractions was then characterized accordingly using standard ASTM/IP designated methods.

**Phase-III:** In this phase, the key fuel properties and compositional study of the resultant fractions in comparison with the standard petro-fuels was carried out.

## **PHASE-I**

This phase was devoted to the preliminary characterization of the crude oils and the surfactants used.

### **3.1. CHARACTERIZATION OF RAW CRUDES AND SURFACTANTS**

#### **3.1.1. Characterization of Raw Crudes**

It is well documented elsewhere that the physical and chemical characteristics of a crude oil vary considerably with its composition [1]. Its composition/quality varies due to its origin and conditions to which it is exposed during transportation and storage [2]. Major groups of compounds present in petroleum are saturated hydrocarbons (straight chained, branched and cyclic hydrocarbons), aromatic hydrocarbons, sulphur bearing compounds, resins and very large aromatic asphaltene compounds [3]. The concentration of different chemical components depends on the type of the crude oil. Light and medium crudes yield more aliphatic/naphthenic components compared to heavy crude oil which yields more heavy compounds, such as aromatic structures, and a high concentration of asphaltenes and resins [4].

**Physico-chemical Characterization:** The raw crudes denoted as RCP-I, RCN-II and RCA-III were characterized and the key physico-chemical properties were determined. The results are given in Table 3.1. As reported elsewhere, K value of 12.5 or higher is reported for paraffinic crude, while 10 or lower value for aromatic crude. For a naphthenic crude, K value vary from 10.5 to 12.9. The K factor or characterization factor is used to classify a crude oil based on its paraffinic, naphthenic, intermediate or aromatic nature. K value of 12.5 or higher indicate that a crude oil is predominantly paraffinic, while 10 or lower value indicate its aromatic nature. For a naphthenic crude, K value vary from 10.5 to 12.9. The correlation index was also calculated and found to be 8.74, 54.08 and 90.82, respectively. The CI values falling between 0 and 15, indicates a predominance of paraffinic hydrocarbons, 15 to 50, indicates predominance of either naphthenes or of mixtures of paraffins, naphthenes, and aromatics, while values more than 50 indicates a predominance of aromatic species [5].

The elemental analysis i.e. the values of CHNSO for the oil samples are given in Table 3.2. It can be seen that the nitrogen and sulphur contents are mostly concentrated in the naphthenic and heavier fractions. The elemental analysis revealed that the amount of carbon increased and the H/C ratio decreased from light to heavier fraction. As reported elsewhere, the total carbon and hydrogen content remains approximately constant (~83%–87% carbon and 11%–14% hydrogen (by weight) across whole crudes of varying density) for light and heavy crudes, the hydrogen-to-carbon ratio (H/C) is significantly lower in the more-aromatic, higher-boiling fractions and resides [6]. Heteroatoms containing compounds such as nitrogen, oxygen, sulfur, are present throughout the entire boiling range of crude oil, but increase in abundance in higher-boiling and non-distillable fractions [7].

All characteristics are typical to most crude oils and agreed to the values of published data [8-11]. The overall results concluded that the RCP-1 is a light crude, RCN-II is medium while RCA-III is heavy crude.

**Table 3.1.** Physico-chemical Properties of Raw Crudes

<b>Property</b>	<b>Unit</b>	<b>RCP-I</b>	<b>RCN-II</b>	<b>RCA-III</b>
base/type of sample	-	paraffinic	naphthenic	aromatic
density	g/cm <sup>3</sup>	0.76	0.85	0.94
API gravity @ 60°F	-	54	35	19
carbon residue	% wt	0.98	0.92	0.99
kinematic viscosity @ 40 °C	mm <sup>2</sup> /s	10.50	08.50	14.40
pour point	°C	-12	-14	-16
flash point	°C	96	93	96
aniline point	°C	86	88	90
Watson constant		12	11	10
Correlation index		8.74	54.08	90.82

**Table 3.2** Elemental Composition (% wt) of Raw Crudes

<b>element (wt %)</b>	<b>RCP-I</b>	<b>RCN-II</b>	<b>RCA-III</b>
Carbon	85.44	85.91	86.10
Hydrogen	11.15	11.30	11.55
Oxygen	1.85	1.21	0.96
Nitrogen	0.11	0.14	0.15
Sulphur	1.45	1.44	1.24

**FTIR Characterization:** Structural analysis of petroleum based products is performed to know about fraction recognition, combustion properties, and efficiency of fuel and quality inspections. It also influences the quality of the marketable products derived from crude products [12]. It has been reported elsewhere that crude oils which have similar physical properties but possess widely varying chemical compositions [13]. FTIR is considered as one of the better techniques for petroleum characterization [14-16].

The infrared region covers the region from 4000- 400  $\text{cm}^{-1}$ . Certain groups of chemical bonding give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule in the IR spectrum. The absorption bands of aliphatic C–H bonds, with additional bands originating from groups containing aromatics, oxygen, sulfur, and nitrogen, usually dominate the spectra of crude oils [30]. The FTIR of the oils under study was carried out. The results are discussed as under:

**RCP-I:** The FTIR analysis of RCP-I was performed. The data is given in Table-3.3. The clear larger size absorption peaks were observed at 2954 and 2822  $\text{cm}^{-1}$  corresponded to the CH and CH<sub>2</sub> stretching vibrations. The other well developed bands centered at 1446 and 1419  $\text{cm}^{-1}$  corresponded to the CH, CH<sub>3</sub> bending vibrations (deformations) were also observed. A medium intensity peak appeared at 727  $\text{cm}^{-1}$  showed CH<sub>2</sub> bending. Another medium intensity band at 1078  $\text{cm}^{-1}$  observed evident the CH bending vibrations [17]. The appearance of these peaks reveals the paraffins characterized by CH, CH<sub>2</sub> and CH<sub>3</sub> vibrations. The results exhibited bands appearing at 852 and 1647  $\text{cm}^{-1}$  due to CH bending and C=C stretching, respectively [18]. A medium peak exhibited at 1725  $\text{cm}^{-1}$  is indicative of carbonyl compounds i.e. ketone. Similarly, a small band observed at 3550  $\text{cm}^{-1}$  due to O-H bond stretching vibrations confirmed the alcoholic contents of the sample under study.

It is clear from the results that the intensities of the bands appeared for paraffins were found to be high which reveals its high concentration in the sample under test. On the other hand, bands, peaks observed for aromatics/olefins and oxygenated compounds have poor intensities which indicate their presence in low concentrations. It may be concluded from the results that the RCP-I possess long chain paraffins as the major constituents and the aromatics/olefins and oxygenated compounds as the minor components.

**RCN-II:** FTIR analysis of RCN-II was undertaken and data have been presented in Table 3.4. Some distinct bands appeared at 2922 and 2852  $\text{cm}^{-1}$  characterizing the CH and  $\text{CH}_2$  stretching vibrations. Peaks observed at 1456 and 1377  $\text{cm}^{-1}$  corresponded to the CH,  $\text{CH}_3$  bending vibrations (deformations) were evident. A moderate intensity peak at 727  $\text{cm}^{-1}$  indicated  $\text{CH}_2$  bending while a peak at 1078  $\text{cm}^{-1}$  showed CH bending vibrations. The observation of these bands implies the existence of paraffins which evidence CH,  $\text{CH}_2$  and  $\text{CH}_3$  vibrations. The aromatics/olefins as constituent of the oil under test was ensured by the appearance of some medium intensity peaks centered at 790 and 1580  $\text{cm}^{-1}$  due to CH bending and C=C stretching, respectively. A small peak exhibited at 1715  $\text{cm}^{-1}$  corresponded to ketone as carbonyl compound. For alcoholic contents, a small intensity peak can be observed at 3525  $\text{cm}^{-1}$  which is due to O-H bond stretching vibrations.

**RCA-III:** The results of FTIR analysis of RCA-III are compiled in Table 3.5. Some strong intensity bands can be observed at 2922 and 2852  $\text{cm}^{-1}$  which indicated the CH and  $\text{CH}_2$  stretching vibrations. Few peaks noticed at 1456 and 1373  $\text{cm}^{-1}$  corresponded to the CH,  $\text{CH}_3$  bending vibrations (deformations). A medium intensity band at 740  $\text{cm}^{-1}$  revealed  $\text{CH}_2$  bending and another medium intensity peak at 1078  $\text{cm}^{-1}$  show CH bending vibrations. The appearance of these peaks indicate the presence of paraffins which represent CH,  $\text{CH}_2$  and  $\text{CH}_3$  vibrations. The aromatics/olefins contents of the oil under test was verified by the appearance of some medium



intensity peaks centered at 795 and 1584  $\text{cm}^{-1}$  which can be attributed to CH bending and C=C stretching, respectively. At 1715  $\text{cm}^{-1}$ , a small peak evidenced the presence of ketone. A band at 3525  $\text{cm}^{-1}$  due O-H bond stretching vibrations can be seen which evident the presence of oxygenates.

The results revealed some larger intensity bands characterized the paraffin content in high concentration of the oils. Conversely, the smaller intensity peaks for aromatics/olefins and oxygenate content accounted for their low concentration. Thus, it may be inferred that the crude under study contained long chain paraffins as the major components and the aromatics/olefins and oxygenate as the least concentrated components.

**GC-MS Characterization:** The chemical and physical properties of petroleum are directly related to its chemical composition, which determines its market value [19]. The GC-MS distinguishes and characterizes crude oil sample according to their compound classes [20]. The chemical compositions in terms of paraffins, naphthenes, aromatics, oxygenates and olefins (PNAOO) of the three crudes were studied by GC-MS. The data was used to calculate the paraffins, olefins, naphthenes, aromatics, sulphur and nitrogen containing hydrocarbon group types. The paraffinic hydrocarbons identified in the RCP-I included mono, di, tri and tetraalkyl paraffines ranging from hexane to octacosane, triacontane and tetratriacontane. Among the naphthenes, the major compounds identified were found to be mostly mono, di and tri alkyl cyclohexanes. Very few olefins recognized to be present included 2, 3, 4-trimethyl-2-pentene, 11-chloro-1-undecene. The aromatics compounds verified in the crude oil mostly included alkyl derivatives of benzene. Some oxygenated hydrocarbons were also present which included alcohol and ketonic derivatives of paraffinic and aromatic hydrocarbons.

The GC-MS data of RCN-II revealed similar results as obtained for RCP-I. Compared with the main NIST library, most of the paraffins verified were found to be polyalkyl derivative of aliphatic hydrocarbons with carbon atoms from 6 to as high as 30 per molecule. Abundantly occurring paraffins were alkylated, hexane, heptane, octane, nonane and decane. The naphthenic hydrocarbon identified were commonly mono, di or tri alkylcyclohexane. Among olefins, the specific compounds identified were found to be 2, 3, 4-trimethyl-2-pentene, 11-chloro-1-undecene. The aromatics identified were solely the alkyl benzene derivatives. A number of largely occurring of oxygenates, including hydroxy and ketonic compounds were also identified.

The GC-MS data of the RCA-III confirmed the presence of the major paraffins including alkylated aliphatic hydrocarbons containing 7 to as high as 30 carbon atoms per molecules. Mostly, these compounds included alkyl derivatives of hexane, heptane, octane, nonane, decane, eicosane, heneicosane, docosane, tricosane, tetracosane, pentacosane, hexacosane, octacosane and triacontane. The naphthenes confirmed were found to be di and tri alkyl cyclohexane. Among the olefins, the specific compounds identified were found to be 2, 3, 4-trimethyl-2-pentene, 11-chloro-1-undecene. The aromatics identified were; sec-butyl benzene, 1-methyl, 2-propyl benzene, 1-4-diethyl benzene, butane, 2-phenyl, 3-hydroxy, 4-cyano, (1, 1-dimethyl propyl benzene), (3, 3-dimethyl butyl) benzene. The oxygenates determined were triasterianone, 3, 3-dimethyl 2-hexanone, 2-butyl octanol.

The relative abundance of the hydrocarbons types was calculated from the data. The results of the RCP-I are provided in Table 3.6. The proportions of the paraffins, naphthenes, aromatic, oxygenates and olefins were found to be 85.67, 6.13, 6.16, 1.43 and 0.73 %, respectively. Based on the results, the original oil contained different hydrocarbons group types as: paraffins >naphthenes >aromatics>oxygenates>olefins. The carbon range hydrocarbons were found to be

C<sub>5</sub>-C<sub>10</sub>, C<sub>11</sub>-C<sub>13</sub>, C<sub>14</sub>-C<sub>18</sub> and C<sub>5</sub>-C<sub>10</sub> in concentration of 25.26, 58.81, 6.21 and 9.72 %, respectively (Table 10). The various carbon number distribution hydrocarbons followed the order: C<sub>11</sub>-C<sub>13</sub>>C<sub>5</sub>-C<sub>10</sub>> C<sub>19</sub>-C<sub>n</sub>>C<sub>14</sub>-C<sub>18</sub>.

The relative abundance of hydrocarbons types i.e. paraffins, olefins, naphthenes and aromatics were calculated in case of the RCN-II. The results are provided in Table 5. The proportions of paraffins, naphthenes, aromatic, oxygenates and olefins were found to be 63.45, 26.20, 7.00, 2.70 and 0.90 %, respectively. On the basis of results, the original oil hydrocarbons distribution followed the order as: paraffins>naphthenes >aromatics>oxygenates>olefins. The different carbon range hydrocarbons determined were C<sub>5</sub>-C<sub>10</sub>, C<sub>11</sub>-C<sub>13</sub>, C<sub>14</sub>-C<sub>18</sub> and C<sub>19</sub>-C<sub>n</sub> in concentrations of 74.40, 16.92, 4.63 and 4.07 %, respectively (Table.3.7). The various carbon number distribution hydrocarbons followed the order of: C<sub>5</sub>-C<sub>10</sub>> C<sub>11</sub>-C<sub>13</sub>> C<sub>14</sub>-C<sub>18</sub>>C<sub>19</sub>-C<sub>n</sub>.

The distribution of the different hydrocarbons range compounds calculated from GC-MS data determined in case of the RCA-III is given in Table 5. The concentrations of the paraffins, naphthenes, aromatic, oxygenates and olefins were found to be 64.52, 14.67, 7.59, 2.70 and 12.08 and 1.14 %, respectively. Based on the results, the RCA III fractional hydrocarbons distribution followed the order of: paraffins>naphthenes >oxygenates> aromatics >olefins. The different carbon range hydrocarbons were i.e. C<sub>5</sub>-C<sub>10</sub> (61.52 %), C<sub>11</sub>-C<sub>13</sub> (18.69), C<sub>14</sub>-C<sub>18</sub> (8.12 %) and C<sub>19</sub>-C<sub>n</sub> (11.67) as per results compiled in the Table.6. The various carbon number distribution hydrocarbons followed the order of: C<sub>5</sub>-C<sub>10</sub>> C<sub>11</sub>-C<sub>13</sub>>C<sub>19</sub>-C<sub>n</sub>>C<sub>14</sub>-C<sub>18</sub>.

It is inferred from the results that all of the three crude oils studied have quite similar chemical compositions in terms of various individual hydrocarbons. However, they differ in paraffinic, olefinic, naphthenic, and aromatic group types with varying carbon range distributions.

The relative abundance of saturated hydrocarbons suggests that the oils are predominantly aliphatic.

**Table: 3.3.** FTIR analysis of RCP-I: Major Absorption Peaks Observed

<b>Position (cm<sup>-1</sup>)</b>	<b>Intensity</b>	<b>Assigned configuration</b>
727	Medium	CH <sub>2</sub> (bend) aliphatic
852	Weak	C-H (bend) aliphatic
1005	Weak	C-H (bend) aliphatic
1273	Medium	C-O(Stretch) Alcohol
1377	Strong	C-H (bend) aliphatic
1446	Strong	CH <sub>3</sub> (bend) aliphatic
1647	Weak	C = C (stretch) aromatic
1725	medium	C=O (stretch) ketone
2822	Strong	CH <sub>2</sub> (bend) aliphatic
2954	Strong	CH (bend) aliphatic

**Table: 3.4.** FTIR analysis of RCN-II:

<b>Position (cm<sup>-1</sup>)</b>	<b>Intensity</b>	<b>Assigned configuration</b>
727	Medium	CH <sub>2</sub> (bend) aliphatic
790	Weak	C-H (bend) aliphatic
1078	Weak	C-H (bend) aliphatic
1155	Medium	C-O(Stretch) Alcohol
1377	Strong	C-H (bend) aliphatic
1456	Strong	CH <sub>3</sub> (bend) aliphatic
1580	Weak	C = C (stretch) aromatic
1715	medium	C=O (stretch) ketone
2852	Strong	CH <sub>2</sub> (bend) aliphatic
2922	Strong	CH (bend) aliphatic

**Table: 3.5.** FTIR analysis of RCA-III:

<b>Position (cm<sup>-1</sup>)</b>	<b>Intensity</b>	<b>Assigned configuration</b>
740	Medium	CH <sub>2</sub> (bend) aliphatic
767	Weak	C-H (bend) aliphatic
1081	Weak	C-H (bend) aliphatic
1168	Medium	C-O(Stretch) Alcohol
1373	Strong	C-H (bend) aliphatic
1456	Strong	CH <sub>3</sub> (bend) aliphatic
1586	Weak	C = C (stretch) aromatic
1718	medium	C=O (stretch) ketone
2851	Strong	CH <sub>2</sub> (bend) aliphatic
2920	Strong	CH (bend) aliphatic

**Table: 3.6.** Hydrocarbon Group Types Distribution Determined in RCP-I, RCN-II and RCA-III Crudes

<b>Concentration (wt%)</b>					
	Paraffins	Naphthenes	Aromatics	Oxygenates	Olefins
<b>Sample</b>					
RCP-I	85.67	6.23	6.26	1.53	0.73
RCN-II	63.45	26.02	7.00	2.71	0.90
RCA-III	64.52	14.67	7.59	12.08	1.14

**Table: 3.7.** Carbon Number Distribution Determined in RCP-I, RCN-II and RCA-III Crudes

<b>Concentration (wt%)</b>				
	C <sub>5</sub> -C <sub>10</sub>	C <sub>11</sub> -C <sub>13</sub>	C <sub>14</sub> -C <sub>18</sub>	C <sub>19</sub> -C <sub>n</sub>
<b>Sample</b>				
RCP-I	25.26	58.81	6.21	9.72
RCN-II	74.40	16.92	4.63	4.07
RCA-III	61.52	18.69	8.12	11.67

### 3.1.2. Characterization of Surfactants

The three surfactants i.e. cationic, anionic and non-ionic surfactants denoted as CTAB, SDS and Triton-100 used in current investigation were selected on the basis of the properties described by the manufacturers including its molecular mass, solubility, critical micelle concentration, polarity, micelle size, etc. The different properties of the surfactants are listed in Table 3.8.

**Table 3.8.** Properties of Various Surfactants

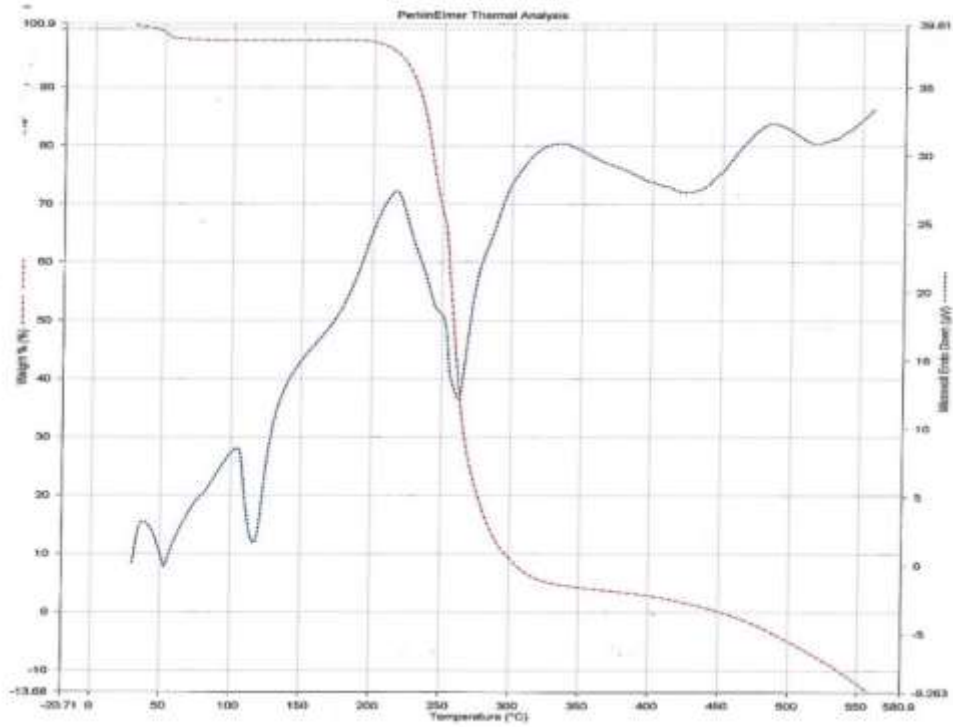
Property	Unit	CTAB	SDS	Triton-X100
Chemical Formula	-	C <sub>19</sub> H <sub>42</sub> BrN	NaC <sub>12</sub> H <sub>25</sub> SO <sub>4</sub>	C <sub>14</sub> H <sub>22</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub>
Type/Charge	-	Cationic	Anionic	Neutral
Molecular mass	Gm	364.45	288.3	647
Critical Micelle Concentration	mM	0.92-1.0	8.2	0.2-0.9
Solubility in methanol		Soluble	Soluble	Soluble

The thermo-gravimetric (TG) study of the three surfactants was carried out in the temperature range of 300-300 °C. The weight losses as a function of temperature were determined at a programmed heating rate of 10°C/min, starting at 30°C under conditions of air. The results are compiled in Table-3.9 and Figs. 3.1-3.3. It can be seen from the data that all samples gave almost similar TG curves with two stages of weight loss. In the first stage, the weight loss observed for CTAB was 3 % while in the second stage, it was 93 %. Similarly, for SDS, the weight losses in the two stages were 2.5 and 66.5 %, respectively. In case of Triton X-100, the weight losses were 10 and 90 %, respectively. It can be seen that the weight loss is not so much profound which is due to the large number of carbon chain present in the surfactants and the variation in three different surfactants can be observed by descending order of carbon chain in different types of surfactants [21], i.e. CTAB > SDS >Triton X-100. Over all, the weight loss is < 10 % which is attributed to the decomposition of hydroxyl (OH) group from the matrix. The results inferred that the three surfactants used are stable thermally in the temperature range selected in the distillation study.

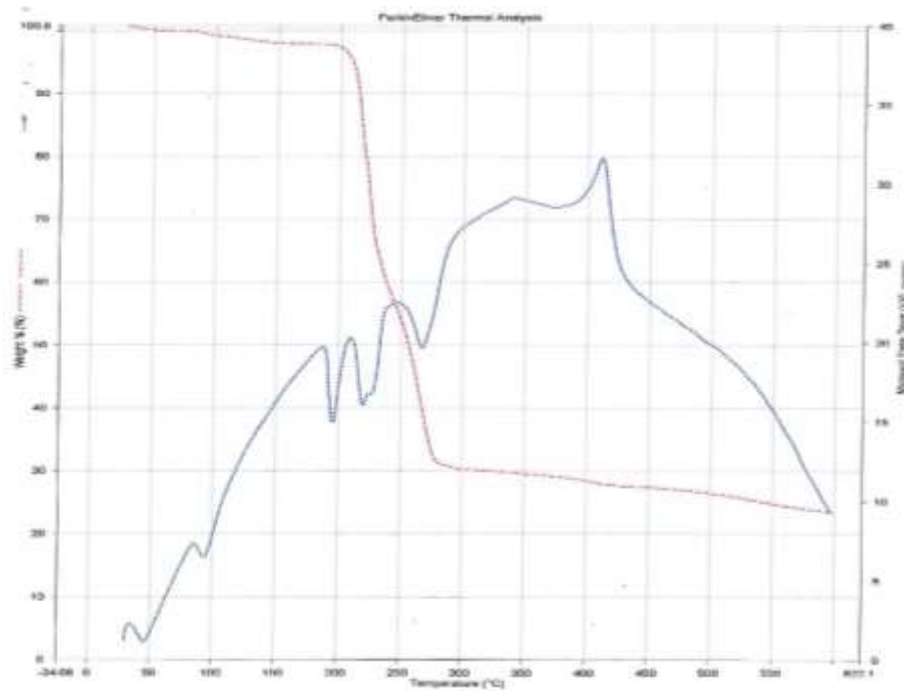
**Table: 3.9.** Thermo-Oxidative Degradation Data of the Surfactants

<b>Sample</b>	<b>Degradation Step</b>	<b>T Onset (°C)</b>	<b>Mass left before deg. step (wt %)</b>	<b>T Offset (°C)</b>	<b>Mass left after deg. step (wt %)</b>	<b>Mass lost per deg.step (wt %)</b>
CTAB	1	50	100	200	97	03
	2	201	97	315	03	93
	3	316	03	450	00	03
SDS	1	50	100	210	97.50	2.50
	2	211	97.50	275	32	65.50
	3	276	32	600	24	8
TX-100	1	30	100	250	95	10
	2	251	95	355	02	88
	3	356	02	500	00	02

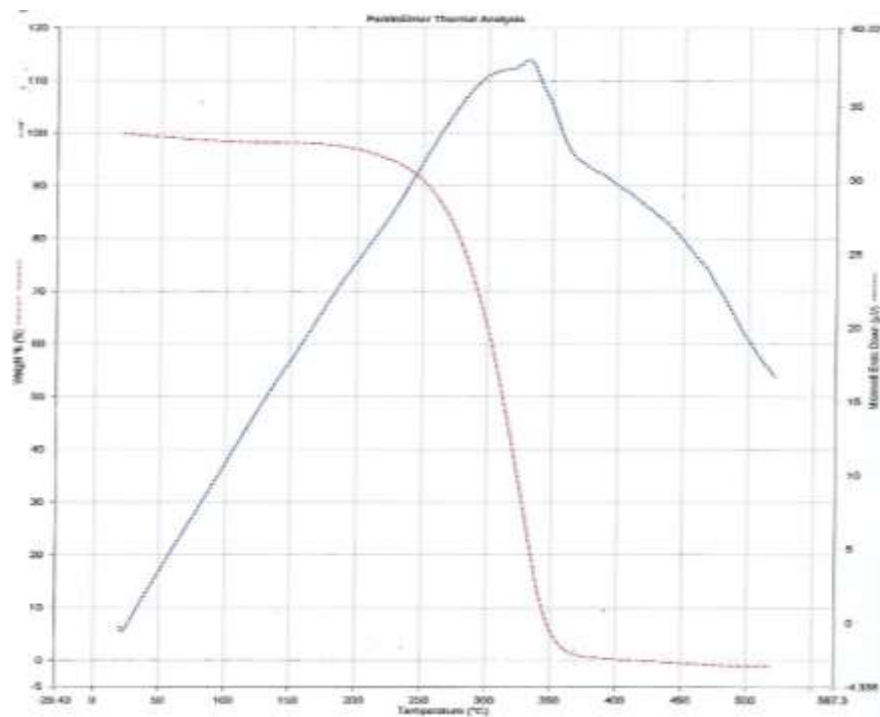




**Fig.3.1.** TG profile of CTAB



**Fig.3.2.** TG profile of SDS



**Fig.3.3.** TG profile of TX-100

## **PHASE-II**

The main factor responsible for poor yields of distillate fractions during atmospheric distillation of petroleum crudes are the heavy molecular weight constituents oil like asphaltenes and resins [22-24]. In this phase, the plain as well as the surfactant-dispersed crude oil samples were subjected to atmospheric distillation and the three main test fractions in the gasoline, diesel and heavy oil range i.e. light oil, middle oil and heavy oil were collected and characterized accordingly using standard ASTM/IP designated methods.

### **3.2. DISTILLATION STUDY OF PLAIN CRUDES**

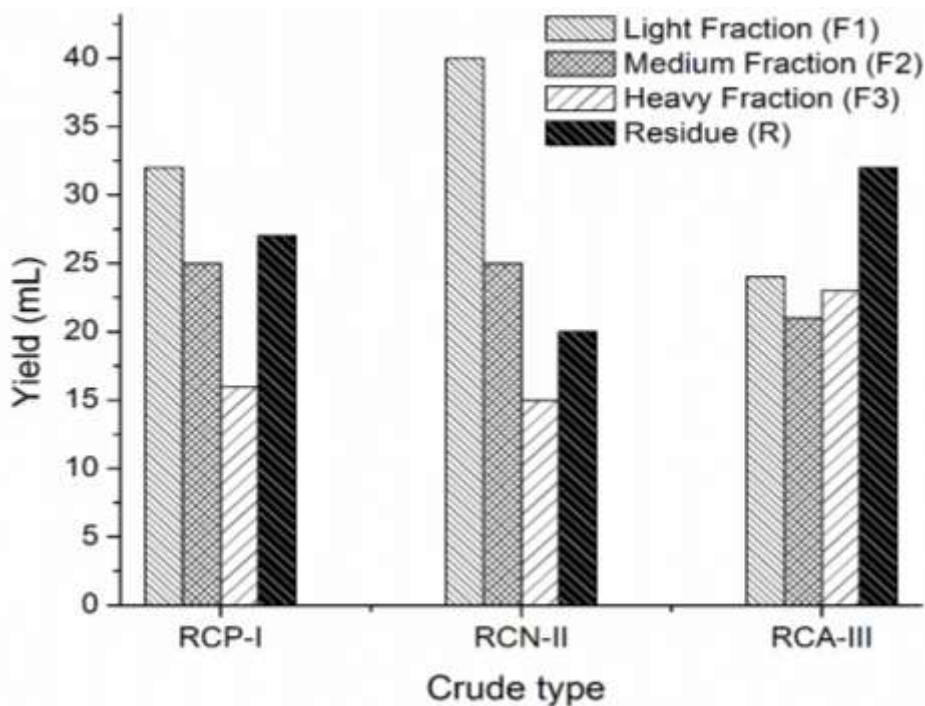
The distillation of each of the crudes under study was carried out so as to collect three fractions namely F1, F2 and F3 and to determine their fuel properties. The temperature readings were recorded correspond to first drop, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 95% of the distilled volume so as to construct the ASTM distillation curves.

#### **3.2.1. Yields of Distillate Fractions**

The distillation of the plain crude oils was carried out and the product distribution of F1, F2, F3 and R was studied. The results are assembled in Fig. 3.4. It can be seen that the RCN-II gave the highest amounts of F1 (IBP to 180 °C), the RCP-I gave highest amount of F2 (180 to 250 °C) while the RCA-III gave the highest amount of F3 (250 to 350 °C). The amounts of residue were observed to be 27, 20 and 22 % for the RCP-I, RCN-II and RCA-III, respectively. Over all, the RCP-I gave 32 % F1, 25 % F2, 16 % F3 and 27% R. The RCN-II gave 40 % F1, 25 % F2, 15 % F3, and 20 % R, while the RCA-III gave 24 % F1, 21% F2, 23 % F3 and 32% R.

The atmospheric residue describes the material at the bottom of the atmospheric distillation, which has an atmospheric equivalent temperature (AET) above 380°C [32]. It can be

seen that all samples contained high amount of residues particularly the heavy crude, which may be correspond to differences in elemental/chemical compositions of the three crudes which in turn may be due to biotic source materials, source rocks, depositional environment, and diagenetic and thermal history. As reported earlier that more-aromatic, higher-boiling fractions and residues, are dominated by polynuclear aromatics, (e.g., multi-ring cycloalkane, aromatic, and polyaromatic structures) with minimal alkyl branching, are less reactive than fractions with higher H/C ratios [33] and gave high yields of residue. The difference in asphaltenes, sulphur and nitrogen containing compounds as well as occluded hydrocarbons may be the other reason. As reported earlier, asphaltene aggregates and hydrocarbons occluded with in asphaltenes frame work are stable at high temperatures, up to 300 °C [34, 35] and concentrate in residues.

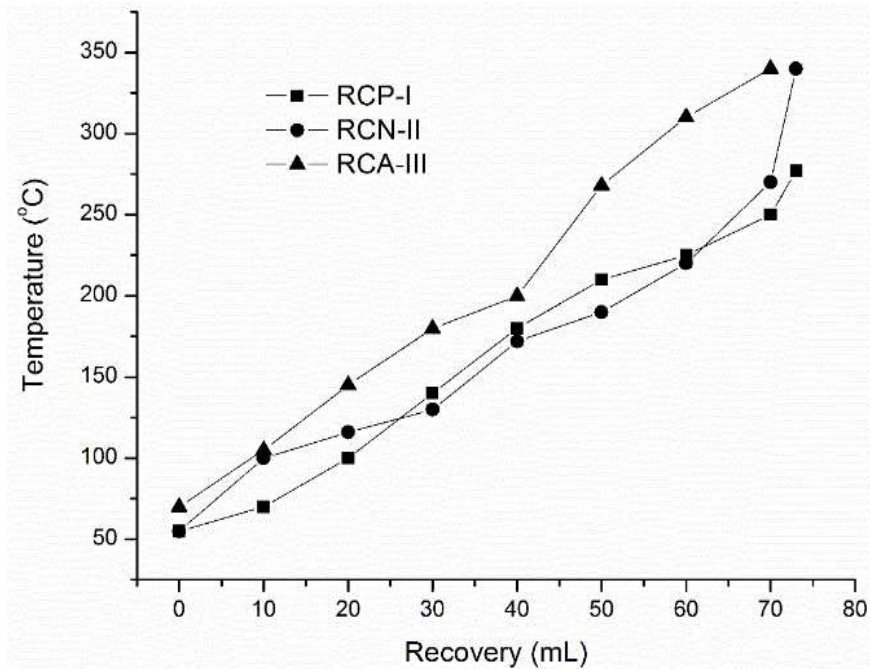


**Fig. 3.4.** Distillation behavior of plain crudes: Yields of distillate fractions

### **3.2.2. Boiling Point Range (BPR) Distribution**

The different marketable products derived from crude oil distillation/fractionation such as fuel gas, light or heavy naphtha, kerosene, aviation fuel, light or heavy gasoil and the amount of residuals, are strongly dependent on the quality of the petroleum which are characterized by the ASTM curves [36]. An ASTM distillation curve is obtained by plotting the cumulative mass or volume distillation fractions with increasing temperature. The shape of the curve depends on the volatility of the components present in each crude oil and is helpful to decide about the suitability of a crude for onward refining operations. As such, the curve gives a “footprint” of the composition of a crude oil [37]. Further, the curve is used to understand the behavior of oil before distillation, when the oil is subjected to a distillation tower on an industrial scale is already known about the percentage of distillate obtained working at a specific temperature [38].

The distillation behaviors of the three crudes under study were evaluated from the distillation curves, displayed in Fig.3.5, which indicate separation of the petroleum fractions or products as a function of temperature. The data collected were; the initial boiling temperature (IBT), the temperature at volume fractions of 10, 20, 30, 40, 50, 60 and 70 %, the final boiling temperature (FBT) and the residue.



**Fig.3.5.** Boiling point range distributions/distillation curves of plain crudes

The IBT, also called initial boiling point (IBP) is the boiling point of the lightest hydrocarbon component. It was observed to be 58 °C for RCP-I while 70 and 55 °C for the RCN-II and RCA-III crudes, respectively. Similarly, the FBT or final boiling point (FBP) which represents the heaviest hydrocarbon component was observed to be 340 °C for all the three crudes. The results depicted broader distillation temperature ranges extended from 58 -340 °C for RCP-I, 70-340 °C for RCN-II while 55-340 °C for RCA-III. Further, a significant amount of the three crudes (85-90 %) was distilled/recovered at a distillation temperature of 340 °C, the rest was considered as residue. As reported elsewhere, to be a good feed stock for petroleum refining, the crude oil primary requirement according to EN 590, is that at 250 °C the distilled liquid fraction must be less than 65 vol % while at 350 °C must be 85 vol %. The 95 vol % of the distilled fraction must be obtained at 360 °C [39]. The results showed conformance to EN 590 requirements and indicated that all of the three crudes are good feed stocks for commercial refining/ distillation.

The values of the distillation ranges/ the distilled fractions are usually based on their refinery product classifications and the temperatures at which 10, 50 and 90 mL recovery is made, characterize the volatility of the fuel as light, medium and heavy fractions. As can be seen from the results, the temperature required for the recovery of each 10-25% volumetric distillate fraction was observed to be lower for RCP-I up to 10 % recovery, while lower for RCN-II after 25 -50%. The pattern of the curve for RCA-III is similar to the RCP-I and RCN-II, however, the temperatures required for the recovery of each 10, 50 and 90 % volumetric distillate fractions were slightly higher than the RCP-I and RCN-II. The RCP-I gave more volatile constituents that boiled off in the early stages of the distillation while the RCN-II, and RCA-III gave less volatile constituents in that temperature range, which evidenced the presence of a different distribution of chemical components.

**Inferences:** As reported earlier, the shape of the curves is dependent on the volatility of components in each crude oil [37]. It can be noticed that the volume of the distillate increased almost linearly from 10 to 90% with the increase in temperature in all three crudes. The given curves showed no multiple inflections or convergences but were rather flat. Some distinct differences, however, persisted among the three curves started from low distillate volumes and magnified at higher distillate volume fraction values, which indicated the difference in the nature and chemical compositions of the crudes under study.

### 3.3. DISTILLATION STUDY OF CHEMICALLY DISPERSED CRUDES

The results of the distillation of the plain crudes revealed that significant amount of the residue was left over in all three crude oils studied. The possible reason may be the residue which comprises of viscous, and high boiling hydrocarbons that usually contain resin and asphaltenes with high levels of heterocyclic aromatic and naphthenic compounds having varying amounts of sulfur, nitrogen, oxygen, and other elements [40]. The chemical surfactants under study were used with the objectives so as to disperse the asphaltenes contents of the sample oils and to open up the occluded phases within the asphaltenes to undergo distillation. The chemical surfactants were used in different dispersant-to-oil ratios (DORs) and the yields of the light, medium and heavy fractions as a function of DOR were studied and discussed in comparison with the control.

#### 3.3.1. Yields of Distillate Fractions

The anionic, cationic and neutral surfactants were employed as dispersants so as to ascertain their role in increasing the yields of distillate fractions, the distillation behavior, the fuel properties and compositions of the test fractions.

**SDS-dispersed Crudes:** In the first step, the SDS was used as a typical anionic surfactant, in different DORs and the yields of the F1, F2 and F3 as a function of DOR was studied so to optimize the DOR. Each of the three crudes i.e. RCP-I, RCN-II and RCA-III, was treated with the dispersant in different DORs i.e. 0:100, 5:100, 10:100, 15:100, 20:100, 25:100 and 30:100 and subsequently distilled. The results are compiled in Fig 3.6 (a), (b) and (c). The optimum DOR was decided from the yields of the test fuels i.e. light distillates (gasoline and diesel). It can be observed that the yields increased with the increase in DOR in RCP-I (Fig. 3.6 a) and RCN-II (Fig.3.6 b)



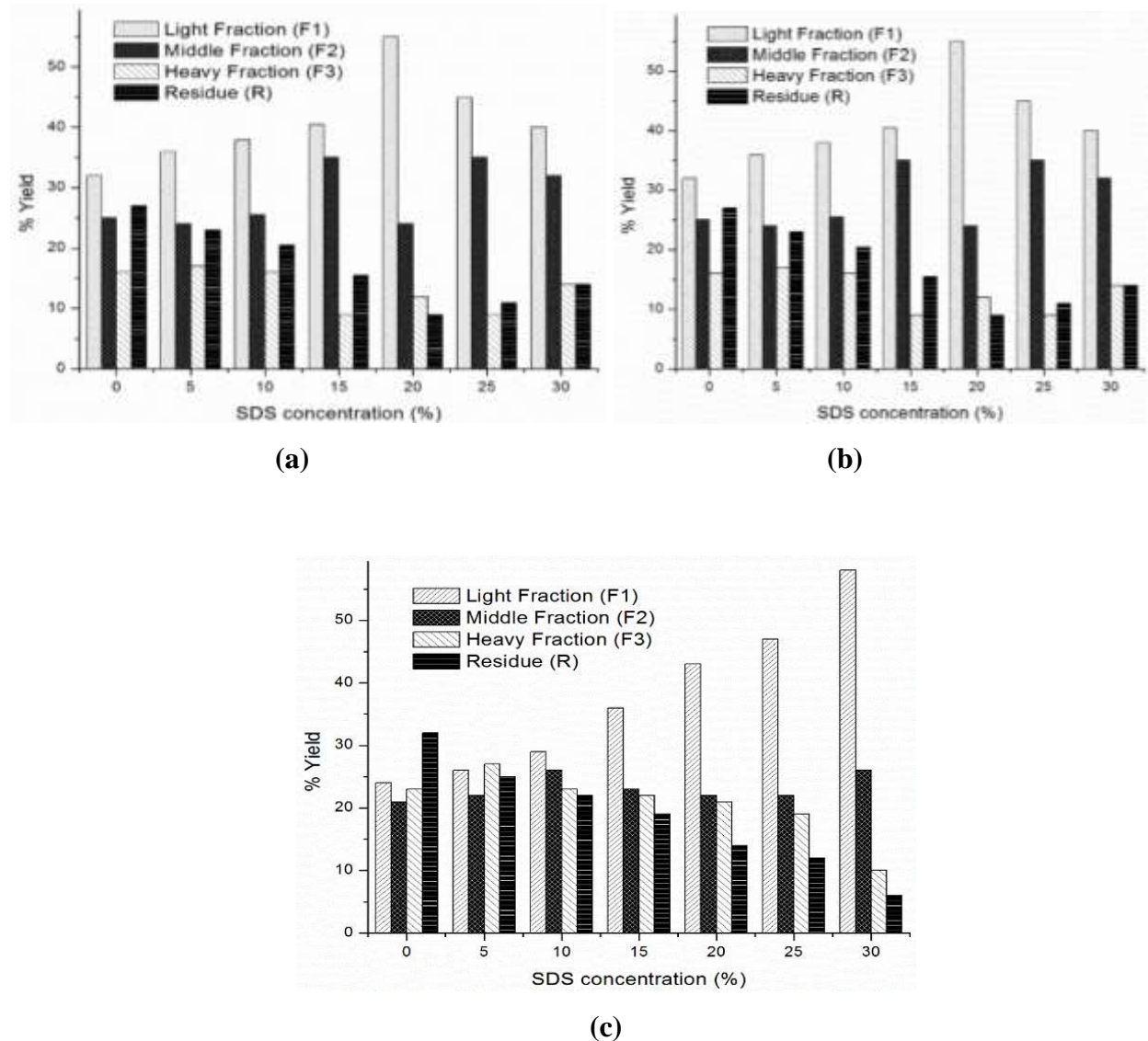
samples where the optimum ratio was found to be 20:100. While the RCA-III (Fig.3.6 c) behaved slightly differently, where 30:100 appeared to be the optimum ratio.

As confirmed from the characterization study of the three crudes, the RCA-III is a heavy crude and thus requires high amount of the dispersant so as to partition/solvate/disperse the high amount of heavy and polar constituents so as to decrease the polarity and vanish the interactions between them and expose the occluded/caged hydrocarbons with in the asphaltene's network to distillation compared to the RCP-I and RCN-II which are paraffinic and naphthenic crudes, respectively containing less amounts of such constituents. As reported earlier the solubility of hydrocarbons increases linearly with the increase in surfactant concentration as a consequence of association between the PAH and micelles above critical micellar concentration, CMC [41]. Further, the heteroatom contents of the RCA-III are also high as can be seen from the elemental analysis. Heteroatom-containing compounds, especially polar molecules, which concentrate in heavy, high-viscosity crudes are responsible for most of the difficulties in refining, and deposit formation of petroleum [42].

As can be seen from the compiled results that at the optimum DOR, the yields of F1 and F2 considerably increased, whereas that of F3 and R decreased in comparison with the plain crudes. The results inferred that the yields of F1 and F2 increased but at the expense of F3 and R. For RCP-I, the % recovery of F1 and F2 increased from 32 and 25 % in plain crudes to 56 and 36 % in SDS-dispersed sample, respectively. On the other hand, the yields of F3 and R decreased to 12 and 9 % from 16 and 26 %, respectively. As RCP-I is a light crude, hence the recovery of F1 was higher in plain distillation which further increased to maximum of 56 % in SDS-dispersed sample. Similar was the case of the RCN-II, which is a medium crude, the yield of F1 increased

from initial of 40 % in control to 46 % in dispersed sample, and the % R decreased from 20 to 7 %. However, the difference in the % recovery of F2 and F3 was less pronounced.

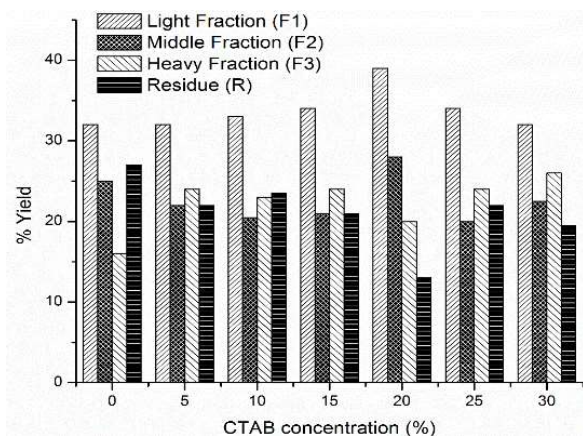
The RCA-III is a heavy crude oil, the effect of SDS-dispersion on distribution of various fractions was very prominent. The % recovery of F1 increased from 24 % in plain crude to 58 % in SDS-dispersed sample. Likewise, the yield of R decreased from 32 % to about 6 %.



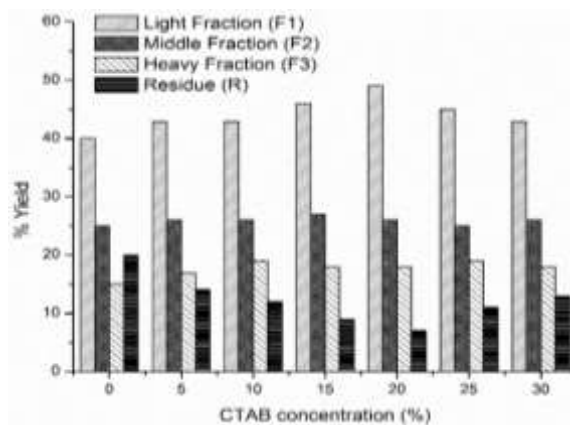
**Fig. 3.6.** Yields of distillate fractions as a function of SDS-to-oil ratio: (a) RCP-I (b) RCN-II and (c) RCA-III.

**CTAB-dispersed Crudes:** In the second step, all the crudes were treated with a cationic surfactant and CTAB was used as a typical dispersant in different ratios so as to study the influence of DORs on the yields of different distillate fractions. Each of the three crudes i.e. RCP-I, RCN-II and RCA-III, was treated with CTAB in different DORs i.e. 0:100, 5:100, 10:100, 15:100, 20:100, 25:100 and 30:100, and subjected to fractional distillation under the same experimental conditions so as to investigate on its optimum ratio required for getting the distillate fractions in high yields. The results are displayed in Figs. 3.7 (a), (b) and (c). As evident from the results, in all of the three crudes, the yield of light fractions linearly increased with the increase in DOR.

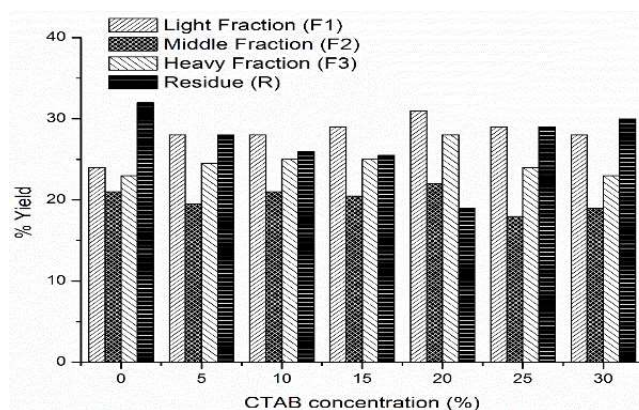
In RCP-I [Fig. 3.7 (a)], a DOR of 20:100 caused a significant increase in the yield of F1 (from 32 to 39 %), whereas the yield of residue decreased from 27 % to 13 %. The yields of F2 and F3 also increased slightly from 25 and 16 % in plain crudes to 28 and 20 % in CTAB-dispersed sample. It can be seen that the yields of distillates increased but at the expense the residue and almost 50 % reduction in the yield of residue can be noticed.



(a)



(b)



(c)

**Fig. 3.7.** Yields of distillate fractions as a function of CTAB-to- oil ratio: (a) RCP-I (b) RCN-II and (c) RCA-III.

The optimum DORs were also determined in RCN-II and RCA-III. The results are compiled in Fig. 3.7 (b) and (c). It was found that a DOR of 20:100 both in RCN-II and RCA-III gave high yields of distilled fractions. In RCN-II, an increase was observed in the yield of F1, which increased from 40 % (plain crude) to 49 %, whereas the yields of F3 slightly increased from 15 % to 18 %, respectively. The yield of F2 remained un-affected and observed to be same as in the plain distillation. The yield of residue encountered major reduction of almost 3 folds, and

declined to 7 % compared to 20 % in the plain distillation. Similarly, in RCA-III, the yield F1 increased from 24 to 31 % and that of F3 from 23 to 28 %, respectively. The yield of F3 remained same as in the plain crude. On the other hand, the yield of residue decreased from 32 to 19 %.

It is evident from the compiled results that in all three crudes, under the optimum DORs, the yields of F1 significantly increased, that of F2 slightly increased, while F3 less influenced. However, the residue decreased significantly. The results showed that CTAB was more effective as compared to SDS and CTAB in reducing the residues in all three crudes. The cationic surfactant was observed to be capable of solvating the hydrocarbons with boiling points close to F1 and F2 fractions, however, it influenced the yield of F3 fraction marginally.

**Triton X-100 dispersed Crudes:** In the third step, the light, medium and heavy crudes were treated with a typical neutral surfactant i.e. Triton X-100 in different DORs. The distributions of F1, F2, F3 and R determined in all the three crudes as function of DOR is shown in Fig. 3.8 (a), (b) and (c).

In RCP-I [Fig. 3.8 (a)], the yield of light fraction increased and that of residue decreased with the increase in DOR. The optimum DOR was found to be 30:100, at which the yield of F1 increased to 39 % (from initial of 32 % in plain crude), and that of residue decreased from 27 to 11 %. At 30:100 ratio, the yields of F2 and F3 increased from 25 and 16 % determined in plain crude to 27 and 23 %, respectively. Like the cationic and anionic surfactants, the TX-100 also decreased the yield of residue by more than 50 % in light crude, which caused an increase in the yields of F2, F2 and F3.

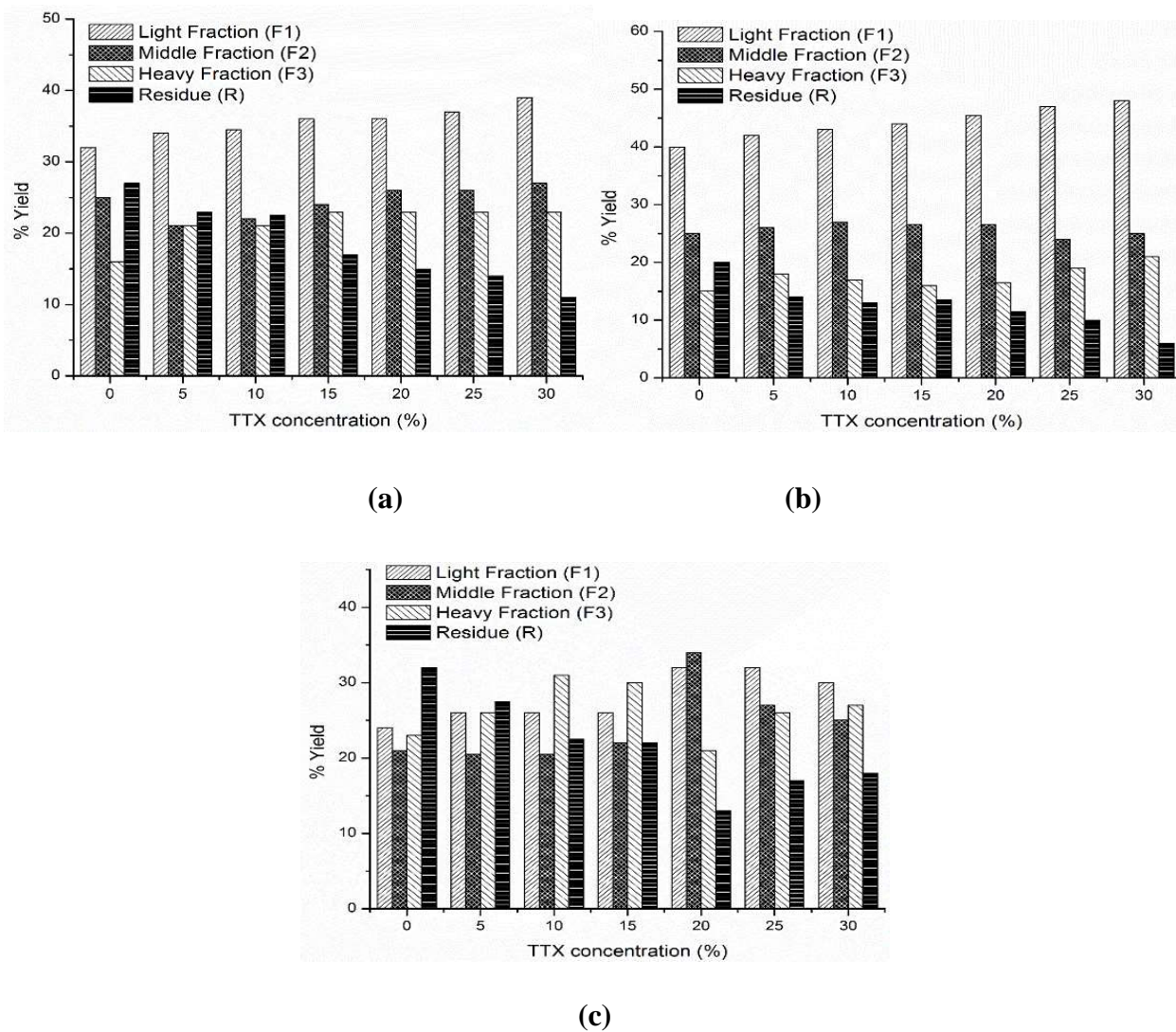
Similar was the case of the medium crude (RCN-II) [Fig. 3.8 (b)], where the optimum DOR was found to be 30:100. Under the optimum ratio, the yield of F1 increased from 40 % (plain

crude) to 48 %, whereas the residue decreased from 20 % to about 06 %. Likewise, the yield of F3 also increased from 15 % in original crude to 21 % in TX-100-dispersed crude, whereas that of F2 remained unchanged.

In heavy crude (RCA-III) Fig. 3.8 (c), the maximum yields of F1 and F2 were obtained at DOR of 20:100. The minimum residue yield was also obtained. Thus, the optimum DOR for RCA-III was found to be 20:100. Under the optimum DOR, the yields of F1 and F2 increased from 24 and 21 % in plain crude to 32 and 34 % in TX-100 dispersed sample, respectively. The yield of the residue decreased from 32 to 13 %. Similarly, the yield of F3 also decreased from 23 to 21 %. Hence, the TX-100 dispersion not only decreased the yield of residue but also the heavy fraction, and increased the yields of F1 and F2. This may be attributed to non-polar (neutral) nature of the surfactant, which may have experienced less hindrances during interaction with heavier molecules in the residue.

**Inferences:** The marked influence of the three surfactants on the yield distribution best describes their performance, where the recovery of the light fraction increased and that of the residue decreased significantly. The composition of the crude oil is a strong factor governing the yields of different distillate fraction particularly the gasoline and diesel range fractions, which may be due to different structural interactions between asphaltenes and paraffins. Such interactions may produce composites with lower dissolution kinetics [43], which leads to poor yields. Asphaltenes are ultra-complex mixtures has a wide diversity of functional groups that promote noncovalent associations, through acid–base interactions (between carboxylic acids and pyridine groups), hydrogen bonding, formation of coordination complexes (due to the presence of vanadium and nickel), generation of hydrophobic pockets (by van der Waals interactions between alkyl and

naphthenic moieties), and  $\pi$ - $\pi$  stacking (due to interactions between parallel aromatic cores) [44, 45]. These interactions vary from crude to crude.



**Fig. 3.8.** Yields of distillate fractions as a function of TX-100-to-oil ratio: (a) RCP-I (b) RCN-II and (c) RCA-III.

### 3.3.2. Boiling Point Range (BPR) Distribution

The influence of the three surfactants/dispersants on the distillation behavior (volatility/shape of the distillation curves) was studied in comparison with the control. Each of the surfactant was used in the previously optimized ratios and the experimental observations have been plotted on the same graph with that of control for ready comparison.

**SDS-dispersed Crudes:** The results are displayed in Fig. 3.9 (a), (b) and (c) which indicated that the two curves started and ends at the same time and showed the same IBP and FBP in all the three crudes. However, after starts, a marked and non-uniform shift in the curves over the course of the distillation can be observed for all of three crudes with variation in temperatures for recovery of each 10-mL fraction which has been considerably lowered in the SDS-dispersed sample. The slopes of the curves indicated an increase in the proportions of the low molecular weight products.

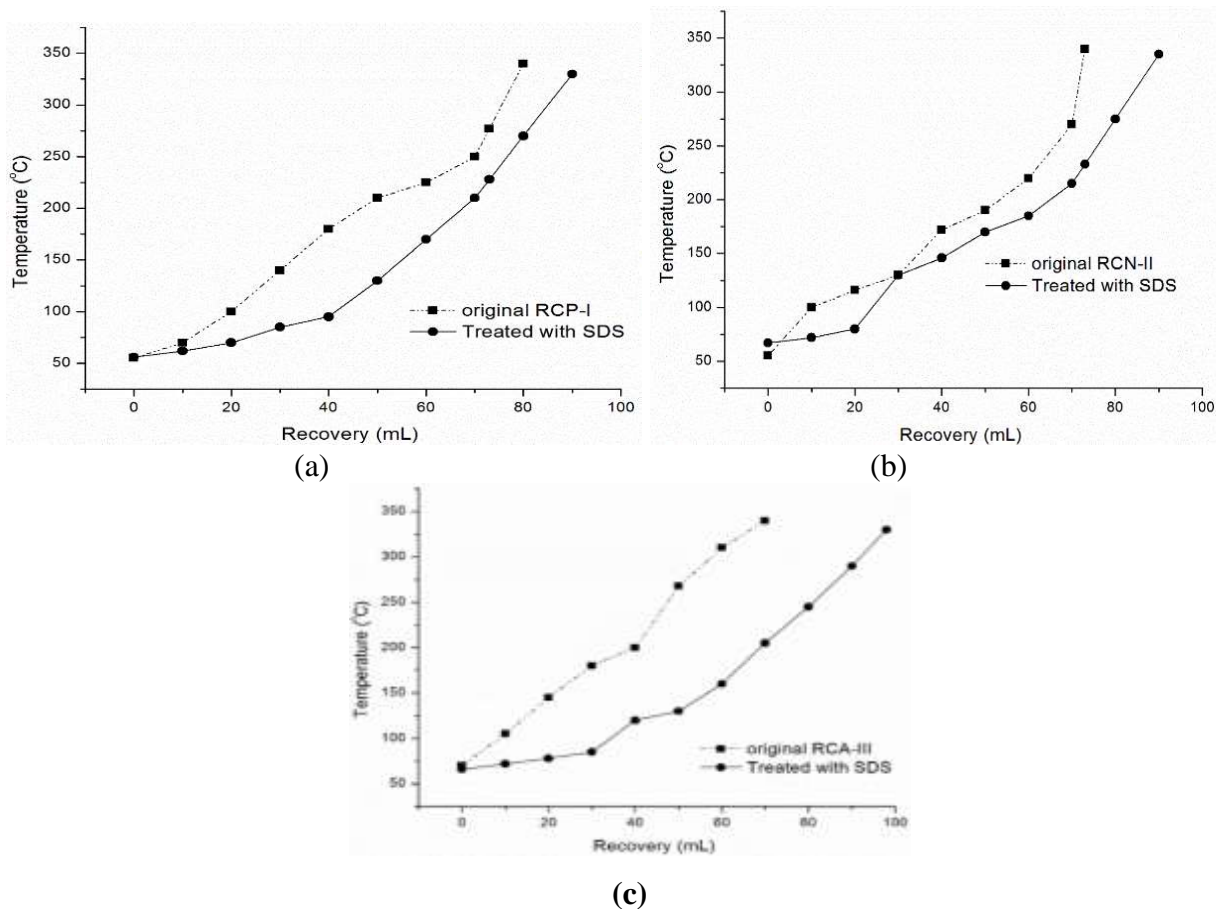
The curve of RCP-I [Fig. 3.9 (a)] indicated no overlapping throughout the distillation except at the initial IBP, hence showed no significant change in IBP, however, as the distillation proceeded, a change in the shape can be observed which can be ascribed to increase in low distillate volumes at relatively low temperatures. A decrease/reduction in temperature for the higher distillate volume fractions can also be observed which indicated that the SDS dispersion assisted in distillation of the oil under study by giving rise to the formation of more distillate fractions.

The effects of the SDS dispersion on the boiling temperatures of each 10-mL fraction in RCN-II and RCA-III [Fig. 3.9 (b) and (c)] were also investigated. It can be seen that the boiling/evaporation temperatures of each 10% v/v (10 mL) fraction has been lowered significantly in RCAN-II at the early stage of distillation, however, in the middle of the distillation, the curve



levelled with that of the control and in the later stage, again diverged. The curve obtained for RCA-III when compared to RCP-I and RCN-II, exhibited significant changes in all stages of the distillation. The different distillation behaviors can be ascribed to the variation in heavy and polar hydrocarbons in the three crudes under study. A high aliphatic hydrocarbon content generally corresponds to lower boiling temperatures, and a high cyclic hydrocarbon content to higher boiling temperatures. The change in hydrocarbon contents over the course of a distillation can explain the slope of the three-distillation curves.

Overall the effect is more pronounced in RCA-III. It can be deduced from the results that dispersing affinity of the SDS is higher towards heavy crude.



**Fig. 3.9** Distillation curves of SDS- dispersed crude oils: (a) RCP-I (b) RCN-II and (c) RCA-III.

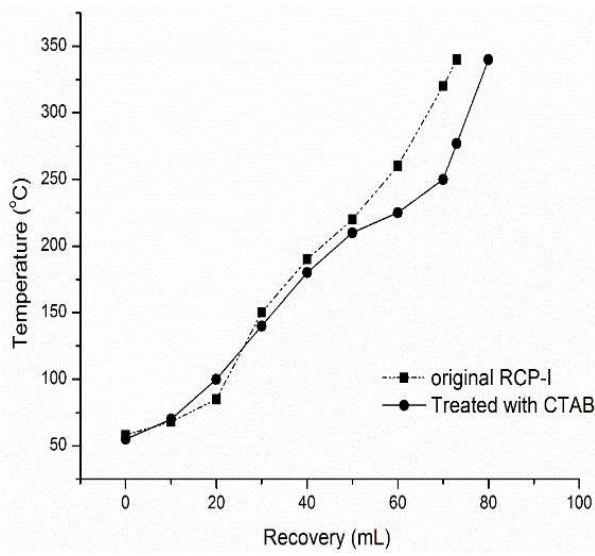
**CTAB- dispersed Crudes:** The distillation profiles (distillation curves) of the crudes under optimum DOR (20:100) of CTAB dispersed samples are provided in Fig. 3.10 (a), (b) and (c) which showed a decrease in the boiling points determined for each 10 mL fractions in comparison with the control with major changes can be observed in the latter stages of distillation. However, the IBP remained same.

In light crude i.e. RCP-I, [Fig. 3.10 (a)], the boiling points of 10 mL fractions up to 50 mL fractions were almost alike but beyond which a marked decrease can be noticed. The BP of 60, 70 and 80 mL fractions showed a decrease of 30 to 50 °C than the control, though the FBP remained unaffected. As afore mentioned that in CTAB-dispersed RCP-I, the yield of residue decreased by about 50 %, which evident that CTAB worked well in exposing the hydrocarbons caged with in the macromolecules constituting the residual fraction.

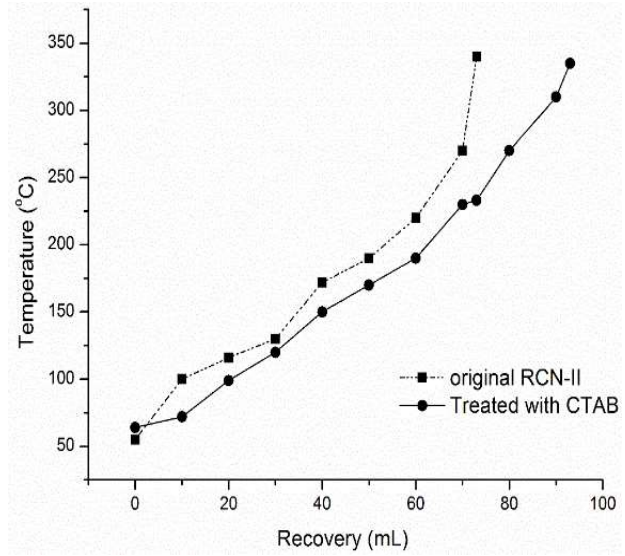
In RCN-II [Fig. 3.10 (b)], the effect is more pronounced, where the distillation curve showed a decrease in the BP of each 10 mL fraction. The difference of BP with the control was less (30 to 50 °C) upto 70 mL recovery, but became more pronounced (upto 100 °C) for 80 mL fraction. Additionally, 98 mL recovery was observed which showed excellent dispersing character of the CTAB for this crude.

In RCA-III [Fig. 3.10 (c)], the distillation curves of the plain and CTAB-dispersed crudes overlapped in the middle. The BPs of initial 10 and 20 mL fractions (light products) and that of 50, 60 and 70 mL fractions (heavy) decreased. The 20 and 30 mL fractions showed no change while 30 and 40 mL fractions exhibited an increase.

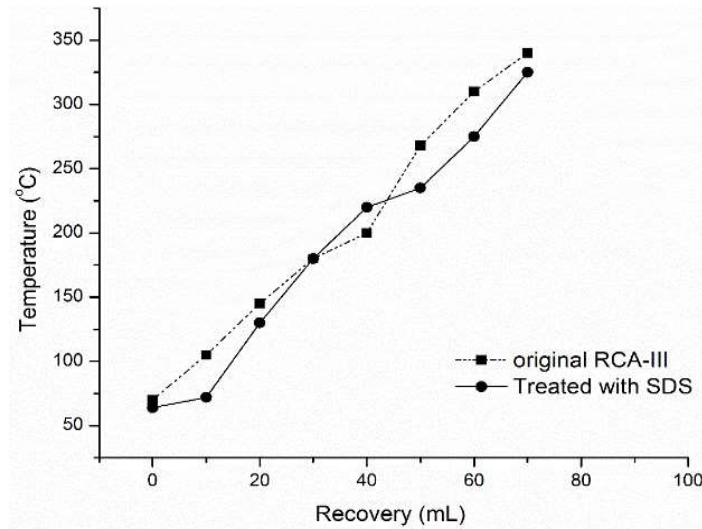
Over all the effect is more pronounced RCN-II. It can be deduced from the results that dispersing affinity of the CTAB is higher towards naphthenic crude.



a)



(b)



(c)

**Fig. 3.10** Distillation curves of CTAB- dispersed crude oils: (a) RCP-I (b) RCN-II and (c) RCA-III.

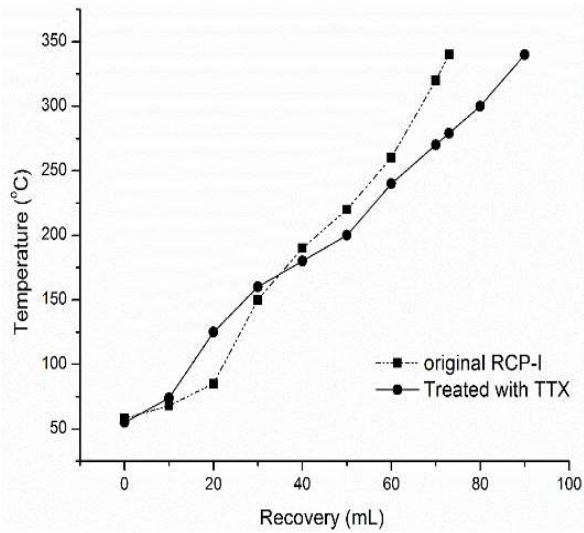
**Titon-X-100-dispersed Crudes:** The ASTM distillation curves of the control and that of the TX-100-dispersed samples (at optimum concentrations) are shown in Fig. 3.11 (a), (b) and (c). It is evident from the displayed results, the curves showed different behaviors in different crudes.

In RCP-I [Fig. 3.11 (a)], the influence is negligible for fractions collected in 10 mL increments up to 40 mL, however, for fractions of 50 mL and beyond, a marked decrease in the boiling points can be seen as compared to plain crudes.

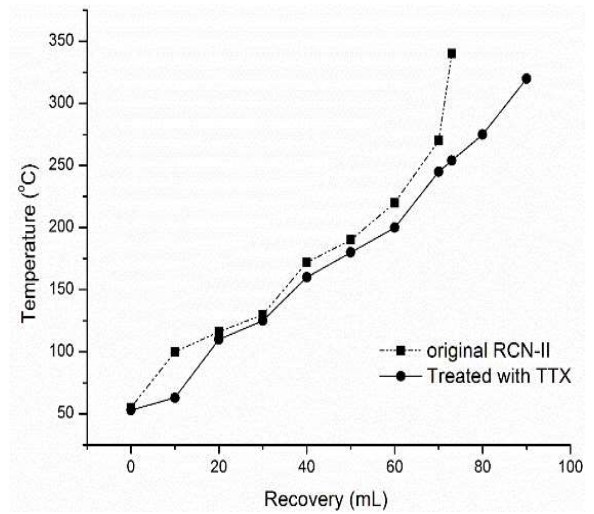
In RCN-II [Fig. 3.11 (b)], the BPs of the all volume wise collected fractions have been lowered. However, the decrease in boiling points was more pronounced in first 10 mL fraction and those fractions obtained beyond 40 mL. For the fractions of 20 mL and 30 mL, no change can be observed. This showed that as compared to light crude (RCP-I) where the BP of only the high boiling fractions was reduced, here, both the light as well as heavy fractions were influenced.

The shape of the curve for the TX-100-dispersed RCA-III [Fig. 3.11 (c)], is quite different from the other crudes, where the boiling points of light fractions decreased, that of medium volume fractions increased while those of heavier cuts decreased in comparison with control. The boiling points of first 10 mL and onward to 50 mL fractions showed a significant decrease, however, those of 20 mL and 30 mL fractions remained unchanged while that of 40 mL fraction increased.

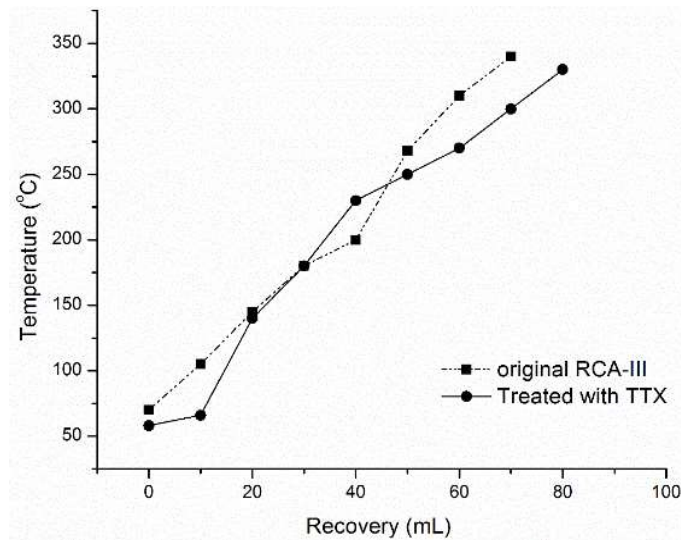
Overall, it may be concluded that the performance of TX-100 was more significant in medium crude, where the BPs of all of the 10 ml fractions decreased.



a)



b)



c)

**Fig. 3.11** Distillation curves of TX-100-100-dispersed crude oils: (a) RCP-I (b) RCN-II and (c) RCA-III

**Inferences:** Remarkable effects of dispersants on the boiling point range and volatility were observed which best describes their performance. The results showed an increased volatility.

Hydrocarbon constituents that were less volatile (remained in the liquid phase) in the plain crudes, begun to vaporize early in the dispersed samples. The reason can be thought is the significant interaction between the dispersant and the components of the oils, which acted to increase the volatility of the oil by vanishing the interactions probably between the asphaltenes constituting the residues and prevented them from forming clusters/aggregates owing to better surface active properties. The better emulsification of different hydrocarbon chains by surfactants under study to influence the distillation behaviors of the three oils may be the cogent reason. Further, the dispersants under study may have assisted in exposing the occluded compounds caged with in the molecular frame work of the asphaltenes to distillation/thermal degradation owing to its amphiphilic characteristics and presence of sulfate group. Amphiphiles with sulphate groups have been found to reduce interfacial tension and reported to be anti-aggregating agents for asphaltenes [46]. Asphaltenes from light crudes have been shown to be different from those obtained from heavy crude oils [47]. Further, heavy crudes contain polycyclic aromatic hydrocarbons (PAHs). The surfactants can have solubilized the PAHs [48].

## **PHASE-III-A**

This phase is devoted to the key fuel properties of the two fractions namely F1 (gasoline range) and F2 (diesel range) obtained in plain as well as in the various dispersant mediated distillation performed under optimum DORs.

### **3.4. KEY FUEL PROPERTIES OF THE DISTILLATE FRACTIONS**

Among several specifications, the ASTM D-396 standard specification for fuel oils is the most widely used standard to qualify fuel oils [49, 50].

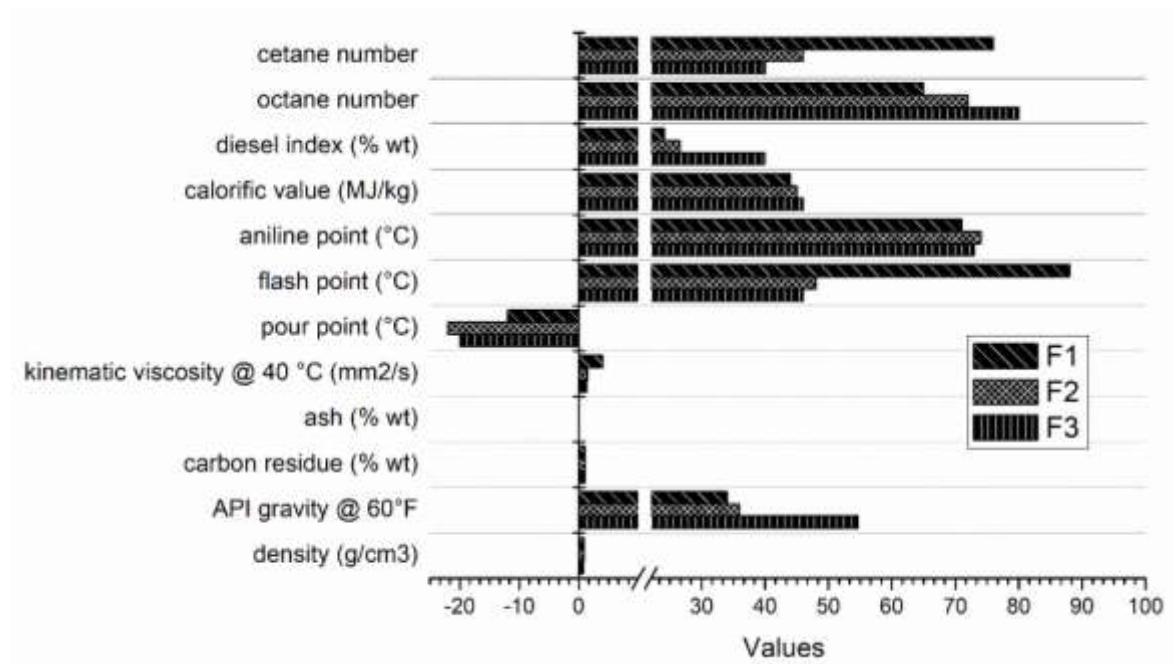
The distillate fractions i.e. light, middle and heavy fractions obtained from the atmospheric plain and mediated distillation of the three crudes were characterized in terms of their physico-chemical parameters including density, specific gravity, API gravity, pour point, kinematic viscosity, carbon residue, ash, flash point, aniline point, diesel index, octane number, cetane number, antiknock index, etc. and the results were compared with the standard specifications.

#### **3.4.1. Fractions from Distillation of Plain Crudes**

The different key fuel properties obtained of the distillate fractions; F1, F2 and F3 derived from plain distillation of RCP-I, were determined. The results are compiled in Fig 3.12. The properties were found to be as followed: density (0.76, 0.84, & 0.85 g/cm<sup>3</sup>); API gravity (54.68, 36, & 34 °API); CCR (0.97, 0.99, & 0.99 % wt); ash (0.034, 0.003, & 0.018 %), viscosity (1.22, 1.44, & 4 cSt); pour point (-20, -22, & -12 °C), flash point (46, 48, & 88°C), aniline point (73, 74 & 71 °C), calorific value (46, 45, & 44Mj/kg), calculated diesel index (39.91, 26.64 & 24.14), octane number (80, 72 & 65) and cetane number (40, 46 & 76), respectively.

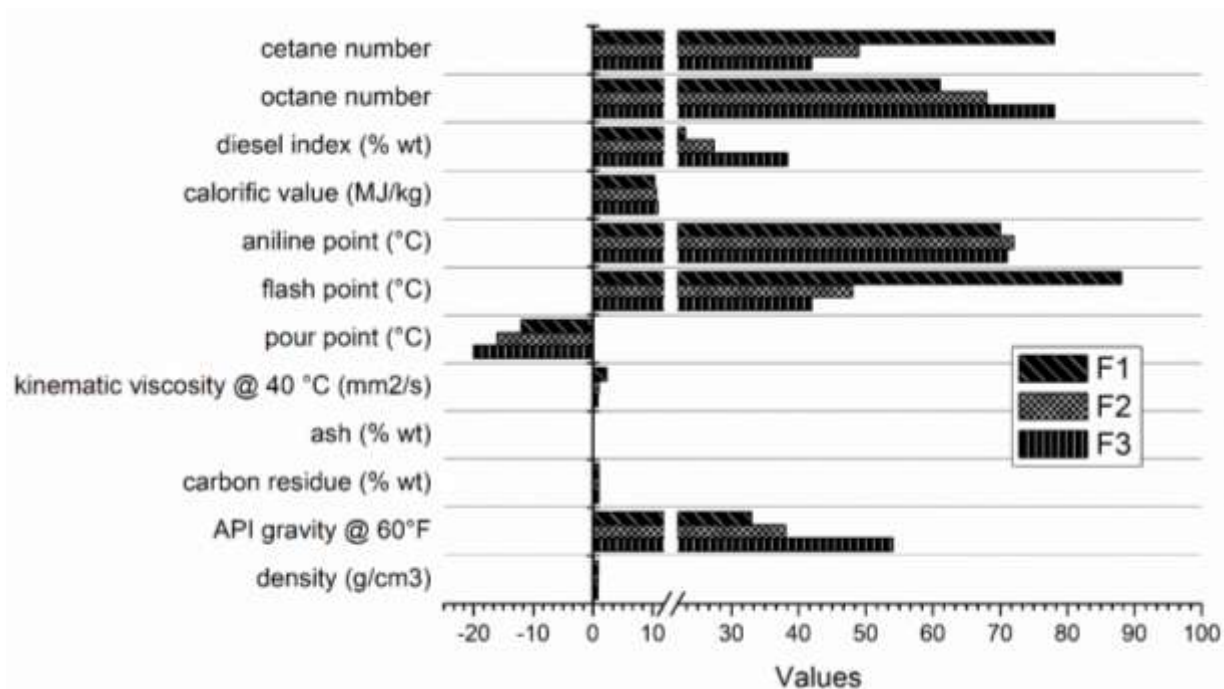
The results of distillate fractions derived from RCN-II crude oil are compiled in Fig 3.13 and found to be as follows: density (0.75, 0.83, & 0.86 g/cm<sup>3</sup>); API gravity (54, 38, & 33 °API); CCR (0.97, 0.99, & 0.99 % wt); ash (negligible), viscosity (0.7, 1.013, & 2.26 cSt); pour point (-20, -16, & -12 °C), flash point (42, 48, & 88°C), aniline point (71, 72 & 70 °C), calorific value (45, 45, & 43 MJ/kg), calculated diesel index (38.34, 27.36 & 23.10), octane number (78, 58 & 61) and cetane number (42,49 & 78), respectively.

The results of distillate fractions derived from RCA-III crude oil are compiled in Fig 3.14 and found to be as followed: density (0.79, 0.83, & 0.86 g/cm<sup>3</sup>); API gravity (47, 39, & 33 °API); CCR (0.99, 0.99, & 0.99 % wt); ash (negligible), viscosity (2.07, 2.23, & 2.50 cSt); pour point (-22, -20, & -15 °C), flash point (46, 48, & 75°C), aniline point (69, 68 & 66 °C), calorific values (47, 46, & 46 MJ/kg), calculated diesel index (32.34, 26.52, & 21.78), octane number (84,75 & 70) and cetane number (45, 46 & 80), respectively.

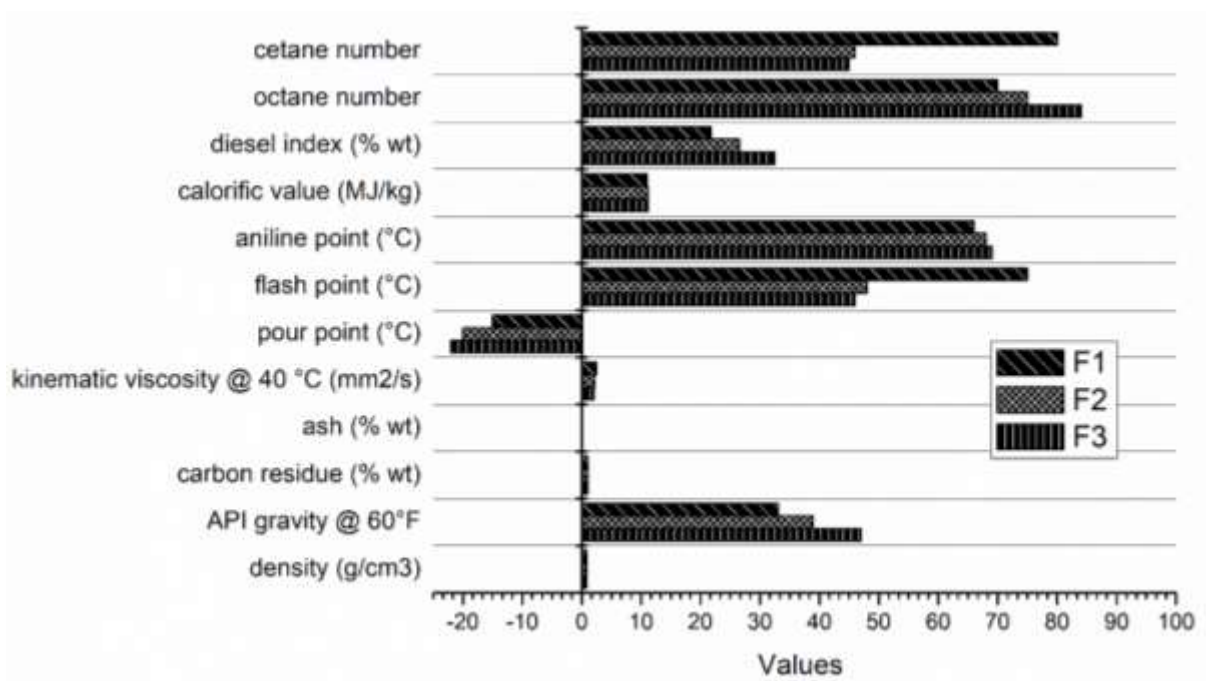


**Fig. 3.12** Physico-chemical properties of distillate fractions of plain RCP-I crude





**Fig. 3.13.** Physico-chemical properties of distillate fractions of plain RCN-II crude



**Fig.3.14.** Physico-chemical properties of distillate fractions of plain RCA-III crude

### 3.4.2. Fractions From Distillation of Chemically Dispersed Crudes

**SDS-dispersed Crudes:** The physico-chemical parameters of the distillate fractions i.e. light, middle and heavy fractions derived from distillation of SDS-dispersed crudes are assembled in Figs 3.15-3.17

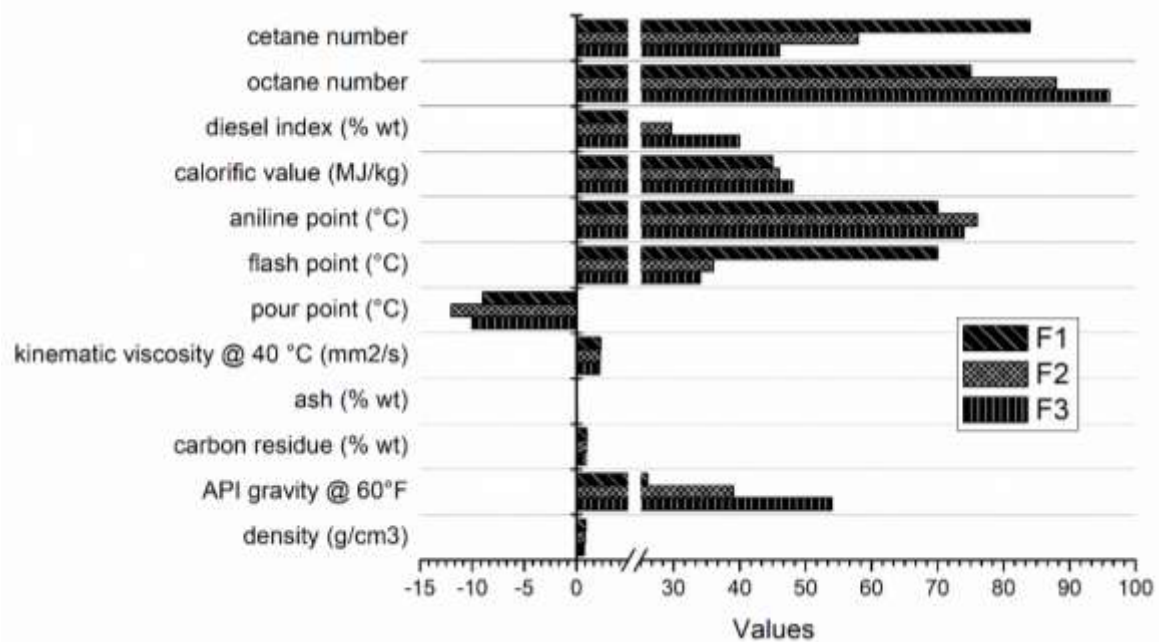
The values for different key fuel properties of the distillate fractions F1 and F2 derived from RCP-I Fig 3.15 are as followed: density (0.76, 0.83, & 0.90 g/cm<sup>3</sup>); API gravity (54, 39, 26 °API); CCR (0.89, 0.96, & 0.98 % wt); ash (negligible), viscosity (2.2, 2.3, & 2.314 cSt); pour point (-10, -12, & -9°C ), flash point (34, 36, & 70 °C), aniline point (74, 76 & 70), calorific value (48,46, &45 MJ/kg), calculated diesel index (39, 29 & 18), octane numbers (96, 88 &75) and cetane numbers (46, 58 & 84), respectively.

The values for different key fuel properties of the distillate fractions F1 and F2 derived from RCN-II [Fig 3.16] are as followed: density (0.78, 0.84, & 0.85 g/cm<sup>3</sup>); API gravity (50, 37, & 35 °API); CCR (0.98, 0.99, & 0.99 % wt); ash (negligible), viscosity (1.2, 1.3, & 1.7 cSt); pour point (-9, -20, & -11°C ), flash point (34, 44, & 65 °C), aniline point (75, 72 & 70), calorific value (47, 46, 45 MJ/kg ), calculated diesel index (37.60, 26.64, &24.50), octane number (98,83 & 73) and cetane number (47,72 & 80), respectively.

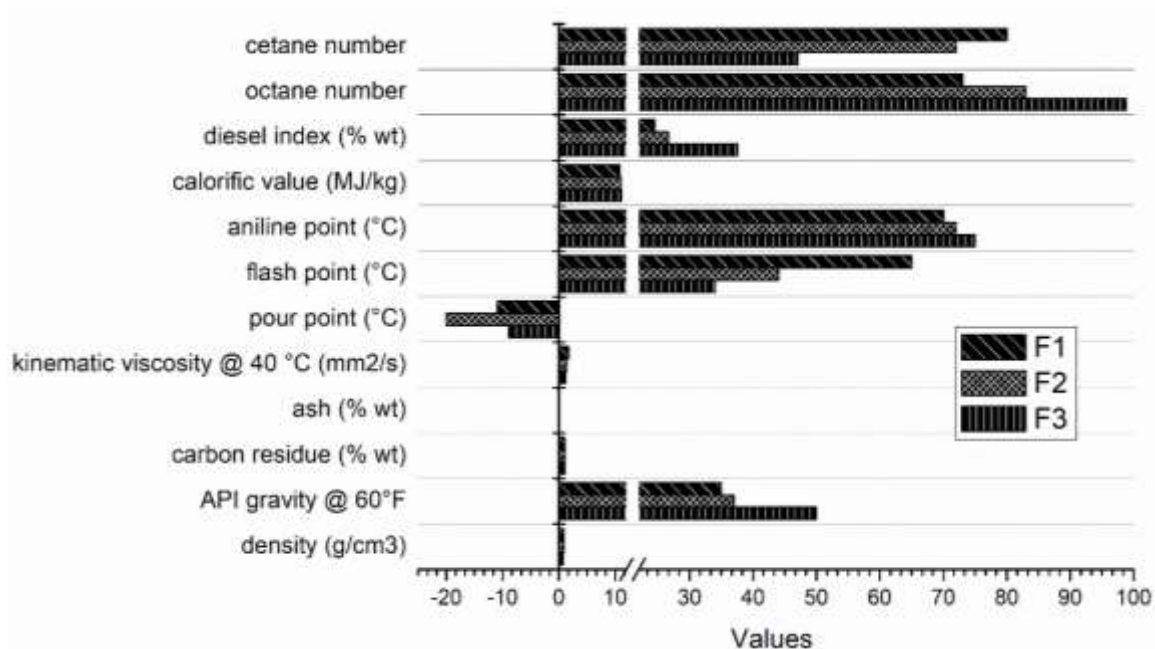
The values for different key fuel properties of the distillate fractions F1 and F2 derived from RCA-III [Fig 3.17] are as followed: density (0.81, 0.84, & 0.87 g/cm<sup>3</sup>); API gravity (42, 36, 31 °API); CCR (0.83, 0.86, & 0.98 % wt); ash (negligible), viscosity (4, 5.6, & 5.8 cSt); pour point (-10, 18, & -12°C ), flash point (34, 30, & 55 °C), aniline point (69, 67 & 65), calculated diesel index (28.98, 24.12 & 20.15), calorific value (48,47, &47 MJ/kg ), octane numbers (94,85 & 81) and cetane numbers (53, 58 & 86), respectively.

The densities and API gravities of the test fuels in the gasoline and diesel boiling range (F1, F2, and F3) are very close to each other and remained in the gasoline, kerosene and diesel range. A difference can be observed in F3 which indicated the removal of lighter occluded hydrocarbons during distillation of the SDS-dispersed samples. The Conradson carbon and ash values are negligible. The viscosity showed lower limits defined for distillate fuels in case of RCP-I and RCN-II while higher limits in distillates derived from RCA-III crudes. The pour points are extremely low in all samples which indicate the absence of waxes and crystallites.

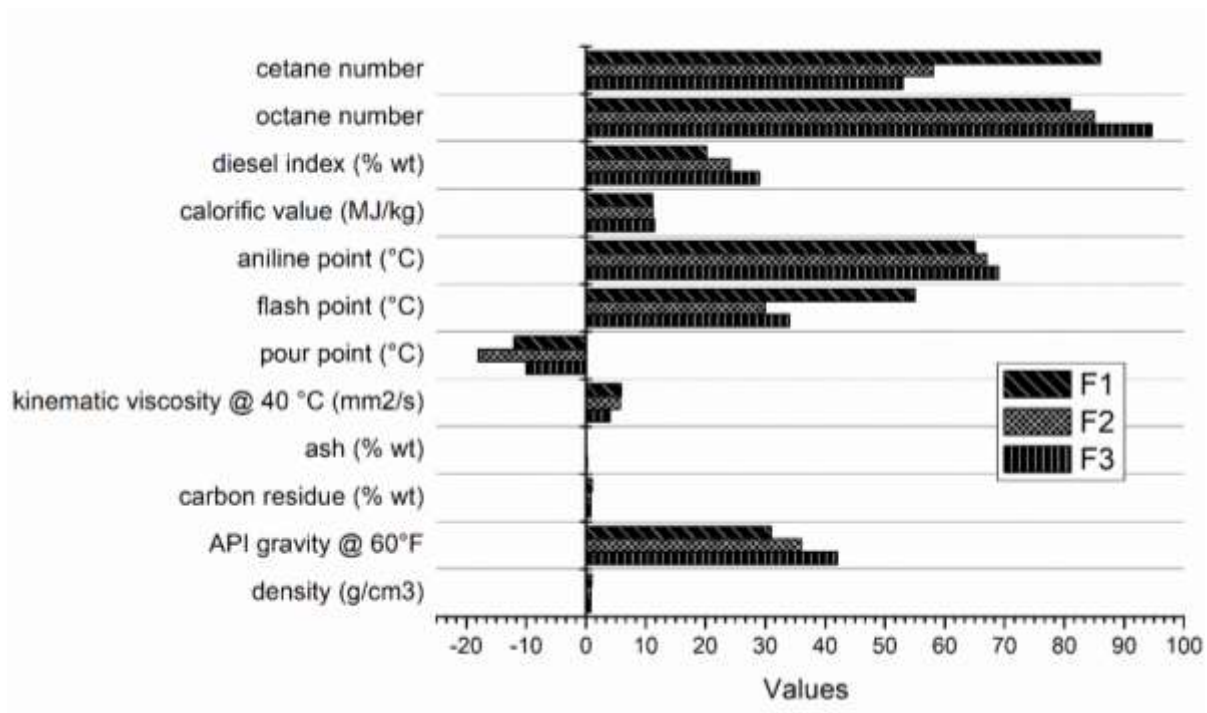
In general, the key properties of the distillate fractions derived from the SDS-dispersed samples exhibited no significant change and showed conformance with the properties of the fractions derived from plain distillation. The results further inferred that SDS mediation caused the yields of gasoline and diesel oil fractions to increase without disturbing their fuel properties, which indicate no harm to the chemical integrity of the resultant distillate fractions in terms of their compositions by SDS.



**Fig. 3.15.** Physico-chemical properties of distillate fractions derived from SDS-dispersed RCP-I crude oil



**Fig.3.16.** Physico-chemical properties of distillate fractions derived from SDS-dispersed RCN-II crude oil



**Fig.3.17.** Physico-chemical properties of distillate fractions derived from SDS-dispersed RCA-III crude oil

**CTAB- dispersed Crudes:** The fuel properties of the distillate fractions derived from distillation of CTAB-dispersed crudes in comparison with the control are shown in Figs. 3.18-3.20.

Fig. 3.18 summarized the properties determined for RCP-I derived F1 and F2 fractions. The results are as followed: density (0.78, 0.87, & 0.91 g/cm<sup>3</sup>); API gravity (50, 30, & 24 °API); CCR (0.99, 0.99, & 0.99 % wt); ash (negligible %), viscosity (3.95, 4.15, & 4.97 cSt); pour point (-20, -18, & -19 °C ), flash point (38, 46, & 95°C), aniline point (73, 74 & 72 °C), calorific value (48, 47, & 46 MJ/kg), calculated diesel index (36.50, 22.94 & 17.28), octane number (94, 85 & 72) and cetane number (45, 56 & 82 ), respectively.

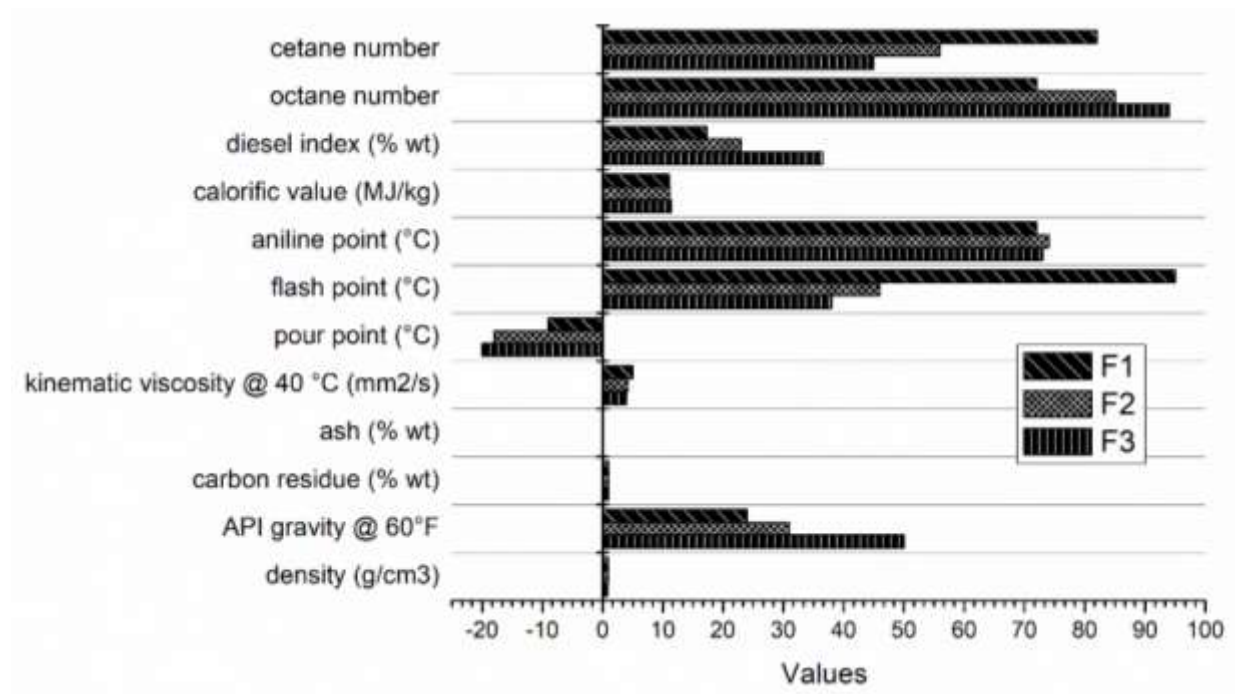
Fig. 3.19 depicts the properties determined for distillate fractions derived from RCN-II and are reported to be as followed: density (0.76, 0.89, & 0.90 g/cm<sup>3</sup>); API gravity (54, 27, & 25

°API); CCR (0.99, 0.99, & 0.99 % wt); ash (negligible %), viscosity (1.3, 1.4, & 1.6 cSt); pour point (-20, -16, & -14 °C), flash point (36, 46, & 92°C), aniline point (73, 72 & 70 °C), calorific values (46,46, & 45 MJ/kg), calculated diesel index (39.43,19.44 &17.99), octane number (88,80 &71) and cetane number (46, 58 & 82 for F2 and F3 fractions), respectively.

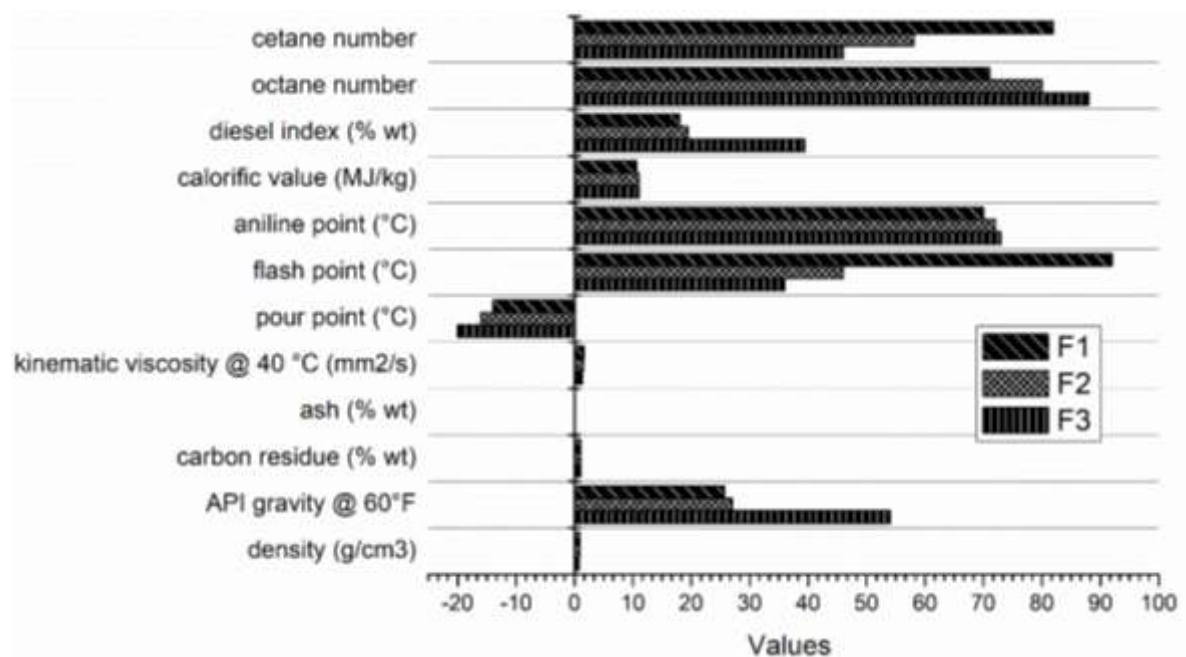
The distillation fractions of RCA-III were also analyzed for the key fuel properties. The results are compiled in Fig.3.20. The properties were as followed: density (0.78, 0.82, & 0.85 g/cm<sup>3</sup>); API gravity (50, 41, & 35 °API); CCR (0.99, 0.99, & 0.99 % wt); ash (negligible %), viscosity (3.3, 3.7, & 4.8 cSt); pour point (-22, -20, & -19 °C), flash point (42, 45, & 75°C), aniline point (72, 71 & 69°C), calorific values (47, 47, & 46 MJ/kg), calculated diesel index (36, 29.11 & 24.15), octane number (98, 78 & 73) and cetane number (62, 58 & 89), respectively.

It can be seen from the data that all of the physicochemical properties occurred close to the distillates fractions of the plain crudes. The properties F1 fractions of all crudes matched well with the standard gasoline and those of F2 and F3 fractions resembles with the kerosene and diesel range products. It can, however, be observed from the data that the some of the properties showed slight higher values than those obtained from plain crudes. The density of the F1, F2 and F3 showed a linear increase, and likewise the API gravities a decrease from 50 to 24. The values of carbon residue and ash content were same as in fractions of plain crudes. The kinematic viscosity of CTAB-dispersed samples showed an increase. Similar are the results for pour point and flash points, which indicated that the distillates contained hydrocarbons with BP in the respective ranges but more complex structures such as long alkyl side chains, aromatics or heteroaromatics, due to which high values of viscosity, pour points and flash points were observed. However, the aniline points of F1 fraction was close to the plain fractions, which indicated that the aromatic content of these fractions remained same. On the other hand, the high octane number of F1 and high cetane

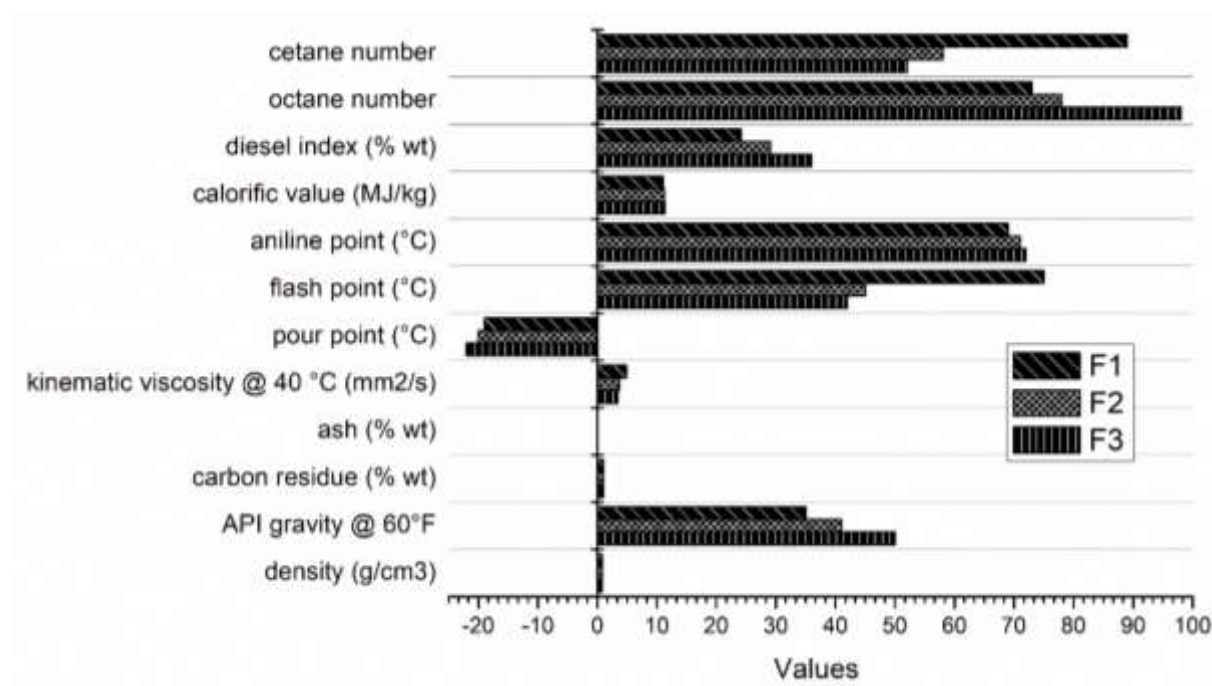
numbers of F2 and F3 fraction showed that these products are superior in ignition properties from those of the original crudes.



**Fig. 3.18.**Physico-chemical Properties of Distillate Fractions Derived From CTAB-dispersed RCP-I Crude Sample



**Fig. 3.19.** Physico-chemical Properties of Distillate Fractions Derived From CTAB-dispersed RCN-II Crude Sample



**Fig. 3.20.** Physico-chemical Properties of Distillate Fractions Derived From CTAB-dispersed RCA-III Crude Sample



**TX-100 dispersed Crudes:** The physico-chemical properties of the light, middle and heavy oil fractions derived from distillation of TX-100-dispersed crudes are presented in Figs.3.21-3.23.

The properties determined for F1, F2 and F3 fractions of RCP-I are summarized in Fig. 3.21. The results were found to be as: density (0.76, 0.83, & 0.90 g/cm<sup>3</sup>); API gravity (54, 39, & 26 °API); CCR (0.89, 0.96, & 0.98 % wt); ash (negligible %), viscosity (2.26, 2.29, & 2.31 cSt); pour point (-10, -12, & -9 °C ), flash point (34, 36, & 70°C), aniline point (74, 76 & 70 °C), calorific values ( 48, 46, & 46 Mj/kg), calculated diesel index (39.96, 29.6 & 18.20), octane number (96,83 & 71) and cetane number (44, 58 & 84), respectively.

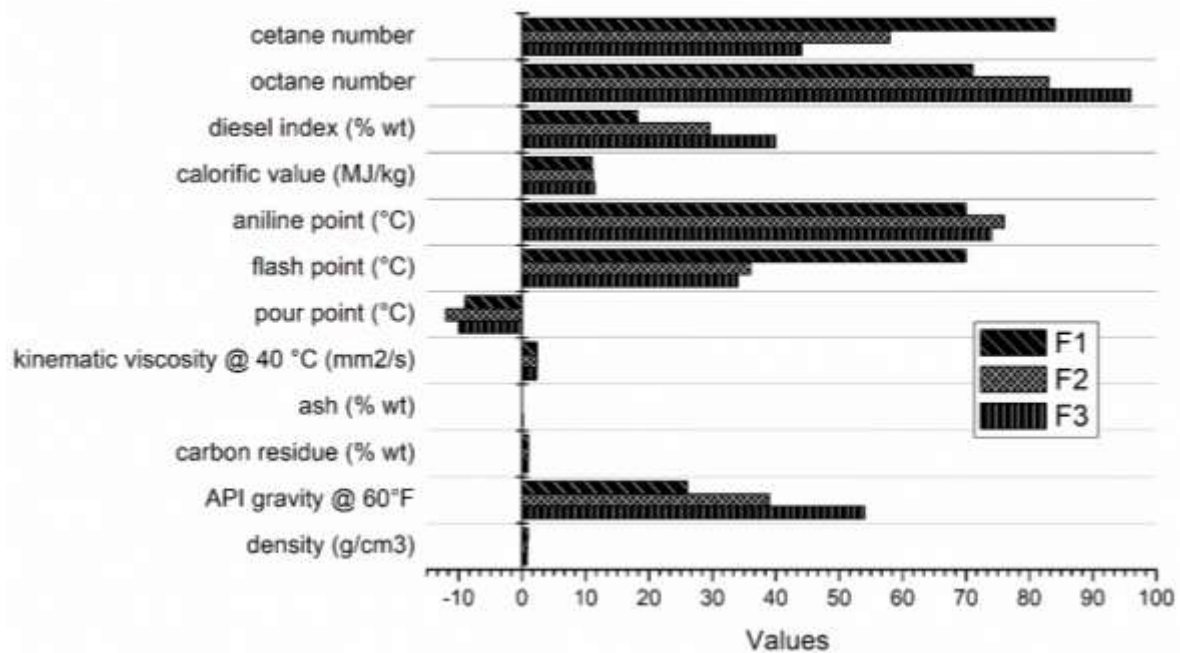
The properties determined for F1, F2 and F3 fractions of RCN-II are assembled in Fig. 3.22 and found to be as followed: density (0.78, 0.84, & 0.85 g/cm<sup>3</sup>); API gravity (50, 37, & 35 °API); CCR (0.98, 0.99, & 0.99 % wt); ash (negligible %), viscosity (1.2, 1.3, & 1.7 cSt); pour point (-9, -20, & -11 °C ), flash point (34, 44, & 65°C), aniline point (75, 72 & 70 °C), calorific values (46,46, & 45 Mj/kg ), calculated diesel index (37.50, 26.84 &24.50), octane number (98.8, 78 &70) and cetane number (44, 72 & 80, respectively.

The properties determined for F1, F2 and F3 fractions of RCA-III are assembled in Fig. 3.23 and found to be as followed: density (0.81, 0.84, & 0.87 g/cm<sup>3</sup>); API gravity (42, 36, & 31 °API); CCR (0.83, 0.86, & 0.98 % wt); ash (negligible %), viscosity (4.0, 5.6, & 5.8 cSt); pour point (-10, 18, & -12 °C ), flash point (34, 30, & 55°C), aniline point (69, 67 & 65 °C), calorific values (47, 48, & 46 Mj/kg ), calculated diesel index (28.98, 24.12 &20.15), octane number (94.6, 77 & 69) and cetane number (50, 58 & 86), respectively.

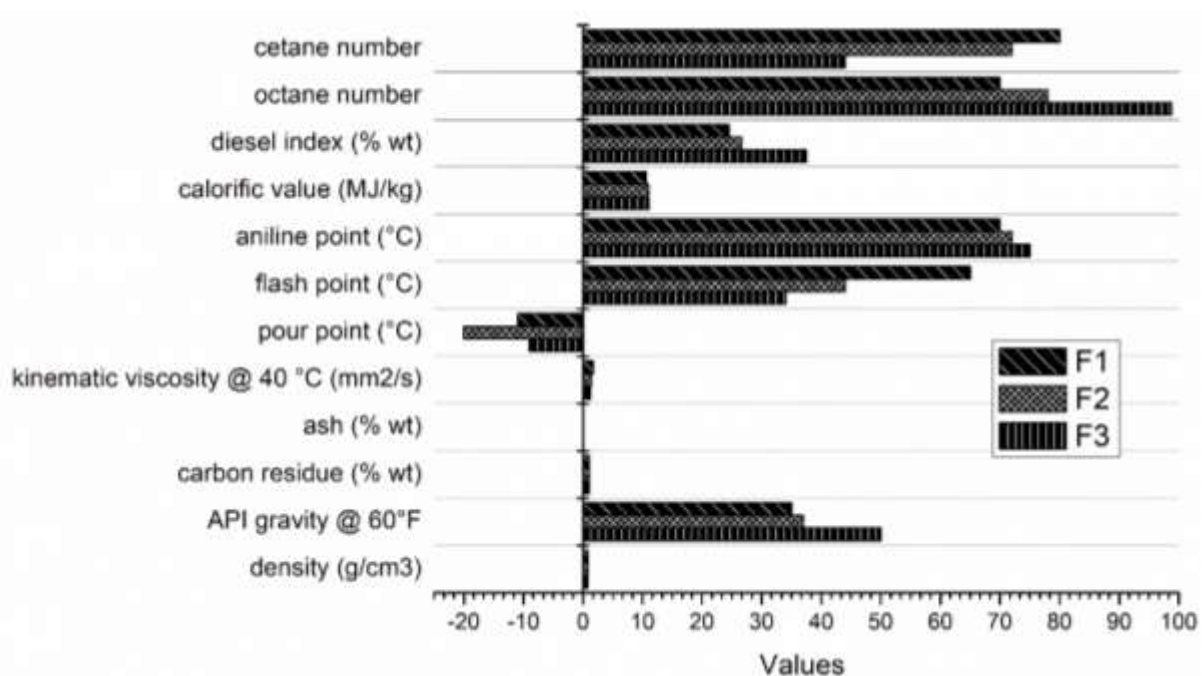
The results indicated that the physico-chemical characteristics of F1 resembled to the gasoline and those of F2 and F3 were close to kerosene and diesel oil. However, it can be observed

slight variations in the properties of the F1, F2 and F3 fractions than those of the plain crudes. In RCP-I, the F1 fractions are similar to the F1 fraction of plain RCP-I, whereas F2 and F3 fractions derived exhibited higher values of some of the key properties. In RCN-II and RCA-III, the values of most of the physico-chemical characteristics were higher than those of the fractions from plain crudes. This may be explained on the basis of the extraction ability of the hydrocarbons from the asphaltene by TX-100 in each crude sample. As in the RCP-I, the CCR residue amount was less than that of light fraction (F1), therefore some of the residue may have been extracted by the neutral surfactant and the extracted hydrocarbons may have added to the F1 and F2 fractions. In TX-100-dispersed samples of RCN-II and RCA-III, the decrease in the yield of residue was higher which increased in the yields of F1 and F2 fractions.

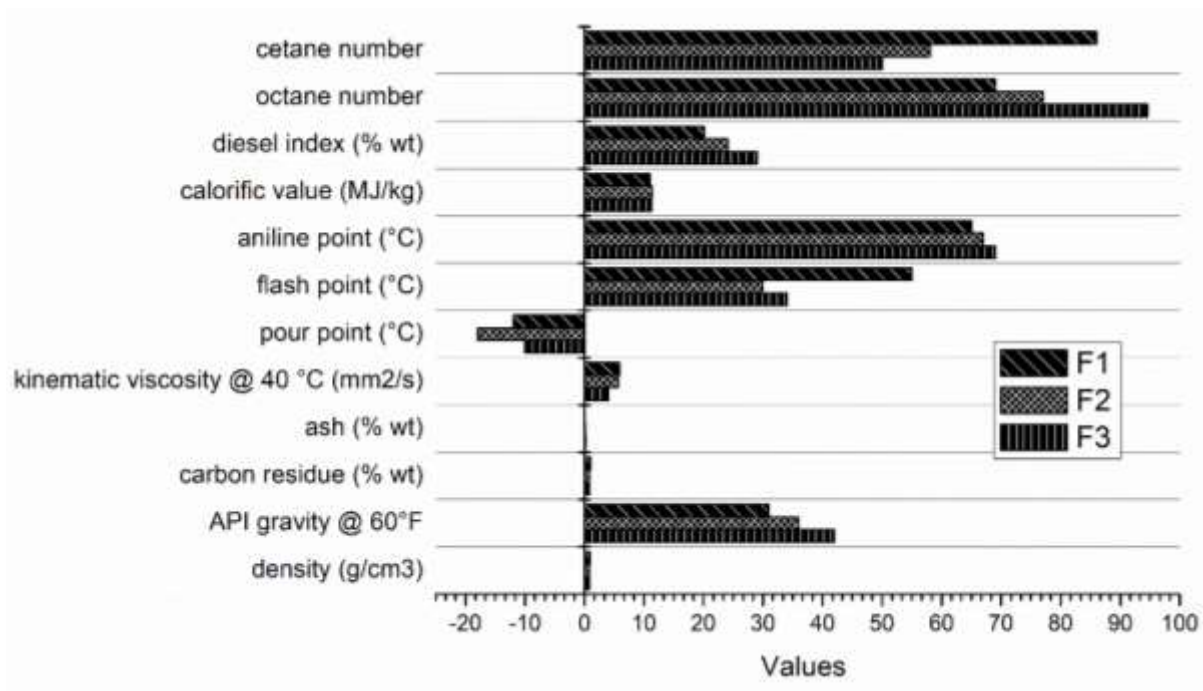
It is worth mentioning that the physico-chemical characteristics of all the F1, F2 and F3 fractions derived from control as well as TX-100-dispersed crudes, occurred within the permissible range of standard gasoline or diesel oil.



**Fig. 3.21.** Physico-chemical properties of distillate fractions derived from TX100-dispersed RCP-I crude oil



**Fig. 3.22.** Physico-chemical properties of distillate fractions derived from TX100-dispersed RCN-II crude oil



**Fig. 3.23.**Physico-chemical properties of distillate fractions derived from TX100-dispersed RCA-III crude oil

**Inferences:** The density of gasoline is reported to be within the range of 720–775 kg/m<sup>3</sup> [51, 52], while that of kerosene as 780–810 kg/m<sup>3</sup> and diesel as 820–860 kg/m<sup>3</sup>. The API gravity of gasoline is reported to be within the range of 51–66, that of while the value for kerosene is 47 °API, while the value for diesel fuels in the range of 30 and 42 [53]. The Conradson carbon residue values are falling within the range of 0.01-0.02 for automotive fuels [54]. The viscosity for unleaded gasoline is reported to be 0.7 mm<sup>2</sup>/s and that of that of kerosene as 2.7 mm<sup>2</sup>/s while that of diesel: 2–4 mm<sup>2</sup>/s [55]. The flash point for gasoline: –43 °C has been reported as [56], while that of that of kersoine as 37- 65 °C and diesel as >55 °C [57]. The kinematic viscosity for diesel fuel as per standard ASTM D396 has been reported to be 2–3.6 cSt and 5.8–26.4 cSt at 38 °C for grade No. 2-D (diesel) and grade No. 4-D (medium distillate), respectively while that reported for low-speed stationary engines, between 13 and 17 cSt [58]. The octane rating of a fuel describes the ability of a fuel to resist auto-ignition and knocking in a spark igniton engines and reflects the ability of a fuel to self-ignite when compressed under standardized conditions [59]. The knock-limited performance of gasoline in most modern engines now tends to be better correlated with octane number [60]. Octane rating recommendations can be found elseweher for gasoline [61].

The results inferred that the key properties are reasonably closer to the values of standard fuels (e.g. gasoline, diesel) and further revealed that all the properties are in good agreement with ASTM standard specifications reported for gasoline, diesel and heavy oils [62-64].

## PHASE-III

### 3.5. COMPOSITIONAL STUDY BY GC-MS ANALYSIS

Petroleum fractions are the products or intermediate products obtained from crude oil through the major processing steps including separation, conversion, and finishing. Each of the fractions is a mixture of thousands of different hydrocarbon molecules i.e. hydrocarbons consisting of hydrogen and carbon atoms only, and hydrocarbons with heteroatoms such as sulfur, nitrogen, oxygen, etc. The complexity of these molecular species increases with boiling point in an exponential way and there are even a number of isomers of an individual hydrocarbon compound. The chemical composition of a fuel has a marked effect on its fundamental ignition behavior [65]. Varying the composition can affect several key parameters, such as vaporization, heat release, reactivity of pollutants [66], ignition delay, *etc.* Therefore, there is a need to identify and quantify different hydrocarbons constituting light and middle fractions such as gasoline and diesel so as to cater to the demand for higher quality products.

The distillates derived in the plain as well as various dispersant-mediated distillation were analyzed by using GC-MS to study the key components present and to ascertain if there were any changes in chemical components during mediated distillation in comparison with the plain distillation. Gas chromatographic- Mass spectrometric analyses were conducted and changes in the individual compounds, the hydrocarbon range products and the hydrocarbon group types in the derived distillates were determined and reported. The identification of compounds was carried out through a comparison of the MS spectra with those in the NIST Mass Spectral Database.

### 3.5.1. Fractions From Distillation of Plain Crudes

The light and medium fractions i.e. F1 and F2 recovered from each crude i.e. RCP-I, RCN-II and RCA-III in plain distillation were characterized so as to study their chemical compositions.

The typical individual hydrocarbon compounds identified in the F1 and F2 are presented in Table 3.10-3.12. The data showed several peaks corresponded to various chemical compounds including paraffins, olefins, naphthenes and aromatics can be observed. Among the paraffins identified were n-heptane, 2,3-dimethyl- hexane, 4-methyl- heptane, octane, 2,4-dimethyl- heptane, iso-nonane, 3-methyl octane, 5,6-dimethyl decane, 4-methyl octane, 2-methyl octane, 3-methyl octane, nonane, 2,2,3,3-tetramethyl pentane, 3-methyl nonane, 2-methyl, 3-ethyl heptane, 2,3,6-trimethyl heptane, 4-methyl nonane, 2-methyl nonane, nonane,3-methyl, decane, 2,5,5-trimethyl heptane, 3-methyl decane, 3,7-dimethyl nonane, 4-methyl decane, octadecane, 2,6,10,14-tetramethyl hexadecane, tetratriacontane, nonadecane, eicosane, octadecane, 2,3,3-trimethyl octane, undecane, dodecane, 3,7-dimethyl decane, 2,3-dimethyl decane, undecane,2-methyl, 2-methyl undecane, tridecane, 2,3,7-trimethyl octane, 2,6,10,14-tetramethyl he3ptadecane, 3-methyl, 5-propyl nonane, 2-methyl, 5-propyl nonane, 2,6,10,14-tetramethyl hexadecane, 2,3,5-trimethyl decane, tetra decane, ,4,6-dimethyl dodecane, pentadecane, 2,6,10,14-tetramethyl pentadecane, heptadecane, octadecane, nonadecane, eicosane, hencosane, docosane, tricosane, tetracosane, pentacosane, hexa cosine, octacosane, triacontane, dotriacontane, tetratriacontane,

Among the naphthenes, the major compounds identified were found to be methyl cyclohexene, 1,2,4-trimethyl cylopentane, 1,3-dimehtyl cyclohexane, P-dimethyl cyclohexane, 1.1-dimethyl cyclohex1-ane, 1,2-dimethyl cyclohexane, 1,1,5-trimethyl cyclohexane, ethyl cyclooctane, 1,3,5-cycloheptatriene, 7-ethyl, 1,2,5-trimethyl cylcohexane, 1-ethyl, 4-methyl

cyclohexane, 1-ethyl, 2-methyl cyclohexane, 1-isopropyl, 1-methyl cyclohexane, propyl cyclohexane, 1,1,2,3-tetra methyl cyclohexane, 1-methyl, 3-propyl cyclohexane, n-butyl cyclohexane, 1-butyl, 2-ethyl cyclopentane, hexane, 1-cyclohexyl, 1-methyl, 2-pentyl cyclohexane, etc. Gasolines are primarily paraffinic containing varying amounts of iso- and n-paraffins [66].

The olefins recognized were 2, 3, 4-trimethyl-2-pentene, 11-chloro-1-undecene. The aromatics verified were; iso-butyl benzene, 1-methyl, 2-propyl benzene, 1-4-diethyl benzene, butane, 2-phenyl, 3-hydroxy, 4-cyano, (1,1-dimethyl propyl benzene, (3,3-dimethyl butyl) benzene. The oxygenates like triasterianone, 3, 3-dimethyl 2-hexane-one, 2-butyl octanol were identified.

Olefins are known to have a role in octane ratings, but are more unstable in the presence of oxygen and can contribute to the production of gum deposits during long-term storage. The aromatic compounds, like olefins, have good octane numbers, but reported to be more toxic and need to meet specific regulations [67, 68].

The composition of the F2 fraction showed that the concentration of paraffinic compounds is very high. The paraffinic compounds were found to be same as in fraction F1, but the concentration of some of the compounds increased than F1. These include 2-Methyl-5-propylnonane, 2,3,5-Trimethyldecane, Tetradecane, 4,6-Dimethyldodecane, Pentadecane, Pentadecane,2,6,10,14-tetramethyl, Hexadecane, Heptadecane, Octadecane, Nonadecane, Eicosane, Heneicosane, and Docosane.

No olefinic and naphthenic compounds were found to be present in F2. Among the aromatics, Sec-Butylbenzene and 1-Methyl-2-propylbenzene were present, whereas the only



oxygenated compound present was triasteranone in concentration higher than F1. The overall results showed that both fractions contained significant concentrations of aliphatic hydrocarbons. The paraffins are desired constituents in diesel range fraction as paraffinic diesel fuels have more combustion efficiency because of the more centered combustion [69].

Fossil fuel oils have been reported to be comprised of various complex mixtures of paraffins, naphthenes, olefins, and aromatics [60]. As earlier reported gasoline contains hundreds of different natural components (divided in paraffinics, olefinics, and aromatics), a few sulfur containing compounds, and some additives and is a complex mixture of hydrocarbons, which are commonly grouped into five major classes, i.e. linear paraffins, branched paraffins, naphthenes, olefins and aromatics [70].

From the GC-MS data, the distribution of different hydrocarbons range compounds was determined and the amounts of hydrocarbons types i.e. paraffins, olefins, naphthenes and aromatics were calculated. The results are provided in Fig. 3.24. The data showed that in F1 fraction, the paraffins, olefins, aromatics, naphthenes and oxygenates were found to be present in amounts of 84.83, 0.73, 5.51, 7.53 and 1.43%, respectively. However, in F2 fraction, olefins and naphthenes were not detected, whereas the yields of paraffins, aromatics and oxygenates were found to be 96.91, 0.24 and 2.85 %, respectively. The RCP-I being a paraffinic crude, gave paraffins in higher amounts in both F1 and F2 fractions. Based on these results, the F1 hydrocarbons distribution followed the given order: paraffins > naphthenes > aromatics > oxygenates > olefins, whereas in F2, the order was; paraffins > oxygenates > aromatics. Paraffins have been reported to present in higher amounts in gasoline and diesel range hydrocarbons [66].

From the GC-MS data, the distribution of different carbon range hydrocarbons was also calculated, and the results are given in Fig. 3.15. In F1 fraction, the concentrations of C<sub>5</sub>-C<sub>10</sub>, C<sub>11</sub>-

C<sub>13</sub>, C<sub>14</sub>-C<sub>18</sub> and C<sub>5</sub>-C<sub>10</sub> range hydrocarbons were found to be 25.26, 58.81, 6.21 and 9.72 %, whereas in F2 fraction these were 3.67, 46.48, 24.96 and 24.89 %, respectively. The results showed that the F1 has high concentration of C<sub>11</sub>-C<sub>13</sub> range hydrocarbons, followed by C<sub>5</sub>-C<sub>10</sub> and C<sub>19</sub>-C<sub>n</sub>, while C<sub>14</sub>-C<sub>18</sub> being in the minimum concentration. Similar was the case of F2, where the concentration of C<sub>11</sub>-C<sub>13</sub> is higher than C<sub>5</sub>-C<sub>10</sub>, however, concentration of C<sub>19</sub>-C<sub>n</sub> range hydrocarbons was higher than C<sub>14</sub>-C<sub>18</sub>. Gasoline and diesel have been reported to have over four hundred liquid hydrocarbons [71, 72] i.e. from 4–12 (gasoline) to 8–24 (diesel) carbon atoms with corresponding boiling points [73].

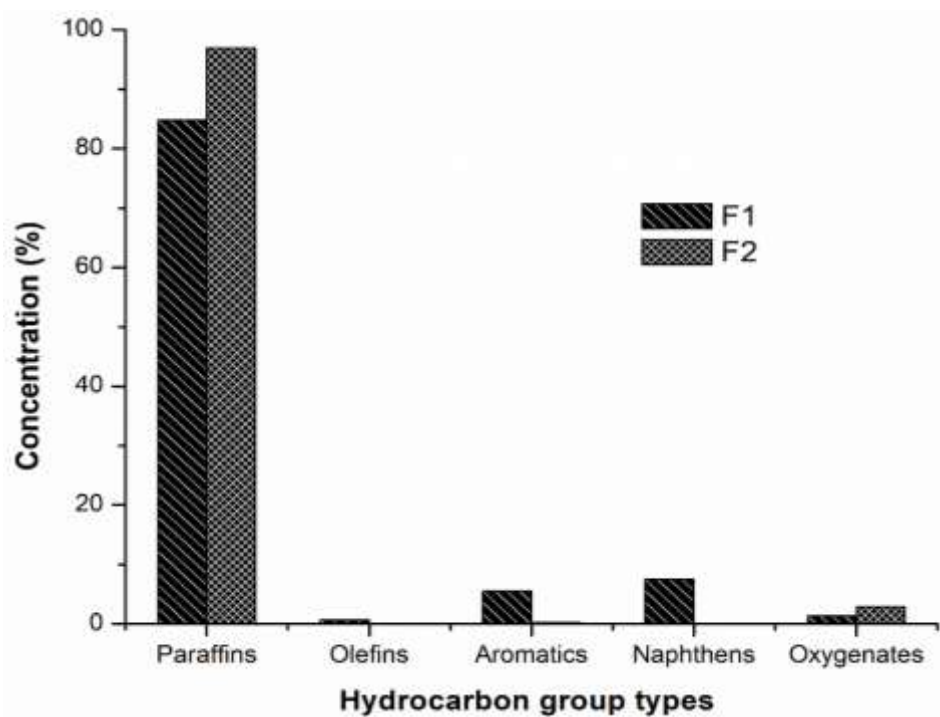
**Table 3.10.** Individual Compounds Determined in Light (F1) and Medium (F2) Distillate Fractions Derived From Distillation of Plain RCP-I Crude

S. #	Compound	F1		F2	
		t <sub>R</sub>	% Conc.	t <sub>R</sub>	% Conc.
<b>Paraffins</b>					
1	Heptane	3.158	0.01	3.148	0.12
2	2,3-Dimethylhexane	4.65	0.01	5.898	0.04
3	3-Methylheptane	5.128	0.01	13.91	0.05
4	Octane	6.173	0.04	14.667	0.11
5	2,4-Dimethylheptane	6.995	0.02	17.304	0.02
6	Isononane	7.304	0.11	18.127	0.05
7	3-Methyloctane	7.534	0.12	18.127	0.05
8	5,6-Dimethyldecane	8.38	0.15	18.43	0.01
9	4-Methyloctane	8.699	0.19	19.446	0.03
10	2-Methyloctane	8.781	0.21	19.642	0.04
11	3-Methyloctane	9.031	0.49	20.518	0.13
12	Nonane	10.186	1.09	20.843	0.35
13	2,2,3,3-Tetramethylpentane	11.091	0.39	22.201	0.05
14	3-Methylnonane	11.476	1.74	22.789	0.18

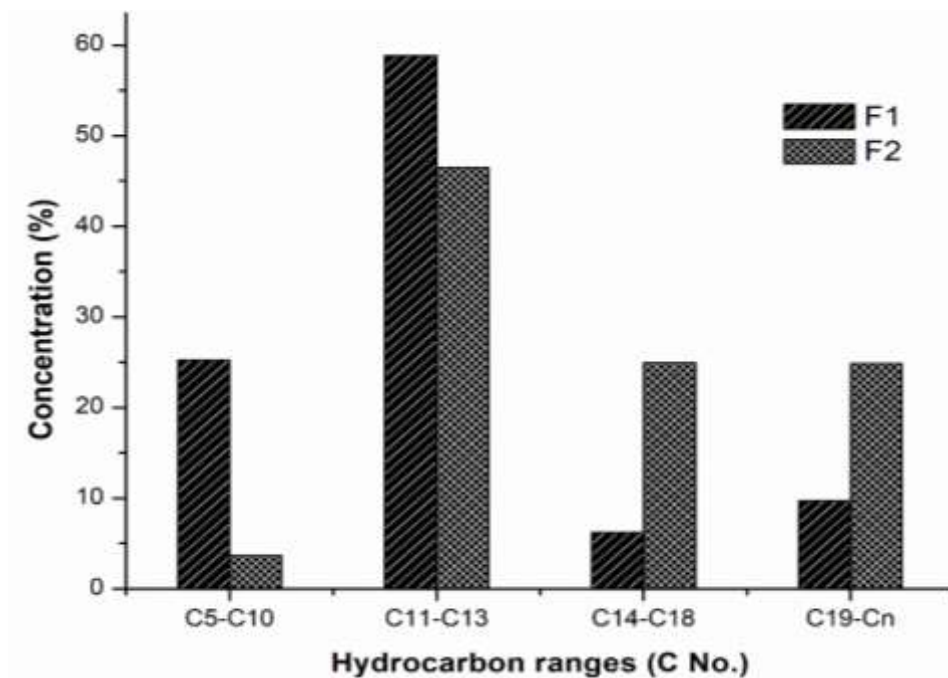
15	2-Methyl-3-ethylheptane	11.664	1.23	24.126	0.05
16	2,3,6-Trimethylheptane	12.238	0.66	24.584	0.09
17	4-Methylnonane	12.524	1.24	25.86	0.04
18	2-Methylnonane	12.66	0.96	26.733	0.05
19	Nonane,3-methyl-	12.888	1.08	29.84	0.09
20	Decane	13.971	4.64	34.767	0.23
21	2,5,5-Trimethylheptane	14.726	3.03	40.199	0.07
22	3-Methyldecane	15.159	0.76	40.199	0.03
23	3,7-Dimethylnonane	15.279	0.69	44.693	0.01
24	4-Methyldecane	16.029	0.86	49.068	0.04
25	2,3,3-Trimethyloctane	16.182	1.45	53.1	0.05
26	3-Methyldecane	16.38	0.72	56.868	0.04
27	Undecane	17.386	7.87	60.413	0.3
28	Dodecane	17.877	0.83	63.776	0.05
29	3,7-Dimethyldecane	18.191	0.98	66.983	0.46
30	2,3-Dimethyldecane	19.339	0.78	70.053	0.46
31	Undecane,2-methyl-	19.516	2.56	73.003	0.62
33	Tridecane	20.6	8.39	75.837	4.16
34	3,6-Dimethylundecane	20.908	4.64	76.45	1.84
35	2,3,7-Trimethyloctane	22.261	4.18	78.593	2.35
36	2,6,10,14-Tetramethylheptadecane	22.855	6.77	78.596	5.68
37	11-Methyldodecane	23.154	1.33	78.599	1
38	3-Methyl-5-propylnonane	24.183	2.12	78.61	2.39
39	2-Methyl-5-propylnonane	24.653	5.97	78.745	8.5
40	2,6,10,14-Tetramethylhexadecane	25.843	1.98	78.876	3.34
41	2-Methyl-5-propylnonane	26.823	4.43	78.976	10.15
42	2,3,5-Trimethyldecane	29.968	2.92	79.123	9
43	Tetradecane	34.799	2.61	79.256	10
44	4,6-Dimethyldodecane	34.933	0.84	79.367	2.8
45	Pentadecane	40.066	1.22	79.523	6.16

46	Pentadecane,2,6,10,14-tetramethyl	40.357	0.31	79.821	2.8
47	Hexadecane	44.846	0.75	80.234	5.14
48	Heptadecane	49.209	0.48	80.465	3.4
49	Octadecane	53.236	0.31	80.597	2.6
50	Nonadecane	57.001	0.22	80.753	3.4
51	Eicosane	60.555	0.14	80.932	2.36
52	Heneicosane	63.918	0.1	81.354	2.42
53	Docosane	67.13	0.06	81.653	1.8
54	Tricosane	70.205	0.04	81.753	0.5
55	Tetracosane	73.166	0.03	81.821	0.3
56	Pentacosane	76.006	0.02	81.998	0.3
57	Hexacosane	78.763	0.01	82.654	0.34
58	Octacosane	81.421	0.01	83.754	0.09
59	Triacontane	83.977	0.01	84.432	0.08
60	Dotriacontane	86.473	0.01	85.543	0.06
61	Tetratriacontane	88.886	0.01	86.587	0.04
			<b>84.83</b>		<b>96.91</b>
<b>Olefins</b>					
1	2,3,4-Trimethyl-2-pentene	6.384	0.01	-	-
2	11, Chloro-1-undecene	16.83	0.72	-	-
			<b>0.73</b>		<b>0.00</b>
<b>Aromatics</b>					
1.	Sec-Butylbenzene	12.817	0.633	13.653	0.13
2.	1-Methyl-2-propylbenzene	13.702	0.33	19.073	0.11
3.	1,4-Diethylbenzene	14.646	0.421	-	-
4.	Butane,2-phenyl-3-hydroxy-4-cyano	15.706	0.328	-	-
5.	(1,1-Dimethylpropyl)benzene	16.538	2.48	-	-
6.	(3,3-Dimethylbutyl)benzene	19.145	1.32	-	-
			<b>5.512</b>		<b>0.24</b>
<b>Naphthenes</b>					

1.	Methylcyclohexane	3.701	0.01	-	-
2.	1,2,3-Trimethylcyclopentane	0	0	-	-
3.	1,2,4-Trimethylcyclopentane	4,340	1	-	-
4.	1,3-Dimethylcyclohexane	5.389	0.01	-	-
5.	p-Dimethylcyclohexane	5.487	0.1	-	-
6.	1,1-Dimethylcyclohexane	5.676	0.1	-	-
7.	1,2-Dimethylcyclohexane	6.384	0.01	-	-
8.	1,3,5-Trimethylcyclohexane	7.646	0.1	-	-
9.	Ethylcyclooctane	8.281	0.06	-	-
10.	1,3,5-Cycloheptatriene,7-ethyl-	8.944	0.2	-	-
11.	1.2.4-Trimethylcyclohexane	9.184	0.06	-	-
12.	1-Ethyl-4-methylcyclohexane	9.663	0.31	-	-
13.	1-Ethyl-2-methylcyclohexane	10.405	0.23	-	-
14.	1-Isopropyl-1-methylcyclohexane	10.548	0.11	-	-
15.	Propylcyclohexane	11.311	0.46	-	-
16.	1,1,2,3-Tetramethylcyclohexane	12.32	0.69	-	-
17.	1-Methyl-3-propylcyclohexane	13.324	0.96	-	-
18.	n-Butylcyclohexane	15.053	0.82	-	-
19.	1-Butyl-2-ethylcyclopentane	17.007	0.56	-	-
20.	Hexane,1-cyclohexyl-	18.495	0.99	-	-
21.	1-Methyl-2-pentylcyclohexane	20.203	0.75	-	-
			<b>7.53</b>		-
<b>Oxygenate</b>					
1.	Triasteranone	9.822	0.12	10.737	2.85
2.	3,3-Dimethyl-2-hexanone	10.8	0.19	-	-
3.	2-Butyloctanol	15.906	1.12	-	-
			<b>1.43</b>		<b>2.85</b>



**Fig. 3.24.** Distribution of various hydrocarbon types in distillate fractions derived from distillation of plain RCP-I crude



**Fig. 3.25.** Distribution of various carbon range compounds in distillate fractions derived from distillation of plain RCP-I crude

The relative abundance of hydrocarbons types i.e. paraffins, olefins, naphthenes and aromatics were calculated in both fractions derived from RCN-II crude. The results are provided in Fig. 3.26. In F1, the proportions of the paraffins, naphthenes, aromatic, oxygenates and olefins were found to be 63.62, 25.51, 7.07, 2.81 and 1.01 %, while in F2 were 96.4, 1.55, 1.22, 0.72 and 0.14 %, respectively. It is evident from the results that in F1 and F2 fractions, the proportions of paraffins and naphthenes were higher, which confirmed that RCN-II is a naphthenic crude. In both fractions, the original oil fractional hydrocarbons distribution followed the order as; paraffins > naphthenes > aromatics > oxygenates > olefins.

The relative distribution of different hydrocarbon range products is displayed in Fig. 3.27. which showed the % amounts of C<sub>5</sub>-C<sub>10</sub>, C<sub>11</sub>-C<sub>13</sub>, C<sub>14</sub>-C<sub>18</sub> and C<sub>19</sub>-C<sub>n</sub> range hydrocarbons in F1 fraction as 74.40, 16.92, 4.63 and 4.07 % respectively, whereas in F2 as 4.29, 40.68, 36.78 and 8.25 %. The data showed that in F1, the distribution of hydrocarbons followed the order: C<sub>5</sub>-C<sub>10</sub> > C<sub>11</sub>-C<sub>13</sub> > C<sub>14</sub>-C<sub>18</sub> > C<sub>19</sub>-C<sub>n</sub> and in F2 fraction, the order was as; C<sub>11</sub>-C<sub>13</sub> > C<sub>14</sub>-C<sub>18</sub> > C<sub>19</sub>-C<sub>n</sub> > C<sub>5</sub>-C<sub>10</sub>. The only difference in both fractions was that F1 is rich in C<sub>5</sub>-C<sub>10</sub> range hydrocarbons, whereas F2 is rich in three carbon range products i.e. C<sub>11</sub>-C<sub>13</sub>, C<sub>14</sub>-C<sub>18</sub> and C<sub>19</sub>-C<sub>n</sub> range hydrocarbons, while C<sub>5</sub>-C<sub>10</sub> range compounds are present in least concentration. All these results conclude that F1 consisted of lighter hydrocarbons, whereas F1 consisted of heavier hydrocarbons.

**Table 3.11.** Individual Compounds Determined in Light (F1) and Medium (F2) Distillate Fractions Derived From Distillation of Plain RCN-II Crude

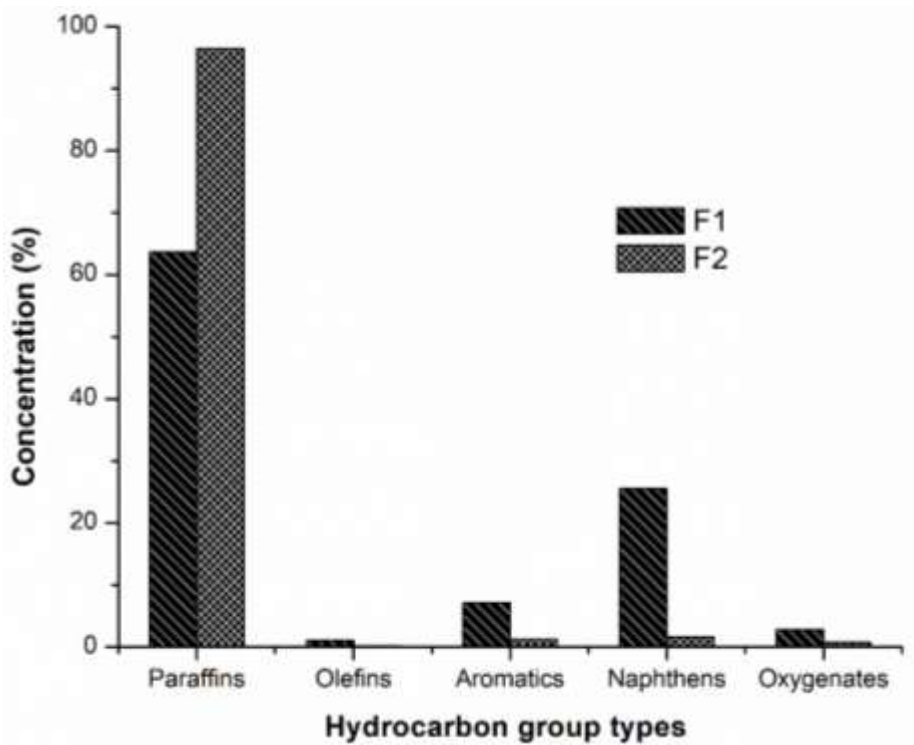
S. #	Compound	F1		F2	
		t <sub>R</sub>	% Conc.	t <sub>R</sub>	% Conc.
<b>Paraffins</b>					
1.	Heptane	3.166	1.77	3.172	0.12
2.	2,3-Dimethylhexane	4.676	0.56	4.718	0.02
3.	3-Methylheptane	5.161	2.71	5.162	0.07
4.	Octane	6.208	4.6	6.202	0.15
5.	2,4-Dimethylheptane	7.015	0.51	7.022	0.01
6.	Isononane	7.33	2.17	7.33	0.05
7.	3-Methyloctane	7.56	2.52	7.56	0.06
8.	5,6-Dimethyldecane	8.396	0.8	8.403	0.02
9.	4-Methyloctane	8.719	1.76	8.72	0.05
10.	2-Methyloctane	8.804	1.91	8.802	0.06
11.	3-Methyloctane	9.056	3.32	9.05	0.1
12.	Nonane	10.214	4.81	10.201	0.19
13.	2,2,3,3-Tetramethylpentane	11.099	0.72	11.104	0.02
14.	3-Methylnonane	11.486	2.13	11.483	0.11
15.	2-Methyl-3-ethylheptane	11.667	0.73	11.673	0.03
16.	2,3,6-Trimethylheptane	12.242	0.63	12.53	0.07
17.	4-Methylnonane	12.531	1.44	12.53	0.07
18.	2-Methylnonane	12.667	1.15	12.664	0.07
19.	3-Methylnonane	12.891	1.09	13.008	0.2
20.	Decane	13.025	0.08	13.963	0.34
21.	2,5,5-Trimethylheptane	13.973	4.08	14.718	0.14
22.	3-Methyldecane	14.719	1.42	15.157	0.05
23.	3,7-Dimethylnonane	15.152	0.4	15.28	0.04



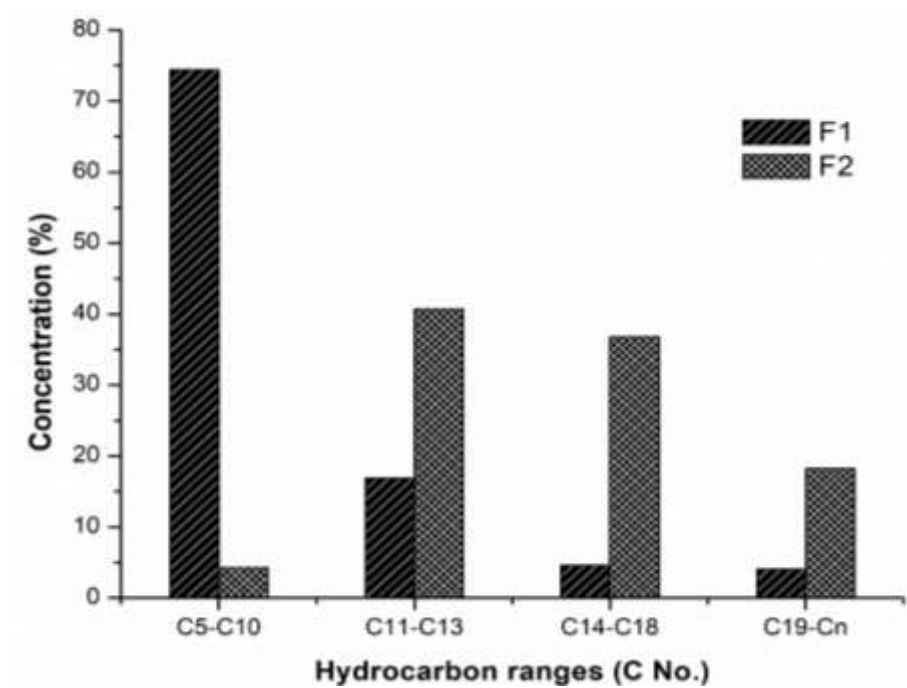
24.	4-Methyldecane	15.274	0.31	16.027	0.06
25.	2,3,3-Trimethyloctane	16.023	0.37	16.178	0.12
26.	3-Methyldecane	16.174	0.63	16.376	0.09
27.	Undecane	16.372	0.45	17.361	0.71
28.	Dodecane	16.961	0.03	17.881	0.02
29.	3,7-Dimethyldecane	17.366	2.44	18.182	0.14
30.	2,3-Dimethyldecane	17.976	0.03	19.332	0.17
31.	Undecane,2-methyl-	18.178	0.26	19.508	0.37
32.	2-Methylundecane	19.326	0.19	19.703	0.27
33.	Tridecane	19.501	0.38	20.579	3.25
34.	3,6-Dimethylundecane	19.698	0.26	20.898	1.88
35.	2,3,7-Trimethyloctane	20.573	2.27	22.255	2.56
36.	2,6,10,14-Tetramethylheptadecane	20.892	1.06	22.846	5.46
37.	11-Methyldodecane	22.244	0.79	23.149	1.04
38.	3-Methyl-5-propylnonane	22.833	1.73	24.181	2.33
39.	2-Methyl-5-propylnonane	23.144	0.24	24.652	7.87
40.	2,6,10,14-Tetramethylhexadecane	24.169	0.38	25.843	3.39
41.	2-Methyl-5-propylnonane	24.632	1.38	26.832	9.05
42.	2,3,5-Trimethyldecane	25.827	0.4	29.993	9.27
43.	Tetradecane	26.8	1.17	34.843	11.23
44.	4,6-Dimethyldodecane	29.943	1.0	34.973	2.92
45.	Pentadecane	34.77	1.27	40.114	7.56
46.	Pentadecane,2,6,10,14-tetramethyl-	34.919	0.33	40.375	1.36
47.	Hexadecane	40.047	0.9	44.877	6.28
48.	Heptadecane	40.336	0.15	49.231	4.84
49.	Octadecane	44.836	0.82	53.247	3.9
50.	Nonadecane	49.196	0.71	57.005	2.84

51.	Eicosane	53.227	0.6	60.546	2.07
52.	Heneicosane	56.991	0.48	63.905	1.38
53.	Docosane	60.536	0.37	67.11	0.57
54.	Tricosane	63.909	0.27	70.187	0.57
55.	Tetracosane	67.112	0.19	73.139	0.36
56.	Pentacosane	70.19	0.15	75.989	0.2
57.	Hexacosane	73.148	0.11	78.723	0.12
58.	Octacosane	75.996	0.08	81.384	0.06
59.	Triacontane	78.75	0.05	83.95	0.03
60.	Dotriacontane	81.403	0.04	86.446	0.02
61.	Tetratriacontane	83.971	0.02	---	0
			<b>63.62</b>		<b>96.4</b>
<b>Olefins</b>					
1.	2,3,4-Trimethyl-2-pentene	6.4	0.98	6.41	0.03
2.	11,Chloro-1-undecene	16.961	0.03	16.831	0.11
			<b>1.01</b>		<b>0.14</b>
<b>Aromatics</b>					
1.	Sec-Butylbenzene	12.825	2.11	12.823	0.15
2.	1-Methyl-2-propylbenzene	13.708	3.09	13.707	0.29
3.	1,4-Diethylbenzene	14.643	0.6	14.649	0.08
4.	Butane,2-phenyl-3-hydroxy-4-cyano	15.7	0.83	15.71	0.12
5.	(1,1-Dimethylpropyl)benzene	16.531	0.22	16.537	0.05
6.	(3,3-Dimethylbutyl)benzene	16.531	0.22	19.139	0.43
			<b>7.07</b>		<b>1.12</b>
<b>Naphthenes</b>					
1.	Methylcyclohexane	-	-	3.172	0.03
2.	1,2,3-Trimethylcyclopentane	4.126	0.3	3.717	0.09

3.	1,2,4-Trimethylcyclopentane	4.335	2.77	4.347	0.01
4.	1,3-Dimethylcyclohexane	4.34	2.08	4.347	0.01
5.	p-Dimethylcyclohexane	5.417	0.67	5.417	0.07
6.	1,1-Dimethylcyclohexane	5.511	0.98	5.516	0.03
7.	1,2-Dimethylcyclohexane	5.699	2.36	5.706	0.01
8.	1,3,5-Trimethylcyclohexane	6.406	0.72	6.202	0.15
9.	Ethylcyclooctane	7.666	7.72	7.668	0.03
10.	1,3,5-Cycloheptatriene,7-ethyl-	8.297	0.32	8.303	0.02
11.	1.2.4-Trimethylcyclohexane	8.971	2.51	8.966	0.36
12.	1-Ethyl-4-methylcyclohexane	9.203	0.69	9.203	0.01
13.	1-Ethyl-2-methylcyclohexane	9.677	0.38	9.68	0.06
14.	1-Isopropyl-1-methylcyclohexane	10.419	1.21	10.42	0.03
15.	Propylcyclohexane	10.558	0.38	10.562	0.02
16.	1,1,2,3-Tetramethylcyclohexane	11.318	0.85	11.321	0.05
17.	1-Methyl-3-propylcyclohexane	12.323	0.57	12.327	0.03
18.	n-Butylcyclohexane	13.327	0.25	13.328	0.07
19.	1-Butyl-2-ethylcyclopentane	15.049	0.35	15.051	0.09
20.	Hexane,1-cyclohexyl-	16.999	0.2	17.003	0.11
21.	1-Methyl-2-pentylcyclohexane	20.391	0.2	18.488	0.27
			<b>25.51</b>		<b>1.55</b>
<b>Oxygenate</b>					
1.	Triasteranone	9.835	2.03	9.841	0.11
2.	3,3-Dimethyl-2-hexanone	10.808	0.27	9.841	0.53
3.	2-Butyloctanol	15.898	0.51	9.841	0.08
			<b>2.81</b>		<b>0.72</b>



**Fig. 3.26.** Distribution of various hydrocarbon types in distillate fractions derived from distillation of plain RCN-II Crude



**Fig. 3.27.** Distribution of various carbon range compounds in distillate fractions derived from distillation of plain RCN-II Crude

The relative abundance of hydrocarbons group types i.e. paraffins, olefins, naphthenes and aromatics were determined in F1 and F2 fractions derived from RCA-III crude oil. The results are provided in Fig. 3.28. The concentrations of the paraffins, naphthenes, aromatic, oxygenates and olefins, in F1 were found to be 65.97, 14.7, 7.59, 0.72 and 12.08 %, respectively, whereas in F2, found to be 97.18, 1.84, 1.38, 0.20 and 0.87 %, respectively. Based on the results, F1 fractional hydrocarbons distribution followed the order given as under: paraffins >naphthenes >oxygenates> aromatics >olefins. However, in F2 the order was; paraffins > naphthenes > aromatics > oxygenates > olefins

The concentration of different hydrocarbon range products i.e. C<sub>5</sub>-C<sub>10</sub>, C<sub>11</sub>-C<sub>13</sub>, C<sub>14</sub>-C<sub>18</sub> and C<sub>19</sub>-C<sub>n</sub> calculated in F1 and F2 are displayed in Fig. 3.29. In F1, the concentration of different carbon range hydrocarbons found were as; C<sub>5</sub>-C<sub>10</sub> (61.52 %), C<sub>11</sub>-C<sub>13</sub> (18.69), C<sub>19</sub>-C<sub>n</sub> (11.67%) and C<sub>14</sub>-C<sub>18</sub> (8.12 %). Similarly, in F2, the concentration of C<sub>5</sub>-C<sub>10</sub> was 5.00 %, C<sub>11</sub>-C<sub>13</sub> was 37.75, C<sub>14</sub>-C<sub>18</sub> was 27.36 and C<sub>19</sub>-C<sub>n</sub> was 29.89 %. The various carbon number distribution hydrocarbons in F1 followed the order as: C<sub>5</sub>-C<sub>10</sub> > C<sub>11</sub>-C<sub>13</sub> > C<sub>19</sub>-C<sub>n</sub> > C<sub>14</sub>-C<sub>18</sub> , whereas in F2, the order was as; C<sub>11</sub>-C<sub>13</sub> > C<sub>19</sub>-C<sub>n</sub> > C<sub>14</sub>-C<sub>18</sub> > C<sub>5</sub>-C<sub>10</sub>.

It can be concluded from these results that F2 fraction is rich in heavier hydrocarbon components, whereas the F1 contained higher proportion of low molecular hydrocarbon compounds.

**Table 3.12.** Individual Compounds Determined in Light (F1) and Medium (F2) Distillate Fractions Derived From Distillation of Plain RCA-III Crude

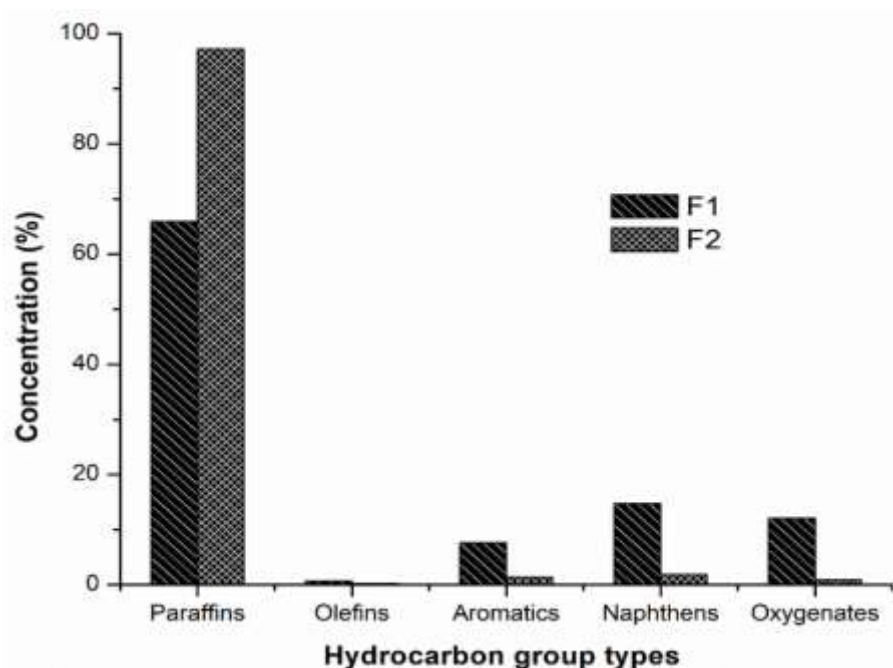
S. #	Compound	F1		F2	
		t <sub>R</sub>	% Conc.	t <sub>R</sub>	% Conc.
<b>Paraffins</b>					
1.	Heptane	3.126	4.73	3.166	0.19
2.	2,3-Dimethylhexane	4.613	0.33	4.621	0.02
3.	3-Methylheptane	5.083	1.7	5.152	0.07
4.	Octane	6.121	3.11	6.193	0.17
5.	2,4-Dimethylheptane	6.94	0.25	7.014	0.01
6.	Isononane	7.248	1.53	7.321	0.07
7.	3-Methyloctane	7.477	0.85	7.551	0.18
8.	5,6-Dimethyldecane	8.472	0.11	8.394	0.03
9.	4-Methyloctane	8.712	1.03	8.71	0.05
10.	2-Methyloctane	8.712	1.03	8.792	0.06
11.	Nonane	10.11	2.47	10.19	0.18
12.	2,2,3,3-Tetramethylpentane	11.014	0.29	11.093	0.02
13.	2-Methyl-3-ethylheptane	11.582	0.48	11.662	0.05
14.	2,3,6-Trimethylheptane	12.441	1.19	12.52	0.11
15.	4-Methylnonane	12.576	0.35	12.52	0.11
16.	2-Methylnonane	12.576	0.65	12.655	0.06
17.	Nonane,3-methyl-	12.804	0.59	12.883	0.25
18.	Decane	12.887	2.33	13.952	0.3
19.	2,5,5-Trimethylheptane	13.875	2.52	14.708	0.17
20.	3-Methyldecane	14.793	0.13	15.149	0.04
21.	3,7-Dimethylnonane	15.193	0.28	15.268	0.05
22.	4-Methyldecane	15.193	0.28	16.015	0.06

23.	2,3,3-Trimethyloctane	15.942	0.32	16.166	0.1
24.	3-Methyldecane	16.291	0.35	16.366	0.07
25.	Undecane	16.291	0.37	17.349	0.84
26.	Dodecane	17.275	2.97	17.863	0.11
27.	3,7-Dimethyldecane	18.097	0.46	18.172	0.19
28.	2,3-Dimethyldecane	18.097	0.46	19.498	0.27
29.	2-Methylundecane	19.732	0.65	19.498	0.49
30.	Tridecane	20.65	0.1	20.567	2.47
31.	3,6-Dimethylundecane	20.823	1.9	20.889	1.74
32.	2,3,7-Trimethyloctane	22.184	1.63	22.247	2.13
33.	2,6,10,14-Tetramethylheptadecane	22.773	3.59	22.835	4.33
34.	11-Methyldodecane	23.081	0.75	22.842	3.81
35.	3-Methyl-5-propylnonane	24.113	1.2	24.173	2.4
36.	2-Methyl-5-propylnonane	24.716	0.23	24.639	6.6
37.	2,6,10,14-Tetramethylhexadecane	25.842	0.45	25.831	3.27
38.	2-Methyl-5-propylnonane	26.87	0.04	26.811	7.59
39.	2,3,5-Trimethyldecane	29.807	3.12	29.963	7.66
40.	Tetradecane	34.683	0.6	34.796	9.93
41.	4,6-Dimethyldodecane	34.733	0.88	34.94	3.78
42.	Pentadecane	40.177	1.2	40.079	7.09
43.	Pentadecane,2,6,10,14-tetramethyl	40.177	1.05	40.343	2.06
44.	Hexadecane	44.669	2.05	44.851	5.71
45.	Heptadecane	49.038	1.81	49.215	4.81
46.	Octadecane	53.067	1.58	53.238	4.03
47.	Nonadecane	56.832	1.51	56.994	3.32
48.	Eicosane	60.384	1.22	60.54	3.51
49.	Henicosane	63.743	1.06	63.898	1.97

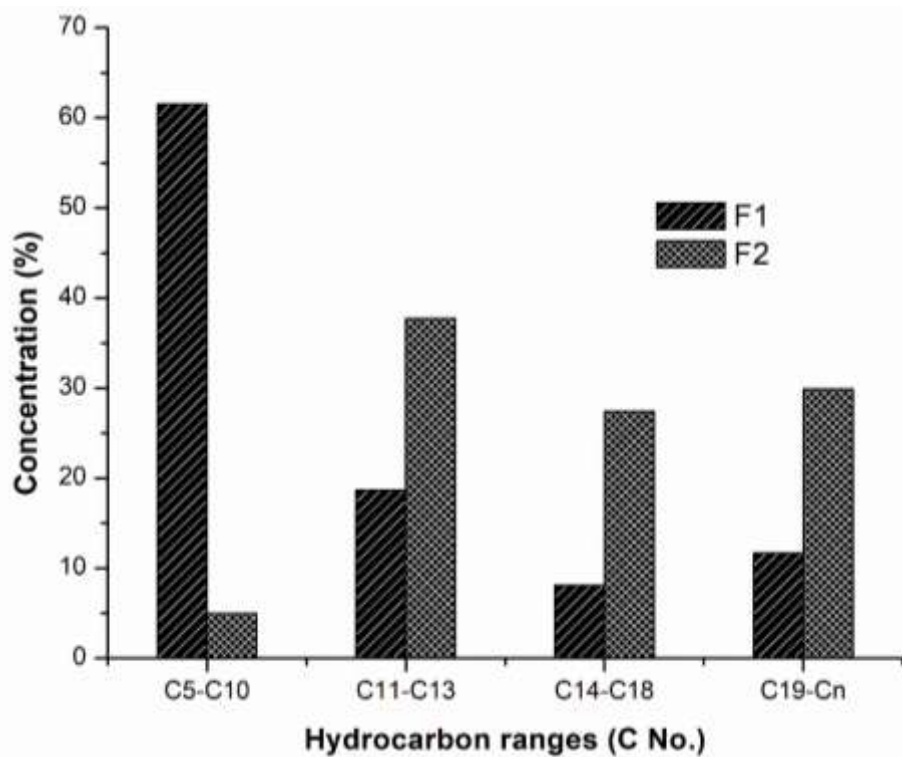
50.	Docosane	66.956	0.83	67.104	1.39
51.	Tricosane	70.03	0.7	70.171	1.07
52.	Tetracosane	72.984	0.54	73.127	0.74
53.	Pentacosane	75.835	0.41	75.973	0.49
54.	Hexacosane	78.571	0.29	78.711	0.34
55.	Octacosane	81.234	0.24	81.362	0.23
56.	Triacontane	83.786	0.12	83.93	0.14
57.	Dotriacontane	83.126	4.73	86.412	0.08
58.	Tetratriacontane	84.613	0.33	88.825	0.05
<b>Total</b>			<b>65.97</b>		<b>97.15</b>
<b>Olefins</b>					
1.	2,3,4-Trimethyl-2-pentene	-	-	6.402	0.03
2.	11, Chloro-1-undecene	16.83	0.72	16.818	0.17
<b>Total</b>			<b>0.72</b>		<b>0.2</b>
<b>Aromatics</b>					
1.	Sec-Butylbenzene	12.725	1.39	12.811	0.11
2.	1-Methyl-2-propylbenzene	13.609	3.72	13.694	0.41
3.	1,4-Diethylbenzene	14.552	0.9	14.636	0.13
4.	Butane,2-phenyl-3-hydroxy-4-cyano	15.782	0.53	15.694	0.22
5.	(1,1-Dimethylpropyl)benzene	16.445	0.36	16.524	0.09
6.	(3,3-Dimethylbutyl)benzene	19.041	0.69	19.127	0.42
<b>Total</b>			<b>7.59</b>		<b>1.38</b>
<b>Naphthenes</b>					
1.	Cyclopentane, 1,2-dimethyl	-	-	3.166	0.06
2.	Methylcyclohexane	3.676	1.08	3.711	0.19
3.	1,2,3-Trimethylcyclopentane	4.088	0.36	4.342	0.01
4.	1,2,4-Trimethylcyclopentane	4.3	0.25	4.342	0.01



5.	1,3-Dimethylcyclohexane	5.462	0.35	5.41	0.08
6.	p-Dimethylcyclohexane	5.463	0.31	5.508	0.03
7.	1,1-Dimethylcyclohexane	5.655	0.52	5.697	0.01
8.	1,2-Dimethylcyclohexane	6.104	0.61	6.402	0.03
9.	1,3,5-Trimethylcyclohexane	7.633	1.27	7.659	0.03
10.	Ethylcyclooctane	8.267	0.62	8.295	0.03
11.	1,3,5-Cycloheptatriene,7-ethyl	8.933	0.51	8.952	0.35
12.	1.2.4-Trimethylcyclohexane	9.177	0.41	9.193	0.01
13.	1-Ethyl-4-methylcyclohexane	9.654	1.12	9.669	0.09
14.	1-Ethyl-2-methylcyclohexane	10.398	1.27	10.41	0.04
15.	1-Isopropyl-1-methylcyclohexane	10.54	0.67	10.548	0.03
16.	Propylcyclohexane	11.305	1.14	11.31	0.07
17.	1,1,2,3-Tetramethylcyclohexane	12.315	0.76	12.317	0.02
18.	1-Methyl-3-propylcyclohexane	13.322	1.23	13.319	0.11
19.	n-Butylcyclohexane	15.051	0.8	15.041	0.1
20.	1-Butyl-2-ethylcyclopentane	17.006	0.34	16.994	0.2
21.	1-Methyl-2-pentylcyclohexane	3.676	1.08	18.477	0.34
<b>Total</b>			<b>14.7</b>		<b>1.84</b>
<b>Oxygenate</b>					
1.	Triasteranone	9.741	2.06	9.827	0.14
2.	3,3-Dimethyl-2-hexanone	10.674	9.54	10.789	0.44
3.	2-Butyloctanol	15.817	0.48	15.893	0.08
4.	(4,6,6-Trimethylbicyclo [3,1,1] hept-3-en-2-yl) acetaldehyde	-	-	17.967	0.21
<b>Total</b>			<b>12.08</b>		<b>0.87</b>



**Fig. 3.28.** Distribution of various hydrocarbon types distillate fractions derived from distillation of plain RCA-III crude



**Fig. 3.29.** Distribution of various carbon range compounds distillate fractions derived from distillation of plain RCA-III crude

### 3.5.2. GC-MS Analysis of Distillate Fractions of Chemically Dispersed Crudes

The GC-MS analysis of the distillate fractions from chemically dispersed crudes was carried out so as to study the influence of the various surfactants on the compositional stabilities of the resultant fractions.

**RCP-I Fractions:** The F1 and F2 fractions derived from distillation of SDS, CTAB and TX-100 dispersed RCP-I crude were analyzed by GC-MS and the major individual hydrocarbons were detected. The data was used to calculate hydrocarbon group types and different carbon range hydrocarbons. The individual hydrocarbons identified in each fraction are indicated in Table 3.13- & Table 3.14. The results showed various hydrocarbon compounds i.e. paraffins, olefins, naphthenes and aromatics. It can be observed that the common paraffins, olefins, aromatics, naphthenes and oxygenated hydrocarbons remained intact and were almost same as determined in the parent crude. However, the relative distribution of some compounds varied with various surfactants. It could be observed that the F1 fraction from SDS-dispersed sample, the paraffins with molecular weight higher than octane and smaller than nonadecane occurred in high concentrations, whereas in the CTAB-dispersed crude, various paraffins smaller than decane range occurred abundantly, while in TX-100-dispersed crude, the middle level paraffins falling between decane to trimethyldecane were present in high concentrations. In case of the F2 fractions obtained from SDS, CTAB and TX-100-dispersed crude, the heavier paraffins i.e. ranging from tridecane to heneicosane were most abundantly present.

The relative distribution of various hydrocarbon groups determined in the fractions are given in Table 3.15. It can be observed, that in F1 fractions, the SDS and TX-100-dispersion led to considerable increase in the paraffinic contents to 78.11 and 89.67 % from 63.62 % in plain RCP-I crude. The dispersion with the same surfactants also resulted a decrease in the olefins,

aromatics, naphthenes and oxygenates. On other hands, CTAB dispersion caused the paraffines to decrease to 58.42 %. The yields of the aromatics, naphthenes and oxygenates were increased compared to plain crude. In case of the F2 fraction, the yields of different hydrocarbons remained close to that of the plain RCP-I. Hence, it may be concluded that the anionic and neutral surfactants efficiently enhanced the yields of saturated hydrocarbons in the paraffinic crude which may be due to the exposure of such hydrocarbons to distillation conditions which were caged in case of plain crudes with in the asphaltene molecules.

Table 3.16 indicates the distribution of various carbon range hydrocarbons, which showed that in F1 fraction, the yield of C<sub>5</sub>-C<sub>10</sub>, C<sub>11</sub>-C<sub>13</sub>, C<sub>14</sub>-C<sub>18</sub>, and C<sub>19</sub>-C<sub>n</sub> range hydrocarbons were 25.26, 58.81, 6.21 and 9.72 % respectively, whereas in F2 fraction the yields were 3.67, 46.48, 24.96 and 24.89 respectively. It is clear from the data that in case of F1 fraction, the SDS-dispersion led to increase in concentration on C<sub>5</sub>-C<sub>10</sub>, C<sub>14</sub>-C<sub>18</sub> and C<sub>19</sub>-C<sub>n</sub> range hydrocarbons to 37.77, 16.96 and 18.83 %, respectively, whereas in F2 fraction, the dispersion enhanced the yields of C<sub>5</sub>-C<sub>10</sub> and C<sub>19</sub>-C<sub>n</sub> range hydrocarbons to 3.92 and 36.77 %, respectively. The CTAB-dispersion caused a substantial increase in C<sub>5</sub>-C<sub>10</sub> range hydrocarbons to 78.2 % in F1 fraction, whereas it also enhanced the concentration of C<sub>14</sub>-C<sub>18</sub> range hydrocarbons to 41.3 % in F2 fraction. Similarly, the TX-100 dispersion increased the concentration of C<sub>14</sub>-C<sub>18</sub> and C<sub>19</sub>-C<sub>n</sub> range hydrocarbons by almost 50 percent to 12.88 and 18.64 % in F1 fraction, however in F2 fraction, it led to a significant increase in concentration of only C<sub>14</sub>-C<sub>18</sub> range hydrocarbons to 45.45 %. The concentration of all other carbon range compounds was slightly reduced at the expense of certain heavy carbon range compounds.

**Table 3.13.** Individual Compounds Determined in Light (F1) Distillate Fractions Derived From Distillation of Chemically Dispersed RCP-I Crude

S. #	Compound	SDS		CTAB		TX-100	
		tr	Conc. (%)	tr	Conc. (%)	tr	Conc. (%)
<b>Paraffins</b>							
1.	Heptane	3.174	1.55	3.16	1.59	3.177	0.11
2.	2,3-Dimethylhexane	4.69	0.31	4.667	0.92	4.694	0.03
3.	3-Methylheptane	5.167	0.9	5.143	2.22	5.172	0.16
4.	Octane	6.21	2.07	6.188	3.37	6.213	0.3
5.	2,4-Dimethylheptane	7.027	0.19	7.009	0.57	7.033	0.07
6.	Isononane	7.336	0.78	7.319	2.23	7.341	0.3
7.	3-Methyloctane	7.566	0.67	7.549	2.04	7.571	0.32
8.	5,6-Dimethyldecane	8.409	0.5	8.395	1.37	8.415	0.28
9.	4-Methyloctane	8.728	0.54	8.714	1.34	8.732	0.27
10.	2-Methyloctane	8.809	0.58	8.796	1.36	8.814	0.28
11.	3-Methyloctane	9.059	1.11	9.046	1.73	9.063	0.61
12.	Nonane	10.212	2.11	10.201	3.89	10.215	0.75
13.	2,2,3,3-Tetramethylpentane	11.111	0.24	11.105	0.59	11.117	0.42
14.	3-Methylnonane	11.494	1.57	11.489	2.41	11.504	1.8
15.	2-Methyl-3-ethylheptane	11.682	0.41	11.677	1.53	11.692	1.55
16.	2,3,6-Trimethylheptane	12.257	0.31	12.252	0.67	12.264	0.65
17.	4-Methylnonane	12.541	0.62	12.537	1.29	12.548	0.92
18.	2-Methylnonane	12.675	0.49	12.672	0.94	12.683	0.66
19.	Nonane,3-methyl-	12.903	0.29	12.9	0.96	12.911	0.82
20.	Decane	13.047	0.17	13.974	4.06	13.985	2.52
21.	2,5,5-Trimethylheptane	13.977	2.4	14.73	0.62	14.745	2.42
22.	3-Methyldecane	14.731	0.73	15.171	0.8	15.178	1.92

23.	3,7-Dimethylnonane	15.169	0.21	15.289	0.32	15.298	0.54
24.	4-Methyldecane	15.289	0.2	16.04	0.37	16.047	0.6
25.	2,3,3-Trimethyloctane	16.039	0.25	16.19	0.62	16.199	1.01
26.	Undecane	16.389	0.34	17.376	3.37	17.394	5.21
27.	Dodecane	17.378	2.93	18.267	0.02	18.001	0.09
28.	3,7-Dimethyldecane	17.886	0.22	18.198	0.29	18.207	0.78
29.	2,3-Dimethyldecane	18.197	0.26	19.524	0.4	19.357	0.62
30.	2-Methylundecane	19.521	0.68	19.721	2.91	19.532	2.02
31.	Tridecane	19.717	0.33	20.909	1.13	20.61	7.03
32.	3,6-Dimethylundecane	20.591	3.38	22.261	0.84	20.921	4.02
33.	2,3,7-Trimethyloctane	20.908	1.57	22.848	1.77	22.271	3.69
34.	2,6,10,14-Tetramethylheptadecane	22.263	1.61	22.868	1.19	22.865	6.35
35.	11-Methyldodecane	22.852	3.76	24.187	0.33	24.194	1.87
36.	3-Methyl-5-propylnonane	24.189	1.14	24.649	1.07	24.665	5.72
37.	2-Methyl-5-propylnonane	24.656	3.89	25.851	0.26	25.86	1.7
38.	2,6,10,14-Tetramethylhexadecane	25.856	1.42	26.826	0.59	26.842	4.26
39.	2-Methyl-5-propylnonane	26.837	3.81	29.979	0.38	30	3.22
40.	2,3,5-Trimethyldecane	29.996	3.48	34.819	0.33	34.846	2.91
41.	Tetradecane	34.847	4.29	34.97	0.08	34.846	2.95
42.	4,6-Dimethyldodecane	34.988	1.64	40.1	0.19	40.116	1.89
43.	Pentadecane	40.12	2.97	40.401	0.06	40.403	0.32
44.	Pentadecane,2,6,10,14-tetramethyl-	40.407	0.61	44.878	0.15	44.899	1.69
45.	Hexadecane	44.896	2.74	49.243	0.13	49.262	1.67
46.	Heptadecane	49.262	2.45	53.271	0.1	53.285	1.71
47.	Octadecane	53.291	2.35	57.036	0.08	57.054	1.63

48.	Nonadecane	57.053	2.06	60.589	0.05	60.604	1.49
49.	Eicosane	60.6	1.9	63.959	0.05	63.976	1.31
50.	Henicosane	63.972	1.63	67.167	0.03	67.182	1.11
51.	Docosane	67.19	1.44	70.239	0.03	70.264	0.99
52.	Tricosane	70.26	1.27	76.058	0.01	73.217	0.91
53.	Tetracosane	73.226	1.12	78.778	0.01	76.066	0.81
54.	Pentacosane	76.074	0.92	81.451	0.01	78.811	0.73
55.	Hexacosane	78.819	0.85	86.516	0.02	81.467	0.59
56.	Octacosane	81.465	0.64	3.16	1.59	84.031	0.46
57.	Triacotane	84.042	0.55	4.667	0.92	86.515	0.3
58.	Dotriacotane	86.528	0.37	5.143	2.22	88.933	0.2
59.	Tetratriacontane	88.94	0.29	-	-	89.177	0.11
<b>Total</b>			<b>78.11</b>		<b>58.42</b>		<b>89.67</b>
<b>Olefins</b>							
1.	2,3,4-Trimethyl-2-pentene	6.417	0.36	6.398	1.05	6.422	0.06
2.	11, Chloro-1-undecene	16.739	0.58	-	-	-	-
<b>Total</b>			<b>0.94</b>		<b>1.05</b>		<b>0.06</b>
<b>Aromatics</b>							
1.	Sec-Butylbenzene	12.836	0.73	12.834	1.7	12.844	0.34
2.	1-Methyl-2-propylbenzene	14.662	1.75	13.719	3.5	13.726	0.55
3.	1,4-Diethylbenzene	15.719	0.69	14.663	1.32	14.668	0.28
4.	Butane,2-phenyl-3-hydroxy-4-cyano	16.551	0.64	15.721	1.24	15.726	0.39
5.	(1,1-Dimethylpropyl)benzene	19.153	0.21	16.553	0.37	16.558	0.2
6.	(3,3-Dimethylbutyl)benzene	12.836	0.6	16.156	0.56	19.164	1.6
<b>Total</b>			<b>4.62</b>		<b>8.69</b>		<b>3.36</b>
<b>Naphthenes</b>							
1.	Methylcyclohexane	3.022	0.31	3.159	0.45	3.026	0.02

2.	1,2,3-Trimethylcyclopentane	3.724	3.29	3.706	7.39	3.726	0.29
3.	1,2,4-Trimethylcyclopentane	4.139	0.4	4.118	1.13	4.143	0.03
4.	1,3-Dimethylcyclohexane	4.352	0.26	4.331	0.82	4.358	0.02
5.	p-Dimethylcyclohexane	5.425	1.23	5.402	3.19	5.43	0.17
6.	1,1-Dimethylcyclohexane	5.523	0.45	5.5	0.97	5.527	0.06
7.	1,2-Dimethylcyclohexane	5.712	0.2	5.691	0.76	5.718	0.04
8.	1,3,5-Trimethylcyclohexane	6.417	0.36	6.398	1.05	6.422	0.06
9.	Ethylcyclooctane	7.676	0.73	7.66	1.48	7.681	0.37
10.	1,3,5-Cycloheptatriene,7-ethyl-	8.309	0.32	8.295	0.79	8.315	0.14
11.	1,2,4-Trimethylcyclohexane	8.974	2.91	8.961	4.69	8.977	0.47
12.	1-Ethyl-4-methylcyclohexane	9.212	0.15	9.201	0.42	9.217	0.12
13.	1-Ethyl-2-methylcyclohexane	9.688	0.73	9.677	0.57	9.693	0.39
14.	1-Isopropyl-1-methylcyclohexane	10.429	0.36	10.42	0.81	10.435	0.31
15.	Propylcyclohexane	10.572	0.16	10.564	0.37	10.578	0.16
16.	1,1,2,3-Tetramethylcyclohexane	11.33	0.59	11.325	1.06	11.339	0.4
17.	1-Methyl-3-propylcyclohexane	12.339	0.36	12.334	0.76	12.348	0.93
18.	n-Butylcyclohexane	13.341	0.5	13.338	0.85	13.489	0.14
19.	1-Butyl-2-ethylcyclopentane	15.064	0.39	15.063	0.53	15.073	0.48
20.	Hexane,1-cyclohexyl-	17.015	0.2	17.017	0.27	17.025	0.36
21.	1-Methyl-2-pentylcyclohexane	18.503	0.35	-	-	18.513	0.74
<b>Total</b>			<b>14.25</b>		<b>28.36</b>		<b>5.7</b>
<b>Oxygenate</b>							
1.	Triasteranone	9.849	1.15	9.839	2.67	9.854	0.2
2.	3,3-Dimethyl-2-hexanone	10.835	0.6	10.814	0.31	10.828	0.22
3.	2-Butyloctanol	15.914	0.33	15.915	0.5	15.923	0.79
<b>Total</b>			<b>2.08</b>		<b>3.48</b>		<b>1.21</b>



**Table 3.14.** Individual Compounds Determined in Middle (F2) Distillate Fractions Derived From Distillation of Chemically Dispersed RCP-I Crude

S. #	Compound	SDS		CTAB		TX-100	
		tr	Conc. (%)	tr	Conc. (%)	tr	Conc. (%)
<b>Paraffins</b>							
1.	Heptane	3.173	0.18	3.16	0.22	3.168	0.25
2.	2,3-Dimethylhexane	-	-	4.701	0.02	4.621	0.02
3.	3-Methylheptane	5.162	0.08	5.152	0.03	5.162	0.05
4.	Octane	6.201	0.19	6.183	0.08	6.193	0.15
5.	2,4-Dimethylheptane	7.019	0.01	7.311	0.02	7.321	0.03
6.	Isononane	7.329	0.06	0	0	7.321	0.03
7.	3-Methyloctane	7.558	0.06	8.397	0.02	7.551	0.01
8.	5,6-Dimethyldecane	8.399	0.04	8.707	0.01	8.394	0.04
9.	4-Methyloctane	8.716	0.04	8.789	0.02	8.711	0.03
10.	2-Methyloctane	8.798	0.05	9.037	0.02	8.792	0.03
11.	3-Methyloctane	9.046	0.1	10.186	0.35	9.04	0.09
12.	Nonane	10.196	0.19	11.093	0.09	10.189	0.15
13.	2,2,3,3-Tetramethylpentane	11.097	0.03	11.66	0.01	11.093	0.01
14.	3-Methylnonane	11.479	0.18	12.52	0.02	11.661	0.03
15.	2-Methyl-3-ethylheptane	11.667	0.05	12.52	0.02	12.519	0.05
16.	2,3,6-Trimethylheptane	12.241	0.04	12.52	0.03	12.519	0.05
17.	4-Methylnonane	12.524	0.07	12.884	0.03	12.519	0.05
18.	2-Methylnonane	12.659	0.05	13.996	0.03	12.881	0.03
19.	Nonane,3-methyl-	-	-	13.954	0.02	12.996	0.18
20.	Decane	13.007	0.05	14.71	0.14	13.95	0.22
21.	2,5,5-Trimethylheptane	13.956	0.35	15.151	0.06	14.706	0.06

22.	3-Methyldecane	14.711	0.05	15.272	0.05	15.148	0.03
23.	3,7-Dimethylnonane	15.152	0.04	16.019	0.02	15.266	0.02
24.	4-Methyldecane	15.272	0.06	16.17	0.02	16.013	0.02
25.	2,3,3-Trimethyloctane	16.02	0.12	16.368	0.05	16.165	0.04
26.	Undecane	16.369	0.1	17.866	0.42	17.347	0.4
27.	Dodecane	17.865	0.1	18.174	0.05	17.93	0.02
28.	3,7-Dimethyldecane	17.865	0.14	19.325	0.07	18.169	0.04
29.	2,3-Dimethyldecane	18.176	0.32	19.498	0.09	19.318	0.05
30.	2-Methylundecane	19.499	0.25	19.695	0.18	19.494	0.11
31.	Tridecane	19.696	2.41	20.888	2.12	20.559	2.69
32.	3,6-Dimethylundecane	20.568	1.8	22.242	1.1	20.883	1.69
33.	2,3,7-Trimethyloctane	20.89	3.67	22.83	1.69	22.239	1.06
34.	2,6,10,14-Tetramethylheptadecane	22.244	5.68	23.139	4.5	22.826	3.12
35.	11-Methyldodecane	22.833	2.29	24.167	1.39	23.135	2.01
36.	3-Methyl-5-propylnonane	24.169	7.55	24.629	1.86	24.164	2.33
37.	2-Methyl-5-propylnonane	24.634	4.66	25.823	6.93	24.624	6.07
38.	2,6,10,14-Tetramethylhexadecane	25.826	8.01	26.798	1.79	25.819	2.01
39.	2-Methyl-5-propylnonane	26.806	8.00	29.941	8.07	26.793	6.05
40.	2,3,5-Trimethyldecane	29.952	12.99	34.768	8.15	29.934	8.00
41.	Tetradecane	34.787	4.26	34.915	11.94	34.757	10.55
42.	4,6-Dimethyldodecane	34.935	7.16	40.051	3.55	34.657	10.7
43.	Pentadecane	40.058	1.41	40.331	7.07	40.043	6.14
44.	Pentadecane,2,6,10,14-tetramethyl-	40.344	7.00	44.832	1.5	40.323	1.45
45.	Hexadecane	44.834	5.64	49.188	7.03	44.82	5.8
46.	Heptadecane	49.193	3.72	53.215	6.01	49.183	5.27
47.	Octadecane	53.221	2.76	56.971	5.09	53.208	4.99
48.	Nonadecane	56.974	2.06	60.512	4.04	56.967	1.07

49.	Eicosane	60.521	2.36	63.879	3.17	60.514	2.93
50.	Henicosane	63.878	0.93	67.084	2.09	63.876	2.56
51.	Docosane	67.091	0.92	70.157	2.74	67.087	1.67
52.	Tricosane	70.164	0.39	73.112	1.22	70.154	1.1
53.	Tetracosane	73.119	0.23	75.959	0.9	73.103	1.78
54.	Pentacosane	75.962	0.14	78.698	0.57	75.951	1.3
55.	Hexacosane	78.705	0.07	81.349	0.4	78.699	1.4
56.	Octacosane	81.357	0.04	83.914	0.23	81.345	0.69
57.	Triacontane	83.926	0.02	86.408	0.14	83.91	0.47
58.	Dotriacontane	86.41	0.01	88.816	0.07	86.4	0.28
59.	Tetratriacontane	88.833	0.01	88.897	0.04	88.808	0.18
<b>Total</b>			<b>96.64</b>		<b>97.59</b>		<b>97.65</b>
<b>Olefins</b>							
1.	2,3,4-Trimethyl-2-pentene	-	-	6.388	0.01	6.422	0.06
2.	11,Chloro-1-undecene	-	-	16.826	0.05	16.154	0.04
<b>Total</b>					<b>0.06</b>		<b>0.1</b>
<b>Aromatics</b>							
1.	Sec-Butylbenzene	12.817	0.08	12.814	0.04	12.81	0.04
2.	1-Methyl-2-propylbenzene	13.701	0.26	13.701	0.11	13.695	0.12
3.	1,4-Diethylbenzene	14.642	0.12	14.641	0.05	14.635	0.05
4.	Butane,2-phenyl-3-hydroxy-4-cyano	15.7	0.14	15.705	0.05	15.695	0.04
5.	(1,1-Dimethylpropyl)benzene	16.531	0.06	16.531	0.02	16.525	0.02
6.	(3,3-Dimethylbutyl)benzene	19.128	0.41	19.128	0.23	19.123	0.13
<b>Total</b>			<b>1.07</b>		<b>0.5</b>		<b>0.4</b>
<b>Naphthenes</b>							
1.	Methylcyclohexane	3.718	0.25	3.16	0.07	3.168	0.07
2.	1,2,3-Trimethylcyclopentane	4.349	0.02	3.703	0.05	3.713	0.06

3.	1,2,4-Trimethylcyclopentane	4.135	0.03	4.118	0	4.128	0.01
4.	1,3-Dimethylcyclohexane	5.418	0.1	5.397	0.02	4.344	0
5.	p-Dimethylcyclohexane	5.516	0.04	5.497	0.01	5.412	0.02
6.	1,1-Dimethylcyclohexane	5.706	0.02	6.388	0.01	5.509	0.01
7.	1,2-Dimethylcyclohexane	6.41	0.03	7.652	0.02	5.412	0.02
8.	1,3,5-Trimethylcyclohexane	7.666	0.06	8.292	0.01	6.401	0.01
9.	Ethylcyclooctane	8.299	0.03	8.957	0.14	7.659	0.03
10.	1,3,5-Cycloheptatriene,7-ethyl-	8.96	0.24	9.664	0.02	8.297	0.01
11.	1,2,4-Trimethylcyclohexane	9.2	0.01	10.405	0.01	8.955	0.1
12.	1-Ethyl-4-methylcyclohexane	9.674	0.07	10.541	0.01	9.664	0.02
13.	1-Ethyl-2-methylcyclohexane	10.415	0.03	11.307	0.02	0	0.01
14.	1-Isopropyl-1-methylcyclohexane	10.557	0.02	12.315	0.02	10.413	0.03
15.	Propylcyclohexane	11.315	0.06	13318	0.03	11.93	0.02
16.	1,1,2,3-Tetramethylcyclohexane	12.322	0.04	15.043	0.03	12.317	0.01
17.	1-Methyl-3-propylcyclohexane	13.323	0.08	16.994	0.05	13.318	0.02
18.	n-Butylcyclohexane	15.044	0.09	18.479	0.14	15.039	0.03
19.	1-Butyl-2-ethylcyclopentane	16.996	0.1	20.188	0.17	16.989	0.03
20.	Hexane,1-cyclohexyl-	18.479	0.25	---	0	18.473	0.4
21.	1-Methyl-2-pentylcyclohexane	20.189	0.26	---	0	20.559	0.07
<b>Total</b>			<b>1.88</b>		<b>0.83</b>		<b>0.98</b>
<b>Oxygenate</b>							
1.	Triasteranone	9.834	0.11	9.83	0.05	9.829	0.05
2.	3,3-Dimethyl-2-hexanone	10.793	0.21	10.78	0.82	10.783	0.73
3.	2-Butyloctanol	15.896	0.08	16.169	0.05	15.89	0.03
4.	4,6,6-Trimethylbicyclo[3,1,1]hept-3-en-2-yl)acetaldehyde	17.744	0.01	17.973	0.1	17.965	0.06
<b>Total</b>			<b>0.41</b>		<b>1.02</b>		<b>0.87</b>

**Table 3.15.** Distribution of Various Hydrocarbon Group Types in Light and Middle Fractions Derived From Distillation of Chemically Dispersed RCP-I Crude

Hydrocarbon group	Plain RCP-I		SDS treated		CTAB treated		TX-100 treated	
	F1	F2	F1	F2	F1	F2	F1	F2
Paraffins	63.62	96.4	78.11	96.64	58.42	97.59	89.67	97.65
Olefins	1.01	0.14	0.94	0.0	1.05	0.06	0.06	0.1
Aromatics	7.07	1.22	4.62	1.07	8.69	0.5	3.36	0.4
Naphthenes	25.51	1.55	14.25	1.88	28.36	0.83	5.7	0.98
Oxygenates	2.81	0.72	2.08	0.41	3.48	1.02	1.21	0.87

**Table 3.16.** Distribution of Various Carbon Range Compounds in Light and Middle Fractions Derived From Distillation of Chemically Dispersed RCP-I Crude

Sample	Concentration (Wt %)							
	C <sub>5</sub> -C <sub>10</sub>		C <sub>11</sub> -C <sub>13</sub>		C <sub>14</sub> -C <sub>18</sub>		C <sub>19</sub> -C <sub>n</sub>	
	F1	F2	F1	F2	F1	F2	F1	F2
Plain RCP-I	25.26	3.67	58.81	46.48	6.21	24.96	9.72	24.89
SDS treated RCP-I	37.77	3.92	26.94	40.27	16.46	36.77	18.83	19.04
CTAB treated RCP-I	78.2	2.7	18.44	34	0.98	41.3	2.38	22
TX-100 treated RCP-I	21.6	3.03	46.88	29.1	12.88	45.45	18.64	22.47

**RCN-II Fractions:** The individual compounds identified in the F1 and F2 fractions of RCN-II crude dispersed with various surfactants. The results are provided in Table 3.17 and Table 3.18, which showed that the profile of individual hydrocarbons is almost same as that of fractions

from plain crude. However, minor variations in relative concentration in different samples can be observed. The data shows that the dispersion with various surfactant led to an increase in the concentration of paraffinic hydrocarbons. In case of F1 fractions derived from distillation of SDS-dispersed crude, the individual paraffinic hydrocarbons presented higher concentrations than the plain oil which included 2,6,10,14-Tetramethylheptadecane, 2-Methyl-5-propylnonane, 2-Methyl-5-propylnonane, 2,3,5-Trimethyldecane, Tetradecane, 4,6-Dimethyldodecane, Pentadecane, Hexadecane, Heptadecane, and Octadecane. In case of CTAB-dispersed crude, the F1 fraction possessed hydrocarbons like 2,6,10,14-Tetramethylheptadecane, 2-Methyl-5-propylnonane, 2,6,10,14-Tetramethyl-hexadecane, 2-Methyl-5-propylnonane, 2,3,5-Trimethyldecane, Tetradecane, 4,6-Dimethyldodecane, Pentadecane, Hexadecane, Heptadecane. In TX-100 dispersion, the F1 fraction, possessed 11-Methyldodecane, 2,6,10,14-Tetramethylhexadecane, 2,3,5-Trimethyldecane, Tetradecane, 4,6-Dimethyldodecane, Pentadecane, 2,6,10,14-tetramethyl, Heptadecane, Octadecane, and Nonadecane. On the other hand, among the aromatic hydrocarbons, the concentration of Sec-Butylbenzene and 1-Methyl-2-propylbenzene was shown to be very high in the F1 fraction of plain RCN-II, however, the concentration of these compounds was found to be decreased in the SDS, CTAB and TX-100-dispersed crude samples.

In case of the F2 fractions, the concentration of paraffinic, naphthenic and some aromatic hydrocarbons was found to be increased as compared to that of plain crude. In SDS-dispersed crude, the F2 fraction possessed the paraffins in higher centration included Nonane 2,2,3,3-Tetramethylpentane, 3-Methylnonane, decane, Undecane and tridecane. Among the naphthenic hydrocarbon, the abundant compounds were found to be 2,3,4-Trimethyl-2-pentene, dimethylcyclohexane, trimethyl cyclohexane and butylcyclohexane. Similarly, in the CTAB-dispersed crude, the major paraffinic compounds identified in the F2 fraction were 3-

Methylnonane, Decane, 2,5,5-Trimethylheptane, 2-Methylundecane, Tridecane, 2,3,7-Trimethyloctane, 3-Methyl-5-propylnonane, 2,6,10,14-Tetramethylhexadecane, 2-Methyl-5-propylnonane and 2,3,5-Trimethyldecane. Out of aromatics, 1-Methyl-2-propylbenzene and (3,3-Dimethylbutyl) benzene, whereas among naphthenes 1-Isopropyl-1-methylcyclohexane, 1-Methyl-3-propylcyclohexane and 1-Butyl-2-ethylcyclopentane were found to be present in higher concentration. In TX-100 treated sample, the major paraffins identified were; Octane, Isononane, 3-Methyloctane, 3-Methyloctane, Nonane, 2,2,3,3-Tetramethylpentane, 3-Methylnonane, Decane, 2,5,5-Trimethylheptane, Undecane, Tridecane and 2,6,10,14-Tetramethylheptadecane. Among aromatics, Sec-Butylbenzene and 1-Methyl-2-propylbenzene, whereas among naphthenes p-Dimethylcyclohexane and 1.2.4-Trimethylcyclohexane were present abundantly.

Table 3.19 presents the relative distribution of various hydrocarbon group types in the F1 and F2 fractions. The data indicated that, in F1 fractions all the dispersions led to an increase in the yield of paraffinic hydrocarbons, out of which the maximum increase was brought about by CTAB followed by SDS and then TX-100, from 63 to 81, 77 and 68 %, respectively. The concentration of the aromatics remained unchanged in the fractions derived from CTAB and TX-100 dispersed crude samples which reduced in fraction derived from the SDS-dispersed crude. The concentration of naphthenes has been found to be sufficiently reduced, whereas a small decrease occurred in the olefins and oxygenates. In case of F2 fractions, marginal increase in the concentration of paraffines occurred in fractions derived from the SDS and TX-100-dispersed samples, however the concentrations of olefins, aromatics, naphthenes and oxygenates were slightly decreased. On the other hand, in case of F2 fraction of CTAB treated crude, a small decrease in the concentration of paraffins can be observed from 96.4 in plain crude to 94.2 %, respectively.

alternately, CTAB has led to a marginal increase in the yields of olefins, aromatics, naphthenes and oxygenates.

The relative distribution of various carbon range hydrocarbons in F1 and F2 fractions of surfactants treated RCN-II samples is displayed in Table 3.20. In case of the F1 fraction, the yield of C<sub>5</sub>-C<sub>10</sub> range hydrocarbons decreased from 74.4 % in plain crude to 41.42 % in the SDS treated crude, 43.5 % in CTAB treated and 68.89 % in TX-100 treated samples. However, the yields of C<sub>11</sub>-C<sub>13</sub>, C<sub>14</sub>-C<sub>18</sub> and C<sub>19</sub>-C<sub>n</sub> range hydrocarbons were sufficiently increased with surfactants treatment. In case of SDS, CTAB and TX-100, the yield of C<sub>11</sub>-C<sub>13</sub> range hydrocarbons was increased from 16.92 % in plain crude to 33.12, 41.71 and 26.55 % respectively. The yield of C<sub>14</sub>-C<sub>18</sub> products was increased from 4.63 % in plain crude to 12.6 and 6.5 % in case of SDS and CTAB treated crudes respectively, however in case of TX-100 this yield was reduced to 1.42 %. Likewise, the yield of C<sub>19</sub>-C<sub>n</sub> range compounds was increased in case of SDS and CTAB from 4.07 to 12.87 and 7.73 %, respectively. It can be concluded from these results that the SDS and CTAB led to large decrease in C<sub>5</sub>-C<sub>10</sub> range compounds but alternately caused major increase in yields of higher range compounds. On the other hand, TX-100 caused a small increase in the yields of C<sub>11</sub>-C<sub>13</sub> range products but led to decrease in the yield of C<sub>5</sub>-C<sub>10</sub>, C<sub>14</sub>-C<sub>18</sub> and C<sub>19</sub>-C<sub>n</sub> range compounds in F1 fraction.

In case of F2 fraction, the SDS treatment caused increase in the yield of C<sub>14</sub>-C<sub>18</sub> range hydrocarbons from 36.78 to 43.96 %, but caused decrease in C<sub>11</sub>-C<sub>13</sub> and C<sub>19</sub>-C<sub>n</sub> range compounds from 40.68 to 37.39 % and 18.25 to 14.45 % respectively, whereas negligible change was observed in the yield of C<sub>5</sub>-C<sub>10</sub> range hydrocarbons. In case of CTAB treated fraction the yields of C<sub>5</sub>-C<sub>10</sub>, C<sub>11</sub>-C<sub>13</sub> and C<sub>14</sub>-C<sub>18</sub> range hydrocarbons was increased by 1-2 %, whereas the yield of C<sub>19</sub>-C<sub>n</sub> range products was decreased from the 18.25 to 14.15 %. In TX-100 treated F2 fraction, the yield of C<sub>14</sub>-



C<sub>18</sub> range hydrocarbons was sufficiently increased from 36.78 to 48.18 %, however the yield of the rest of carbon range products was decreased by 3 to 6 % from the plain crude. It can be concluded that TX-100 caused greater increase in the middle range compounds, and small decrease to the rest, but CTAB caused small increase in the yields of all carbon range products, except higher range i.e. C<sub>19</sub>-C<sub>n</sub> range products where yield was decreased. On the other hands SDS treatment led to increase in yield of C<sub>14</sub>-C<sub>18</sub> range compounds, but decrease to the rest of compounds, except light range product was not changed.

**Table 3.17.** Individual Compounds Determined in Light (F1) Distillate Fractions Derived From Distillation of Chemically Dispersed RCN-II Crude

S. #	Compound	SDS		CTAB		TX-100	
		t <sub>R</sub>	Conc. (%)	t <sub>R</sub>	Conc. (%)	t <sub>R</sub>	Conc. (%)
<b>Paraffins</b>							
1.	Heptane	3.163	0.14	3.177	0.12	3.165	0.2
2.	2,3- Dimethylhexane	4.668	0.01	4.522	0.01	4.71	0.02
3.	3-Methylheptane	5.144	0.06	5.176	0.02	4.883	0.01
4.	Octane	6.186	0.16	6.208	0.08	5.161	0.02
5.	2,4-Dimethylheptane	7.007	0.01	7.028	0.01	6.191	0.04
6.	Isononane	7.316	0.05	7.335	0.04	7.322	0.01
7.	3-Methyloctane	7.544	0.06	7.565	0.03	7.322	0.01
8.	5,6-Dimethyldecane	8.387	0.02	8.407	0.03	7.551	0.01
9.	4-Methyloctane	8.706	0.05	8.725	0.04	8.393	0.01
10.	2-Methyloctane	8.789	0.06	8.806	0.05	8.711	0.01
11.	3-Methyloctane	9.036	0.11	9.053	0.1	8.793	0.02
12.	Nonane	10.187	0.23	10.203	0.29	9.04	0.04
13.	2,2,3,3- Tetramethylpentane	11.092	0.03	11.105	0.04	10.193	0.08
14.	3-Methylnonane	11.472	0.15	11.487	0.25	11.096	0.01
15.	2-Methyl-3-ethylheptane	11.66	0.03	11.674	0.11	11.475	0.18
16.	2,3,6-Trimethylheptane	12.236	0.05	12.249	0.07	11.664	0.02
17.	4-Methylnonane	12.519	0.08	12.532	0.15	12.241	0.02
18.	2-Methylnonane	12.654	0.07	12.666	0.13	12.525	0.04
19.	Nonane, 3-methyl-	12.883	0.06	12.894	0.13	12.658	0.03
20.	3-Methylnonane	12.999	0.07	13.011	0.09	12.887	0.03
21.	Decane	13.952	0.36	13.964	0.91	12.006	0.03
22.	2,5,5-Trimethylheptane	14.709	0.12	14.719	0.39	13.958	0.19
23.	3-Methyldecane	15.147	0.04	15.16	0.1	14.712	0.08
24.	3,7-Dimethylnonane	15.268	0.03	15.279	0.09	15.152	0.02

25.	4-Methyldecane	16.017	0.04	16.027	0.14	15.271	0.02
26.	2,3,3-Trimethyloctane	16.169	0.07	16.178	0.26	16.021	0.03
27.	3-Methyldecane	16.367	0.05	16.376	0.21	16.172	0.05
28.	Undecane	17.35	0.45	17.362	1.74	16.371	0.04
29.	Dodecane	17.863	0.05	17.873	0.17	17.354	0.46
30.	3,7-Dimethyldecane	18.174	0.07	18.183	0.22	17.867	0.04
31.	2,3-Dimethyldecane	19.324	0.09	19.334	0.23	18.177	0.05
32.	Undecane, 2-methyl-	19.498	0.21	19.507	0.46	19.3326	0.07
33.	2-Methyl undecane	19.695	0.16	19.704	0.36	19.5	0.15
34.	Tridecane	20.571	2.31	20.576	1.93	19.697	0.11
35.	3,6-Dimethyundecane	20.892	1.47	20.896	2.05	20.567	1.68
36.	2,3,7-Trimethyloctane	22.248	2.14	22.25	2.56	20.89	1
37.	2,6,10,14-Tetramethylheptadecane	22.84	3.81	22.84	3.86	22.244	1.65
38.	11-Methyldodecane	23.142	1.01	23.146	1.46	22.832	4.7
39.	3-Methyl-5-propylnonane	24.176	2.26	24.174	2.22	23.142	0.72
40.	2-Methyl-5-propylnonane	24.649	7.52	24.641	7.64	24.17	1.91
41.	2,6,10,14-Tetramethylhexadecane	25.838	2.35	25.835	3.09	24.634	7.44
42.	2-Methyl-5-propylnonane	26.829	8.95	26.813	8.16	25.828	2.98
43.	2,3,5-Trimethyldecane	29.987	9.54	29.964	9.3	26.807	9.03
44.	Tetradecane	34.841	12.77	34.798	11.69	29.956	9.45
45.	4,6-Dimethyldodecane	34.979	4.26	34.798	11.99	34.792	12.04
46.	Pentadecane	40.112	9.03	40.071	5.23	34.936	2.6
47.	Pentadecane, 2,6,10,14-tetramethyl-	40.377	1.29	40.343	1.14	40.064	8.42
48.	Hexadecane	44.877	6.69	44.844	4.15	40.334	1.55
49.	Heptadecane	49.232	6.19	49.205	3.11	44.84	8.53
50.	Octadecane	53.249	5.02	53.233	2.38	49.198	7.22
51.	Nonadecane	57.005	2.09	56.992	1.69	53.22	6.12
52.	Eicosane	60.541	1.28	60.537	1.22	56.975	2.9

53.	Heneiconsane	63.904	1	63.907	0.78	60.525	1.93
54.	Docosane	67.114	1.06	67.116	0.53	63.882	1.07
55.	Tricosane	70.185	0.71	70.191	0.34	67.085	1.34
56.	Tetracosane	73.136	0.46	73.142	0.23	70.157	0.88
57.	Pentacosane	75.978	0.22	75.999	0.19	73.111	0.55
58.	Hexacosane	78.719	0.18	78.736	0.09	75.966	0.31
59.	Octacosane	81.374	0.11	81.393	0.05	78.704	0.17
60.	Triacontane	83.938	0.07	83.964	0.03	81.357	0.09
61.	Dotriacontane	86.433	0.04	86.446	0.01	83.933	0.04
62.	Tetratriacontane	88.837	0.02	88.872	0.01	86.413	0.02
<b>Total</b>			<b>97.09</b>		<b>94.2</b>		<b>98.49</b>
<b>Olefins</b>							
1.	2,3,4-Trimethyl-2-pentene	6.395	0.02	6.416	0.01	6.396	0.01
2.	11,Chloro-1-undecene	16.823	0.07	16.831	0.28	16.829	0.04
<b>Total</b>			<b>0.09</b>		<b>0.29</b>		<b>0.05</b>
<b>Aromatics</b>							
1.	Sec-Butylbenzene	12.812	0.18	12.824	0.24	12.817	0.06
2.	1-Methyl-2-propylbenzene	13.698	0.33	13.708	0.71	13.701	0.13
3.	1,4-Diethylbenzene	14.64	0.07	14.649	0.34	14.645	0.04
4.	Butane,2-phenyl-3-hydroxy-4-cyano	15.7	0.1	15.709	0.36	15.705	0.06
5.	(1,1-Dimethylpropyl)benzene	16.529	0.03	16.539	0.14	16.534	0.02
6.	(3,3-Dimethylbutyl)benzene	19.129	0.25	19.137	0.6	19.131	0.18
<b>Total</b>			0.96		2.39		0.49
<b>Naphthenes</b>							
1.	Cyclopentane, 1,2-dimethyl-	-	-	3.025	0.06	3.709	0.02
2.	Methylcyclohexane	3.163	0.04	3.724	0.02	4.122	0
3.	1,2,3-Trimethylcyclopentane	3.706	0.13		0		0
4.	1,2,4-Trimethylcyclopentane	4.12	0.01	4.142	0	5.409	0.01
5.	1,3-Dimethylcyclohexane	4.333	0.01	5.425	0.02	5.505	0

6.	p-Dimethylcyclohexane	5.402	0.07	5.524	0.01	5.409	0.01
7.	1,1-Dimethylcyclohexane	5.5	0.03	5.52	0.01	6.396	0.01
8.	1,2-Dimethylcyclohexane	5.69	0.01	6.416	0.01	7.658	0.01
9.	1,3,5-Trimethylcyclohexane	6.395	0.02	7.673	0.04	8.292	0.01
10.	Ethylcyclooctane	7.653	0.04	8.307	0.03	8.962	0.1
11.	1,3,5-Cycloheptatriene,7-ethyl-	8.288	0.03	8.971	0.21	9.671	0.02
12.	1.2.4-Trimethylcyclohexane	8.951	0.37	9.203	0.01	9.488	0.01
13.	1-Ethyl-4-methylcyclohexane	9.189	0.01	9.683	0.09	10.412	0.01
14.	1-Ethyl-2-methylcyclohexane	9.666	0.07	10.422	0.05	10.554	0.01
15.	1-Isopropyl-1-methylcyclohexane	10.406	0.03	10.565	0.02	11.313	0.03
16.	Propylcyclohexane	10.548	0.02	11.323	0.12	12.319	0.02
17.	1,1,2,3-Tetramethylcyclohexane	11.308	0.06	12.329	0.1	13.322	0.04
18.	1-Methyl-3-propylcyclohexane	12.315	0.03	13.331	0.18	15.046	0.03
19.	n-Butylcyclohexane	13.318	0.07	15.052	0.22	16.997	0.04
20.	1-Butyl-2-ethylcyclopentane	15.04	0.07	17.004	0.17	18.48	0.1
21.	Hexane,1-cyclohexyl-	16.994	0.06	18.888	0.38	20.19	0.17
22.	1-Methyl-2-pentylcyclohexane	18.478	0.14	20.196	0.33	-	-
<b>Total</b>			<b>1.32</b>		<b>2.08</b>		<b>0.65</b>
<b>Oxygenate</b>							
1.	Triasteranone	9.827	0.14	9.844	0.13	9.835	0.04
2.	3,3-Dimethyl-2-hexanone	10.783	0.28	9.844	0.41	10.789	0.19
3.	2-Butyloctanol	15.894	0.06	9.844	0.18	15.898	0.03
4.	(4,6,6-Trimethylbicyclo [3,1,1]hept-3-en-2-yl)acetaldehyde	17.971	0.08	9.844	0.32	17.974	0.06
<b>Total</b>			<b>0.56</b>		<b>1.04</b>		<b>0.32</b>

**Table 3.18.** Individual Compounds Determined in Middle (F2) Distillate Fractions Derived From Distillation of Chemically Dispersed RCN-II Crude

S. #	Compound	SDS		CTAB		TX-100	
		t <sub>R</sub>	Conc. (%)	t <sub>R</sub>	Conc. (%)	t <sub>R</sub>	Conc. (%)
<b>Paraffins</b>							
1.	Heptane	3.163	0.14	3.177	0.12	3.165	0.2
2.	2,3- Dimethylhexane	4.668	0.01	4.522	0.01	4.71	0.02
3.	3-Methylheptane	5.144	0.06	5.176	0.02	4.883	0.01
4.	Octane	6.186	0.16	6.208	0.08	5.161	0.02
5.	2,4-Dimethylheptane	7.007	0.01	7.028	0.01	6.191	0.04
6.	Isononane	7.316	0.05	7.335	0.04	7.322	0.01
7.	3-Methyloctane	7.544	0.06	7.565	0.03	7.322	0.01
8.	5,6-Dimethyldecane	8.387	0.02	8.407	0.03	7.551	0.01
9.	4-Methyloctane	8.706	0.05	8.725	0.04	8.393	0.01
10.	2-Methyloctane	8.789	0.06	8.806	0.05	8.711	0.01
11.	3-Methyloctane	9.036	0.11	9.053	0.1	8.793	0.02
12.	Nonane	10.187	0.23	10.203	0.29	9.04	0.04
13.	2,2,3,3- Tetramethylpentane	11.092	0.03	11.105	0.04	10.193	0.08
14.	3-Methylnonane	11.472	0.15	11.487	0.25	11.096	0.01
15.	2-Methyl-3-ethylheptane	11.66	0.03	11.674	0.11	11.475	0.18
16.	2,3,6-Trimethylheptane	12.236	0.05	12.249	0.07	11.664	0.02
17.	4-Methylnonane	12.519	0.08	12.532	0.15	12.241	0.02
18.	2-Methylnonane	12.654	0.07	12.666	0.13	12.525	0.04
19.	Nonane, 3-methyl-	12.883	0.06	12.894	0.13	12.658	0.03
20.	3-Methylnonane	12.999	0.07	13.011	0.09	12.887	0.03
21.	Decane	13.952	0.36	13.964	0.91	12.006	0.03
22.	2,5,5-Trimethylheptane	14.709	0.12	14.719	0.39	13.958	0.19
23.	3-Methyldecane	15.147	0.04	15.16	0.1	14.712	0.08

24.	3,7-Dimethylnonane	15.268	0.03	15.279	0.09	15.152	0.02
25.	4-Methyldecane	16.017	0.04	16.027	0.14	15.271	0.02
26.	2,3,3-Trimethyloctane	16.169	0.07	16.178	0.26	16.021	0.03
27.	3-Methyldecane	16.367	0.05	16.376	0.21	16.172	0.05
28.	Undecane	17.35	0.45	17.362	1.74	16.371	0.04
29.	Dodecane	17.863	0.05	17.873	0.17	17.354	0.46
30.	3,7-Dimethyldecane	18.174	0.07	18.183	0.22	17.867	0.04
31.	2,3-Dimethyldecane	19.324	0.09	19.334	0.23	18.177	0.05
32.	Undecane, 2-methyl-	19.498	0.21	19.507	0.46	19.332 6	0.07
33.	2-Methyl undecane	19.695	0.16	19.704	0.36	19.5	0.15
34.	Tridecane	20.571	2.31	20.576	1.93	19.697	0.11
35.	3,6-Dimethyundecane	20.892	1.47	20.896	2.05	20.567	1.68
36.	2,3,7-Trimethyloctane	22.248	2.14	22.25	2.56	20.89	1
37.	2,6,10,14-Tetramethylheptadecane	22.84	3.81	22.84	3.86	22.244	1.65
38.	11-Methyldodecane	23.142	1.01	23.146	1.46	22.832	4.7
39.	3-Methyl-5-propylnonane	24.176	2.26	24.174	2.22	23.142	0.72
40.	2-Methyl-5-propylnonane	24.649	7.52	24.641	7.64	24.17	1.91
41.	2,6,10,14-Tetramethylhexadecane	25.838	2.35	25.835	3.09	24.634	7.44
42.	2-Methyl-5-propylnonane	26.829	8.95	26.813	8.16	25.828	2.98
43.	2,3,5-Trimethyldecane	29.987	9.54	29.964	9.3	26.807	9.03
44.	Tetradecane	34.841	12.77	34.798	11.69	29.956	9.45
45.	4,6-Dimethyldodecane	34.979	4.26	34.798	11.99	34.792	12.04
46.	Pentadecane	40.112	9.03	40.071	5.23	34.936	2.6
47.	Pentadecane, 2,6,10,14-tetramethyl	40.377	1.29	40.343	1.14	40.064	8.42
48.	Hexadecane	44.877	6.69	44.844	4.15	40.334	1.55
49.	Heptadecane	49.232	6.19	49.205	3.11	44.84	8.53
50.	Octadecane	53.249	5.02	53.233	2.38	49.198	7.22
51.	Nonadecane	57.005	2.09	56.992	1.69	53.22	6.12

52.	Eicosane	60.541	1.28	60.537	1.22	56.975	2.9
53.	Heneiconsane	63.904	1	63.907	0.78	60.525	1.93
54.	Docosane	67.114	1.06	67.116	0.53	63.882	1.07
55.	Tricosane	70.185	0.71	70.191	0.34	67.085	1.34
56.	Tetracosane	73.136	0.46	73.142	0.23	70.157	0.88
57.	Pentacosane	75.978	0.22	75.999	0.19	73.111	0.55
58.	Hexacosane	78.719	0.18	78.736	0.09	75.966	0.31
59.	Octacosane	81.374	0.11	81.393	0.05	78.704	0.17
60.	Triacontane	83.938	0.07	83.964	0.03	81.357	0.09
61.	Dotriacontane	86.433	0.04	86.446	0.01	83.933	0.04
62.	Tetratriacontane	88.837	0.02	88.872	0.01	86.413	0.02
<b>Total</b>			<b>97.09</b>		<b>94.2</b>		<b>98.49</b>
<b>Olefins</b>							
1.	2,3,4-Trimethyl-2-pentene	6.395	0.02	6.416	0.01	6.396	0.01
2.	11,Chloro-1-undecene	16.823	0.07	16.831	0.28	16.829	0.04
<b>Total</b>			<b>0.09</b>		<b>0.29</b>		<b>0.05</b>
<b>Aromatics</b>							
1.	Sec-Butylbenzene	12.812	0.18	12.824	0.24	12.817	0.06
2.	1-Methyl-2-propylbenzene	13.698	0.33	13.708	0.71	13.701	0.13
3.	1,4-Diethylbenzene	14.64	0.07	14.649	0.34	14.645	0.04
4.	Butane,2-phenyl-3-hydroxy-4-cyano	15.7	0.1	15.709	0.36	15.705	0.06
5.	(1,1-Dimethylpropyl)benzene	16.529	0.03	16.539	0.14	16.534	0.02
6.	(3,3-Dimethylbutyl)benzene	19.129	0.25	19.137	0.6	19.131	0.18
<b>Total</b>			0.96		2.39		0.49
<b>Naphthenes</b>							
1.	Cyclopentane, 1,2-dimethyl-			3.025	0.06	3.709	0.02
2.	Methylcyclohexane	3.163	0.04	3.724	0.02	4.122	0
3.	1,2,3-Trimethylcyclopentane	3.706	0.13		0		0
4.	1,2,4-Trimethylcyclopentane	4.12	0.01	4.142	0	5.409	0.01



5.	1,3-Dimethylcyclohexane	4.333	0.01	5.425	0.02	5.505	0
6.	p-Dimethylcyclohexane	5.402	0.07	5.524	0.01	5.409	0.01
7.	1,1-Dimethylcyclohexane	5.5	0.03	5.52	0.01	6.396	0.01
8.	1,2-Dimethylcyclohexane	5.69	0.01	6.416	0.01	7.658	0.01
9.	1,3,5-Trimethylcyclohexane	6.395	0.02	7.673	0.04	8.292	0.01
10.	Ethylcyclooctane	7.653	0.04	8.307	0.03	8.962	0.1
11.	1,3,5-Cycloheptatriene,7-ethyl-	8.288	0.03	8.971	0.21	9.671	0.02
12.	1,2,4-Trimethylcyclohexane	8.951	0.37	9.203	0.01	9.488	0.01
13.	1-Ethyl-4-methylcyclohexane	9.189	0.01	9.683	0.09	10.412	0.01
14.	1-Ethyl-2-methylcyclohexane	9.666	0.07	10.422	0.05	10.554	0.01
15.	1-Isopropyl-1-methylcyclohexane	10.406	0.03	10.565	0.02	11.313	0.03
16.	Propylcyclohexane	10.548	0.02	11.323	0.12	12.319	0.02
17.	1,1,2,3-Tetramethylcyclohexane	11.308	0.06	12.329	0.1	13.322	0.04
18.	1-Methyl-3-propylcyclohexane	12.315	0.03	13.331	0.18	15.046	0.03
19.	n-Butylcyclohexane	13.318	0.07	15.052	0.22	16.997	0.04
20.	1-Butyl-2-ethylcyclopentane	15.04	0.07	17.004	0.17	18.48	0.1
21.	Hexane,1-cyclohexyl-	16.994	0.06	18.888	0.38	20.19	0.17
22.	1-Methyl-2-pentylcyclohexane	18.478	0.14	20.196	0.33	0	0
<b>Total</b>			<b>1.32</b>		<b>2.08</b>		<b>0.65</b>
<b>Oxygenate</b>							
1.	Triasteranone	9.827	0.14	9.844	0.13	9.835	0.04
2.	3,3-Dimethyl-2-hexanone	10.783	0.28	9.844	0.41	10.789	0.19
3.	2-Butyloctanol	15.894	0.06	9.844	0.18	15.898	0.03
4.	4,6,6-Trimethylbicyclo[3,1,1]hept-3-en-2-yl)acetaldehyde	17.971	0.08	9.844	0.32	17.974	0.06
<b>Total</b>			<b>0.56</b>		<b>1.04</b>		<b>0.32</b>

**Table 3.19.** Distribution of Various Hydrocarbon Group Types in Light and Middle Fractions Derived From Distillation of Chemically Dispersed RCN-II Crude

Hydrocarbon group	Plain RCP-I		SDS treated		CTAB treated		TX-100 treated	
	F1	F2	F1	F2	F1	F2	F1	F2
<b>Paraffins</b>	63.62	96.4	77.56	97.07	81.07	94.2	68.52	98.49
<b>Olefins</b>	1.01	0.14	0.94	0.09	0.71	0.29	0.91	0.05
<b>Aromatics</b>	7.07	1.22	4.77	0.96	7.25	2.39	7.69	0.49
<b>Naphthenes</b>	25.51	1.55	14.65	1.32	9.57	2.08	20.56	0.65
<b>Oxygenates</b>	2.81	0.72	2.08	0.56	1.47	1.04	2.37	0.32

**Table 3.20.** Distribution of Various Carbon Range Compounds in Light and Middle Fractions Derived From Distillation of Chemically Dispersed RCN-II Crude

.Sample	Concentration (wt%)							
	C5-C10		C11-C13		C14-C18		C19-C <sub>n</sub>	
	F1	F2	F1	F2	F1	F2	F1	F2
<b>Plain RCN-II</b>	74.4	4.29	16.92	40.68	4.63	36.78	4.07	18.25
<b>SDS treated RCN-II</b>	41.42	4.2	33.12	37.39	12.6	43.96	12.87	14.45
<b>CTAB treated RCN-II</b>	43.5	6.45	41.71	42	6.5	37.4	7.73	14.15
<b>TX-100 treated RCN-II</b>	68.89	1.64	26.55	34.57	1.42	48.18	3.13	15.61

**RCA-III Fractions:** The individual compounds, identified in F1 and F2 fractions derived from chemically dispersed RCA-III fractions were identified. The results are assembled in Table 3.21 and Table 3.22 which indicated that the majority of the individual compounds were similar to that of F1 and F2 fractions derived from plain crude. However, like other crudes, their relative concentrations were changed upon dispersion with the surfactants under study. Overall, the total concentration of the paraffinic compounds in the F1 fractions increased. In F1 fraction derived from distillation of SDS-dispersed the paraffinic compounds with increased concentrations included Isononane, 3-Methyloctane, 3-Methylnonane, 4-Methylnonane, Decane, 2,5,5-Trimethylheptane, Undecane, 2-Methylundecane, Tridecane, 3,6-Dimethylundecane, 2,3,7-Trimethyloctane, and 11-Methyldodecane. The SDS-dispersion also led to increase in concentration of some naphthenes, which included 1,3,5-Trimethylcyclohexane and 1-Ethyl-4-methylcyclohexane. In case of CTAB-dispersed crude sample, the paraffinic hydrocarbons with increased concentration included; 4-Methylnonane, Decane, 3,7-Dimethylnonane, 4-Methyldecane, Undecane, 2-methyl, 2,6,10,14-Tetramethylheptadecane, 11-Methyldodecane, 3-Methyl-5-propylnonane, 2-Methyl-5-propylnonane, 2-Methyl-5-propylnonane, Tetradecane, 4,6-Dimethyldodecane, 2-Methyl-5-propylnonane, Tetradecane, and 4,6-Dimethyldodecane. The concentration of some aromatic compounds i.e. 1-Methyl-2-propylbenzene, Butane,2-phenyl-3-hydroxy-4-cyano, (3,3-Dimethylbutyl)benzene was also increased. Similarly, in case of fractions derived from TX-100-dispersed sample, the concentration of paraffinic compounds including 3-Methyloctane, 3-Methyloctane, Nonane, 3-Methylnonane, 4-Methylnonane, Decane, 2,5,5-Trimethylheptane, Undecane, Tridecane and 2,6,10,14-Tetramethylheptadecane enhanced. Among aromatics, the abundant compounds included, Sec-Butylbenzene, and 1-Methyl-2-propylbenzene.

In case of F2 fraction, the overall concentrations of aromatics and naphthenes were slightly increased but those of paraffinic compounds significantly increased. However, some common paraffinic compounds found to be present in high concentrations compared to the F2 fraction of plain RCA-III crude which included Tridecane, 2,6,10,14-Tetramethylheptadecane, 11-Methyldodecane, 2-Methyl-5-propylnonane, 2,6,10,14-Tetramethylhexadecane, 2-Methyl-5-propylnonane, 2,3,5-Trimethyldecane, Tetradecane and 4,6-Dimethyldodecane.

The hydrocarbon group types distribution of various hydrocarbon groups types in the F1 and F2 fractions is shown in Table 3.23. The data showed that in F1 fractions, the yields of paraffins increased by the SDS, CTAB and TX-100 dispersion from 65.97 % in plain RCA-III to 73.91, 82.46 and 72.96 % respectively. The yield of olefins was also marginally increased in some cases i.e. TX-100 dispersion (from 0.72 % to 1.32 %) and SDS dispersion (0.79 %), and decreased in CTAB dispersion (to 0.08 %). The concentration of aromatics decreased in case of SDS and CTAB dispersed samples from 7.59 % in plain crude to 4.72 and 6.7 %, respectively, however, increased to 8.16 % in TX-100 dispersed sample. The naphthenes increased in SDS and TX-100 dispersed samples from 14.7 % in plain to 19.3 and 15.39 %, respectively, but decreased in CTAB dispersed sample to 9.35 %. The concentration of oxygenated hydrocarbons decreased in case of all surfactants from 12.08 to 1.28, 1.41 and 2.17 % respectively. It can be concluded that SDS led to an increase in the paraffins and naphthenes, and a decrease in olefins, aromatics and oxygenates. The CTAB caused a considerable increase in paraffins but decreased the rest of the products. On the other hand, the TX-100 caused an increase in all hydrocarbon groups, except oxygenates.

In case of F2 fractions, the yield of paraffins was considerably reduced in case of SDS-dispersed sample from 97.18 % in plain to 84.01 %, whereas slightly decreased in case of CTAB and TX-100-dispersed samples to 96.31 and 95.75 %, respectively. The olefins were less affected. An

increase in the yield of naphthenes can be observed in case of all the surfactant dispersed samples, that is from 1.84 % in plain crude to 3.95 % in SDS, 1.87 % in CTAB and 2.01 in TX-100-dispersed samples. Similarly, the oxygenates increased to 7.42 and 1.1 % from 0.87 % in plain crude with SDS and TX-100 dispersion. It can be suggested that SDS caused a slight decrease in paraffins but increased the rest of hydrocarbon group types marginally. The CTAB and TX-100 caused negligible changes in paraffins, but resulted in a decrease in olefins and aromatics, whereas the yield of naphthenes and oxygenates also enhanced marginally.

The distribution of different carbon range products is given in the Table 3.24. The data showed that in case of F1 fraction, the concentrations of C<sub>5</sub>-C<sub>10</sub> range hydrocarbons decreased from 61.52 % in plain to 60 % in TX-100-, 56.69 % in SDS- and 39.03 % in CTAB- dispersed samples. Similarly, the concentration of C<sub>14</sub>-C<sub>18</sub> range products decreased from 37.75 % to 35.19, 33.9 and 32.29 %, respectively. The yields of C<sub>19</sub>-C<sub>n</sub> range products also found to be decreased with CTAB, SDS and TX-100 from 11.67 to 8.94, 6.54 and 6.24 % respectively. However, the yields of C<sub>11</sub>-C<sub>13</sub> components increased with all surfactants. The maximum increment from 18.69 % to 47.46 % can be observed in case of CTAB, followed by 32.39 % in SDS and 26.23 % in TX-100 dispersions.

In F2 fractions, the yields of C<sub>5</sub>-C<sub>10</sub> and C<sub>14</sub>-C<sub>18</sub> range hydrocarbons increased whereas that of C<sub>11</sub>-C<sub>13</sub> and C<sub>19</sub>-C<sub>n</sub> range hydrocarbons decreased. The yield of C<sub>5</sub>-C<sub>10</sub> range products increased from 5 % to 21.1 % in SDS-, 6.09 % in TX-100- and 5.08 % in CTAB-dispersed samples. Similarly, the yields C<sub>14</sub>-C<sub>18</sub> range hydrocarbons increased from 27.36 % to 37.38 in TX-100-, 36.08 % in CTAB- and 29.22 % in SDS-dispersed samples. On the other hand, the yield of C<sub>11</sub>-C<sub>13</sub> and C<sub>19</sub>-C<sub>n</sub> range hydrocarbons reduced from 37.75 and 29.89 % in F2 fractions of plain crude to 33.9 and 15.78 % in SDS-, 32.29 and 6.24 % TX-100- and 35.19 and 8.94 % in CTAB-dispersed

samples. It can be concluded from the results that CTAB treatment led to substantial increase in middle range hydrocarbons in F1 and F2 fractions, whereas SDS led to an increase in yield of smaller carbon range products in F2 fraction as well as in middle range products in F1 fractions.

**Table 3.21.** Individual Compounds Determined in Light (F1) Distillate Fractions Derived From Distillation of Chemically Dispersed RCA-III Crude

S. #	Compound	SDS		CTAB		TX-100	
		tr	Conc. (%)	tr	Conc. (%)	tr	Conc. (%)
<b>Paraffins</b>							
5.	Heptane	3.136	0.06	3.177	0.01	3.152	0.07
6.	2,3-Dimethylhexane	4.632	0.51	4.692	0.03	4.655	0.21
7.	3-Methylheptane	5.108	1.13	5.02	0.01	5.133	1.04
8.	Octane	6.152	0.74	5.17	0.1	6.182	1.7
9.	2,4-Dimethylheptane	6.976	0.59	6.21	0.17	7.002	0.44
10.	Isononane	7.292	2.76	7.032	0.15	7.318	1.96
11.	3-Methyloctane	7.521	1.91	7.341	0.85	7.549	2.09
12.	5,6-Dimethyldecane	8.366	0.88	7.571	0.62	8.392	0.79
13.	4-Methyloctane	8.688	1.38	7.681	0.56	8.715	1.63
14.	2-Methyloctane	8.77	1.22	8.316	0.3	8.8	1.64
15.	3-Methyloctane	9.021	2.95	8.415	0.38	9.051	3.19
16.	Nonane	10.178	1.77	8.735	0.98	10.214	3.78
17.	2,2,3,3-Tetramethylpentane	11.084	0.88	8.816	0.65	11.109	0.91
18.	3-Methylnonane	11.476	4.34	9.066	1.57	11.5	3.1
19.	2-Methyl-3-ethylheptane	11.66	1.99	10.219	1.42	11.682	1.23
20.	2,3,6-Trimethylheptane	12.233	0.91	11.123	0.71	12.256	0.88
21.	4-Methylnonane	12.522	2.56	11.512	3.63	12.547	2.08
22.	2-Methylnonane	12.655	1.23	11.695	1.56	12.684	1.44
23.	Nonane,3-methyl-	12.884	0.31	12.269	0.87	12.909	1.41
24.	Decane	13.963	3.31	12.556	2.43	13.996	4.6

25.	2,5,5-Trimethylheptane	14.725	4.05	12.69	1.23	14.746	2.58
26.	3-Methyldecane	15.156	0.64	12.917	1.35	15.177	0.62
27.	3,7-Dimethylnonane	15.277	0.8	13.994	3.63	15.298	0.55
28.	4-Methyldecane	16.026	0.79	14.757	4.59	16.047	0.62
29.	2,3,3-Trimethyloctane	16.178	1	15.186	0.82	16.2	0.94
30.	3-Methyldecane	16.376	0.83	15.306	0.97	16.398	0.71
31.	Undecane	17.37	4.1	16.055	0.96	17.398	4.47
32.	Dodecane	17.876	0.67	16.207	1.3	18.003	0.06
33.	3,7-Dimethyldecane	18.188	1.01	16.405	1.07	18.208	0.55
34.	2,3-Dimethyldecane	19.511	0.79	16.858	0.62	19.358	0.36
35.	Undecane,2-methyl-	19.707	0.58	17.401	5.65	19.532	0.64
36.	2-Methylundecane	20.585	4.29	17.903	0.93	19.726	0.45
37.	Tridecane	20.902	2.86	18.217	1.39	20.604	3.56
38.	3,6-Dimethylundecane	22.254	2.03	19.54	1.16	20.918	1.89
39.	2,3,7-Trimethyloctane	22.842	3.27	19.734	0.84	22.269	1.39
40.	2,6,10,14-Tetramethylheptadecane	24.179	1.05	20.611	6.13	22.857	2.55
41.	11-Methyldodecane	24.642	2.61	20.926	4.24	24.192	0.64
42.	3-Methyl-5-propylnonane	25.837	0.86	22.275	3.23	24.657	1.95
43.	2-Methyl-5-propylnonane	26.813	1.76	22.865	5.08	25.856	0.56
44.	2,6,10,14-Tetramethylhexadecane	29.957	1.16	24.197	1.73	26.834	1.37
45.	2-Methyl-5-propylnonane	34.79	1.09	24.665	4.3	29.995	1.14
46.	2,3,5-Trimethyldecane	34.942	0.28	25.863	1.4	34.843	1.88
47.	Tetradecane	40.072	0.84	26.841	2.95	34.843	1.97
48.	4,6-Dimethyldodecane	40.358	0.23	29.998	2.29	40.117	1.08
49.	Pentadecane	44.852	0.78	34.841	1.52	40.407	0.19
50.	Pentadecane,2,6,10,14-tetramethyl-	49.212	0.74	34.983	0.39	44.894	1.02
51.	Hexadecane	53.236	0.65	40.115	0.82	49.259	0.93
52.	Heptadecane	57	0.57	40.4	0.2	53.281	0.85

53.	Octadecane	60.556	0.43	44.89	0.65	57.054	0.7
54.	Nonadecane	63.922	0.35	49.25	0.62	60.594	0.59
55.	Eicosane	67.133	0.24	53.28	0.57	63.964	0.46
56.	Henicosane	70.207	0.18	57.05	0.52	67.18	0.47
57.	Docosane	73.17	0.12	60.594	0.41	70.254	0.28
58.	Tricosane	76.011	0.09	63.957	0.36	73.214	0.22
59.	Tetracosane	78.76	0.06	67.167	0.26	76.061	0.16
60.	Pentacosane	81.414	0.05	70.246	0.21	78.813	0.12
61.	Hexacosane	83.977	0.03	73.202	0.14	81.46	0.08
62.	Octacosane	86.467	0.02	76.048	0.12	84.033	0.05
63.	Triacontane	88.877	0.01	78.797	0.7	86.521	0.03
64.	Dotriacontane	89.136	0.06	81.447	0.07	88.939	0.02
65.	Tetratriacontane	89.632	0.51	84.016	0.04	89.152	0.07
<b>Total</b>			73.91		82.46		72.96
<b>Olefins</b>							
1.	2,3,4-Trimethyl-2-pentene	6.363	0.79	6.42	0.08	6.39	0.53
2.	11,Chloro-1-undecene	---	0	----	0	16.852	0.79
<b>Total</b>			<b>0.79</b>		<b>0.08</b>		<b>1.32</b>
<b>Aromatics</b>							
1.	Sec-Butylbenzene	12.813	0.78	12.849	0.84	12.843	1.98
2.	1-Methyl-2-propylbenzene	13.699	1.4	13.731	1.61	13.728	2.97
3.	1,4-Diethylbenzene	---	0	14.675	0.61	14.668	0.75
4.	Butane,2-phenyl-3-hydroxy-4-cyano	15.705	0.38	15.733	1.22	15.728	1.12
5.	(1,1-Dimethylpropyl)benzene	16.538	1.38	16.565	0.48	16.559	0.35
6.	(3,3-Dimethylbutyl)benzene	19.143	0.78	19.172	1.94	19.164	0.99
<b>Total</b>			<b>4.72</b>		<b>6.7</b>		<b>8.16</b>
<b>Naphthenes</b>							
1.	Methylcyclohexane	3.676	1.08	3.026	0.01	3.152	0.02
2.	1,2,3-Trimethylcyclopentane	4.088	0.36	3.724	0.05	3.694	0.37



3.	1,2,4-Trimethylcyclopentane	4.3	0.25	4.143	0.01	4.108	0.12
4.	1,3-Dimethylcyclohexane	5.462	0.35	4.356	0.01	4.321	0.08
5.	p-Dimethylcyclohexane	5.463	0.38	5.427	0.13	5.393	1.14
6.	1,1-Dimethylcyclohexane	5.655	0.58	5.525	0.03	5.49	0.35
7.	1,2-Dimethylcyclohexane	6.104	0.95	5.714	0.04	5.68	0.3
8.	1,3,5-Trimethylcyclohexane	7.633	2.27	6.42	0.08	6.39	0.53
9.	Ethylcyclooctane	8.267	0.89	8.979	0.35	7.659	1.34
10.	1,3,5-Cycloheptatriene,7-ethyl-	8.933	0.51	9.222	0.19	8.293	0.69
11.	1,2,4-Trimethylcyclohexane	9.177	0.49	9.697	1.13	8.961	1.96
12.	1-Ethyl-4-methylcyclohexane	9.654	2.12	10.439	0.7	9.203	0.36
13.	1-Ethyl-2-methylcyclohexane	10.398	1.27	10.582	0.38	9.681	1.68
14.	1-Isopropyl-1-methylcyclohexane	10.54	0.67	11.343	0.83	10.425	0.9
15.	Propylcyclohexane	11.305	1.14	12.35	0.64	10.566	0.48
16.	1,1,2,3-Tetramethylcyclohexane	12.315	0.76	13.356	1.76	11.33	1.25
17.	1-Methyl-3-propylcyclohexane	13.322	1.83	15.082	0.9	12.339	0.61
18.	n-Butylcyclohexane	15.051	0.8	18.523	1	13.346	1.38
19.	1-Butyl-2-ethylcyclopentane	17.006	0.74	20.226	1.05	15.074	0.81
20.	Hexane,1-cyclohexyl-	18.492	0.78		0.01	17.026	0.44
21.	1-Methyl-2-pentylcyclohexane		1.08	3.026	0.05	18.514	0.58
<b>Total</b>			<b>19.3</b>		<b>9.35</b>		<b>15.39</b>
<b>Oxygenate</b>							
1.	Triasteranone	----	0	---	0	9.838	1.03
2.	3,3-Dimethyl-2-hexanone	10.792	0.38	10.832	0.28	10.817	0.35
3.	2-Butyloctanol	15.902	0.9	15.932	1.13	15.924	0.79
<b>Total</b>			<b>1.28</b>		<b>1.41</b>		<b>2.17</b>

**Table 3.22.** Individual Compounds Determined in Middle (F2) Distillate Fractions Derived From Distillation of Chemically Dispersed RCA-III Crude

S. #	Compound	SDS		CTAB		TX-100	
		t <sub>R</sub>	Conc. (%)	t <sub>R</sub>	Conc. (%)	t <sub>R</sub>	Conc. (%)
<b>Paraffins</b>							
1.	Heptane	3.138	1.49	3.169	0.45	3.167	0.07
2.	2,3- Dimethylhexane	-	-	4.624	0.06	4.62	0.21
3.	3-Methylheptane	5.10	7.269	5.159	0.08	5.154	1.04
4.	Octane	6.139	0.48	6.197	0.26	6.191	1.7
5.	2,4-Dimethylheptane	-	-	7.325	0.07	7.016	0.44
6.	Isononane	7.279	0.16	7.325	0.07	7.319	1.96
7.	5,6-Dimethyldecane	-	-	8.396	0.03	8.397	2.09
8.	4-Methyloctane	-	-	8.714	0.06	8.707	0.79
9.	2-Methyloctane	-	-	8.796	0.06	8.789	1.63
10.	3-Methyloctane	8.99	0.41	9.043	0.2	9.037	1.64
11.	Nonane	10.143	0.62	10.195	0.19	10.186	3.19
12.	2,2,3,3- Tetramethylpentane	-	-	11.094	0.01	11.086	3.78
13.	3-Methylnonane	-	-	11.473	0.25	11.466	0.91
14.	2-Methyl-3-ethylheptane	-	-	11.66	0.05	11.656	3.1
15.	2,3,6-Trimethylheptane	12.474	0.41	12.207	0.07	12.198	1.23
16.	4-Methylnonane	12.475	0.41	12.519	0.08	12.511	0.88
17.	2-Methylnonane	12.611	0.38	12.652	0.04	12.647	2.08
18.	Nonane, 3-methyl-	-	-	12.881	0.04	12.874	1.44
19.	3-Methylnonane	12.611	0.38	12.999	0.13	12.991	1.41
20.	Decane	13.91	1.21	13.951	0.22	13.942	4.6
21.	2,5,5-Trimethylheptane	14.667	0.89	14.706	0.12	14.7	2.58
22.	3-Methyldecane	15.973	0.36	15.147	0.01	15.26	0.62
23.	3,7-Dimethylnonane	-	-	15.266	0.04	15.26	0.55
24.	4-Methyldecane	-	-	16.012	0.04	16.007	0.62

25.	2,3,3-Trimethyloctane	16.126	0.22	16.163	0.06	16.157	0.94
26.	3-Methyldecane	16.128	0.22	16.363	0.03	16.355	0.71
27.	Undecane	17.307	2.55	17.347	0.47	17.339	4.47
28.	Dodecane	17.822	0.14	17.86	0.06	17.853	0.06
29.	3,7-Dimethyldecane	18.128	0.44	18.168	0.11	18.161	0.55
30.	2,3-Dimethyldecane	19.449	0.46	19.493	0.15	19.114	0.36
31.	Undecane, 2-methyl-	19.648	0.39	19.493	0.15	19.683	0.64
32.	2-Methyl undecane	19.648	0.39	19.69	0.12	20.554	0.45
33.	Tridecane	20.523	4.28	20.56	1.54	20.878	3.56
34.	3,6-Dimethyundecane	20.848	2.73	20.883	1.19	22.233	1.89
35.	2,3,7-Trimethyloctane	22.205	2.45	22.238	1.49	22.82	1.39
36.	2,6,10,14-Tetramethylheptadecane	22.792	5.39	22.825	3.97	22.833	2.55
37.	11-Methyldodecane	-	-	22.839	3.22	24.159	2.64
38.	3-Methyl-5-propylnonane	24.131	2.3	24.163	2.02	24.618	1.95
39.	2-Methyl-5-propylnonane	24.586	5.74	24.622	6.28	25.812	4.56
40.	2,6,10,14-Tetramethylhexadecane	25.865	0.81	25.817	2.85	26.781	2.37
41.	2-Methyl-5-propylnonane	26.732	4.65	26.786	7.27	29.915	5.14
42.	2,3,5-Trimethyldecane	29.835	4.29	29.922	9.79	34.889	5.88
43.	Tetradecane	34.611	6.97	34.736	8.42	35.067	4.97
44.	4,6-Dimethyldodecane	34.783	4.87	34.847	4.31	40.019	3.08
45.	Pentadecane	40.127	3.42	40.025	7.15	40.306	3.09
46.	Pentadecane, 2,6,10,14-tetramethyl-	40.127	2.15	40.313	1.79	44.796	1.02
47.	Hexadecane	44.694	4.94	44.808	6.04	49.162	0.93
48.	Heptadecane	49.068	4.26	49.172	5.41	53.187	0.85
49.	Octadecane	53.096	4.78	53.197	4.75	56.95	0.7
50.	Nonadecane	56.866	2.35	56.952	4.01	60.502	0.59
51.	Eicosane	60.418	1.85	60.5	3.14	63.862	0.46
52.	Heneiconsane	63.777	3.32	63.868	2.44	67.073	0.36

53.	Docosane	66.977	1.19	67.078	1.71	70.146	0.28
54.	Tricosane	70.049	0.72	70.147	1.27	73.096	0.22
55.	Tetracosane	-	-	73.096	0.88	75.939	0.16
56.	Pentacosane	-	-	75.951	0.61	78.689	0.12
57.	Hexacosane	-	-	78.692	0.4	81.346	0.08
58.	Octacosane	-	-	81.344	0.28	83.92	0.05
59.	Triacontane	-	-	83.905	0.15	86.394	0.03
60.	Dotriacontane	89.632	0.51	86.398	0.09	88.815	0.02
61.	Tetra triacontane			88.804	0.06	89.167	0.07
<b>Total</b>			<b>84.01</b>		<b>96.31</b>		<b>95.75</b>
<b>Olefins</b>							
1.	2,3,4-Trimethyl-2-pentene	-	-	6.403	0.05	6.399	0.05
2.	11-chloro-1-undecene	16.77	0.45	16.822	0.1	-	-
			<b>0.45</b>		<b>0.15</b>		<b>0.05</b>
<b>Aromatics</b>							
1.	Sec- Butyl benzene	12.766	0.45	12.814	0.07	12.804	0.11
2.	1-Methyl-2-propylbenzene	13.652	1.52	13.7	0.3	13.689	0.48
3.	1,4-Diethylbenzene	14.596	0.49	15.701	0.11	14.628	0.12
4.	Butane,2-phenyl-3-hydroxyl-4-cyano-	15.653	0.87	16.527	0.05	15.691	0.14
5.	(1,1-Dimethylpropyl)benzene	16.484	0.23	19.124	0.26	16.517	0.07
6.	(3,3-Dimethylbutyl)benzene	19.077	0.61	19.424	0.07	19.114	0.24
			<b>4.17</b>		<b>0.86</b>		<b>1.16</b>
<b>Naphthenes</b>							
1.	Cyclopentane, 1,2-dimethyl-	-	-	3.169	0.13	3.711	0.17
2.	Methylcyclohexane	3.676	0.84	3.714	0.15	4.344	0.03
3.	1,2,3-Trimethylcyclopentane	-	-	4.345	0.01	5.409	0.09
4.	1,3-Dimethylcyclohexane	5.356	0.3	5.412	0.08	5.505	0.03
5.	p-Dimethylcyclohexane	5.356	0.34	5.509	0.03	5.409	0.09
6.	1,2- Dimethylcyclohexane	-	-	5.7	0.06	6.399	0.05

7.	1,3,5-Trimethylcyclohexane	8.905	0.72	7.66	0.03	7.657	0.05
8.	Ethylcyclooctane	-	-	8.294	0.02	8.294	0.03
9.	1,3,5-Cycloheptatriene, 7-ethyl-	-	-	8.963	0.28	8.953	0.43
10.	1-Ethyl-4-methylcyclohexane	9.619	0.36	9.671	0.1	9.664	0.15
11.	1-Ethyl-2-methylcyclohexane	-	-	10.412	0.04	10.408	0.06
12.	1-Isopropyl-1-methylcyclohexane	-	-	10.415	0.05	10.409	0.08
13.	Propylcyclohexane	11.315	0.25	11.309	0.07	11.302	0.1
14.	1,1,2,3-Tetramethylcyclohexane	-	-	12.325	0.01	13.309	0.12
15.	1-Methyl-3-propylcyclohexane	13.051	0.42	13.315	0.1	15.032	0.06
16.	n-Butylcyclohexane	14.006	0.35	15.038	0.05	16.984	0.1
17.	1-Butyl-2-ethylcyclopentane	16.492	0.37	16.988	0.1	18.466	0.17
18.	Hexane,1-cyclohexyl-1-Methyl-2-pentylcyclohexane	-	-	18.472	0.18	19.711	0.17
19.	1-Methyl-2-pentylcyclohexane	-	-	20.183	0.38	19.944	0.03
<b>Total</b>			3.95		1.87		2.01
<b>Oxygenate</b>							
1.	Triasteranone	-	-	9.836	0.14	9.826	0.2
2.	3,3-Dimethyl-2-hexanone	10.792	7.18	10.787	0.62	10.781	0.81
3.	2-Butyloctanol	15.902	0.24	16.163	0.05	15.883	0.09
<b>Total</b>			7.42		0.81		1.1

**Table 3.23.** Distribution of Various Hydrocarbon Group Types in Light and Middle Fractions Derived From Distillation of Chemically Dispersed RCA-III Crude

Hydrocarbon group	Plain RCP-I		SDS treated		CTAB treated		TX-100 treated	
	F1	F2	F1	F2	F1	F2	F1	F2
<b>Paraffins</b>	65.97	97.18	73.91	84.01	82.46	96.31	72.96	95.75
<b>Olefins</b>	0.72	0.2	0.79	0.45	0.08	0.15	1.32	0.05
<b>Aromatics</b>	7.59	1.38	4.72	4.17	6.7	0.86	8.16	1.16
<b>Naphthenes</b>	14.7	1.84	19.3	3.95	9.35	1.87	15.39	2.01
<b>oxygenates</b>	12.08	0.87	1.28	7.42	1.41	0.81	2.17	1.1

**Table 3.24.** Distribution of Various Carbon Range Compounds in Light and Middle Fractions Derived From Distillation of Chemically Dispersed RCA-III Crude

Sample	Concentration (wt%)							
	C <sub>5</sub> -C <sub>10</sub>		C <sub>11</sub> -C <sub>13</sub>		C <sub>14</sub> -C <sub>18</sub>		C <sub>19</sub> -C <sub>n</sub>	
	F1	F2	F1	F2	F1	F2	F1	F2
<b>Plain RCA-III</b>	61.52	5.00	18.69	37.75	8.12	27.36	11.67	29.89
<b>SDS treated RCA-III</b>	56.69	21.1	32.39	33.9	4.38	29.22	6.54	15.78
<b>CTAB treated RCA-III</b>	39.03	5.08	47.46	35.19	4.57	36.08	8.94	23.65
<b>TX-100 treated RCA-III</b>	60.00	6.09	26.23	32.29	7.53	37.38	6.24	23.03

**Inferences:** The results inferred that both F1 and F2 derived from distillations of plain crudes have quite complex compositions of low and high molecular weight aliphatic, naphthenic and aromatic hydrocarbons. The aliphatic compounds were found predominately in the two fractions with similar paraffinic makeup. However, some fractions have high olefinic contents. Olefins to certain concentration are desirable in diesel fuel applications [74]. Alkane rich fuel formulations have superior ignition properties and are considered as good fuels for Advanced Combustion Engines [75, 76]. The product distribution of F1 consisted mostly of hydrocarbons in the gasoline boiling range ( $C_6$ – $C_{13}$  hydrocarbons), while that of F2 in the diesel rang. The presences of aromatics in F1 are desired as they act as octane boosters. Dispersants are used to accelerate the removal of oil from the surface of the sea by greatly enhancing the rate of natural dispersion of oil and thus prevent it from coming ashore. Dispersed oil will also be more rapidly biodegraded by naturally occurring microorganisms. The rationale for dispersant use is that dispersed oil is likely to have less overall environmental impact than oil that persists on the surface of the sea, drifts and eventually contaminates the shoreline [77].

The GC-MS results of the chemically dispersed crudes interpreted that the main compositions of the studied fractions (F1 and F2) were alkanes, alkenes, cycloalkanes, while aromatics were also present in low concentrations. A high degree of compositional similarity with the distillates derived from the plain can be observed. All hydrocarbons present in distillates from plain crudes can also be observed but with different values/concentrations.

The concentration of lighter hydrocarbons ( $C_5$ - $C_{13}$ ) increased significantly in F1 fractions compared to the plain crudes. This could be due to the beneficial effect of the dispersants in terms of their abilities to expose the hydrocarbons occluded or caged with in the asphaltene molecular frame work. However, in the heavier crude (RCA-III), the fractions characterized by decrease in

aromatic species with increase in aliphatic contents with a higher degree of branching and relatively higher amounts of bi- and polycyclic aliphatics. The fractions were also detected to have low contents of oxygenates, sulphur and nitrogen compounds. The low concentration of SON and aromatic contents ensures a cleaner-burning fuel.

Over all, the GC-MS results on the compositional data obtained from the various distillates was found to be superimposed for the plain and chemically dispersed samples and revealed a wide range of same/identical core structures with an almost uninterrupted continuum hydrocarbon group type's distributions.

### **3.6. FTIR STUDY OF ASPHALTENES**

The FTIR, being a versatile analysis technique, has been used to determine the aliphatic, aromatic CH content or to identify other functional groups in asphaltene [78]. The FTIR analysis of the asphaltene derived from the three crude oils was performed so as to verify the possible functional groups which may have involved in interactions with the surfactants under study. The results are displayed in Fig. 3.30 (a), (b) and (c). The characteristic bands for the different phases are summarized in Table 3.25. The presence of acid groups (such as COOH, OH, and SH) or basic groups (such as pyridinic groups) were identified in crude oils under study in addition to the rest of frame work.

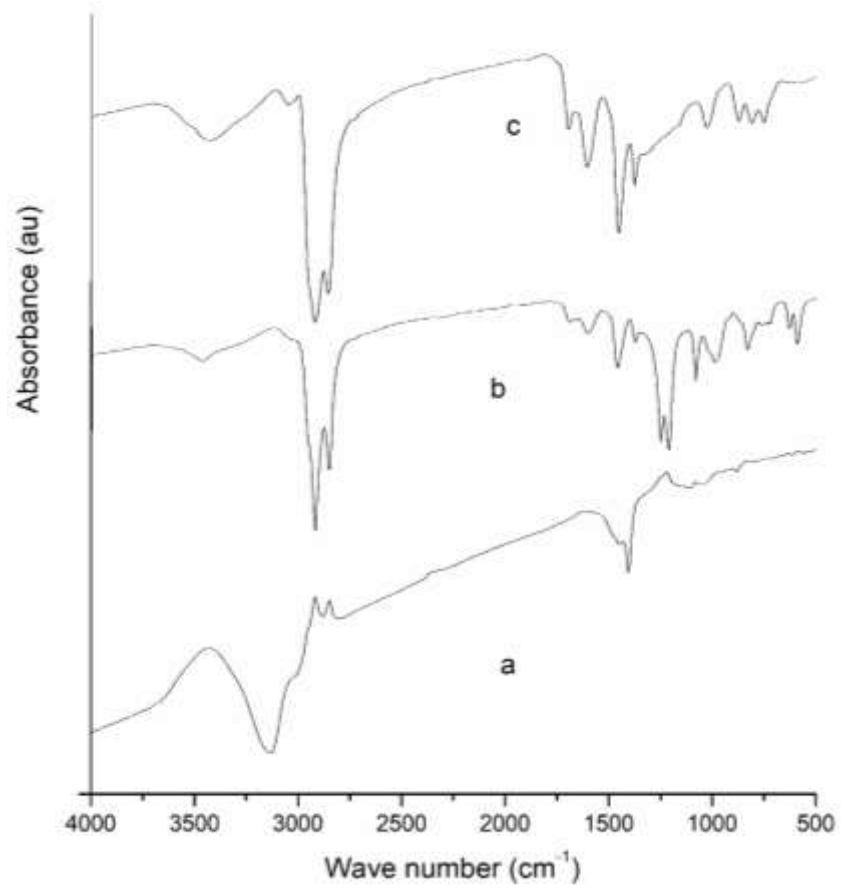
The FTIR spectrum of the asphaltene derived from RCP-I crude is provided in Fig.3.30 (a). A number of absorption bands of aliphatic C–H bonds, supplemented with additional bands corresponded to groups containing aromatics, oxygen, sulfur, and nitrogen [79, 80] can be seen including peaks centered at 3135, 3004, 2896, 2806, 1461, 1403, and 1090  $\text{cm}^{-1}$ . Among the several peaks, a sharp peak corresponded to O-H carboxylic can be seen at 3135  $\text{cm}^{-1}$ . The absorption at



the  $3135\text{ cm}^{-1}$  which corresponded to the presence of a small amount of phenolic functional groups [81].

The FTIR analysis of the asphaltenes derived from the RCN-II was also carried out and the corresponding spectrum is provided in Fig 3.30 (b). The spectrum exhibited bands centered at 3425, 3045, 2913, 2838, 1601, 1484, 1444, 1353, 1007, 883, and  $792\text{ cm}^{-1}$ . Strong absorption peaks between  $3600\text{--}3100\text{ cm}^{-1}$  can be observed, which indicated that it has high concentrations of O–H and N–H groups. Band corresponded to the aliphatic  $\text{--CH}_2$  and  $\text{--CH}_3$  bending vibrations at  $1484\text{ cm}^{-1}$  can be evidently observed. The spectrum displayed some peaks of high intensity while other poor intensity. Differences in the relative intensities of the bands indicated structural variations. Bands corresponded to oxygen functional groups, aromatic amines, amides ( pyrrolic type) and quinones can be seen. The band around  $1601\text{ cm}^{-1}$  was attributed to the stretching vibrations of carbonyl groups, predominantly in carboxylic acids. The intensity of this band was generally poor. Absorption peaks near  $3045\text{ cm}^{-1}$  and  $1601\text{ cm}^{-1}$  related to aromatic C–N stretching vibration and C=C stretching vibration of the skeleton, respectively, showed the presence of the aromatic structures. For the nitrogen-containing functional groups, their absorption peaks of aromatic amines C–N stretching vibration ( $1353\text{ cm}^{-1}$ ) and heterocyclic skeleton vibrations ( $1444\text{ cm}^{-1}$ ) can be seen. The weak absorbance at  $1007\text{ cm}^{-1}$ , related to sulfoxide (S=O) functional groups [82], can also be observed.

The spectrum of the asphaltenes derived from RCA-III crude is provided in Fig 3.30 (c) which exhibited several peaks centered at 3127, 2996, 2880, 2798, 1452, 1394, 1115, and  $859\text{ cm}^{-1}$ . These peaks corresponded to the presence of alkanes, aromatic rings, phenyl rings, alcohols, ethers, carboxylic acids, esters, aldehydes, ketones, anhydrides, organic sulfoxides, sulfate salts, thiobenzophenones, amines, and nitro compounds [83, 84].



**Fig 3.30.** FTIR spectra of asphaltenes derived from plain crudes: (a) RCP-I (b) RCN-II and (c) RCA-III

**Table 3.25.** FTIR Absorption Peaks (cm<sup>-1</sup>) and Assigned Configurations of Asphaltenes Derived from Plain Crudes

<b>RCP-I</b>	<b>RCN-II</b>	<b>RCA-III</b>	<b>Assigned configurations</b>
-	3425	-	O-H Alcoholic/Phenolic, N-H amines
3135	-	3127	O-H Carboxylic
3004	3045	-	=C-H Aromatics
2896	2913	2996	C-H (CH <sub>3</sub> Aliphatic)
2806	2838	2880	C-H (CH <sub>2</sub> Aliphatic)
-	-	2798	C-H (Aldehyde), S-H thiol
-	1601	-	C=C (Aromatic/Olefinic)
1461	1484	1452	C-H (CH <sub>2</sub> bending)
1403	1444	1394	O-H (Bending)
-	1353	-	C-O (acyl/ Phenol)
1090	1007	1115	C-O (alkoxy) / S=O sulfoxide
-	883	859	C-H (CH <sub>2</sub> bending) aromatic
-	792	-	S-OR esters

### **3.7. EFFECT OF SURFACTANT TREATMENT ON METALS REMOVAL/LEACHING**

The concentration of various metals was analyzed in the residual fractions of all of the plain and various surfactant treated crudes, in order to investigate the effect of each individual surfactant on the removal/leaching of the inorganic elements/metals from the corresponding crude oil samples. As mentioned in the section 3.4, that the ash contents of all of the crude samples were negligible, wherein some samples showed ash content upto 0.003 %. The ash content was too small to be analyzed by the EDX, therefore, the residues of all of the samples were partially carbonized and then analyzed by the XRF. The concentration of the various inorganic elements determined in residues of the plain and surfactant treated crudes are given in Table 3.26. According to the results, only Cu, Fe, Ca and Zn were detected in all samples. In plain and SDS treated RCP-I crude samples, the same metals were not detected even in trace amount. However, in CTAB treated RCP-I crude, Cu and Zn were found to be present in concentration of 119.534 and 50.043 ppm, respectively. Whereas in TTX treated RCP-I, Fe was found to be 24.607 ppm. It can be suggested that all of the samples were rich while others were lean in terms of lithophilic, chalcophilic and siderphilic inorganic elements. The high concentration in the surfactant treated samples may be due to the obvious reason of the exposure of the trapped hydrocarbon due to structure relaxation of the giant asphaltene molecules.

In case of plain RCN-II crude, Cu concentration was found to be 69.077 ppm, whereas no other metal was detected. However, in the SDS treated crude, 84.058, 54.947 and 73.908 ppm of Cu, Zn and Ca were detected. Similarly, in the CTAB treated crude, 59.162 ppm of Zn was found, whereas in the TTX treated RCN-II crude, no elements was detected.

In plain RCA-III crude, 58.906 ppm Cu was detected. Interestingly, only Cu was found to be present in surfactants treated RCA-III crude, except SDS treated sample wherein 25.163 ppm Zn

was detected. The concentrations of the Cu in the SDS, CTAB and TTX treated RCN-III crude oil samples were found to be 76.631, 63.129 and 56.216 ppm, respectively. The surfactant treated crude showed slightly high concentration of Cu as compared to the plain crude. This may be attributed to the removal of most asphaltic components in the treated sample, due to which high molecular weight resins increased in concentration, hence concentration of Cu metal also increased.

**Table 3.26.** Concentration of Various Inorganic Elements (ppm)in Residues of Plain and Various Surfactant Treated Crudes

Sample Name	Concentration (ppm)			
	Cu	Zn	Fe	Ca
RCP-I Crude				
Plain RCP-I	BDL	BDL	BDL	BDL
SDS treated RCP-I	BDL	BDL	BDL	BDL
CTAB treated RCP-I	119.534	50.043	BDL	BDL
TTX treated RCP-I	BDL	BDL	24.607	BDL
RCN-II crude				
Plain RCN-II	69.077	BDL	BDL	BDL
SDS treated RCN-II	84.058	54.947	BDL	73.908
CTAB treated RCN-II	59.162	BDL	BDL	BDL
TTX treated RCN-II	BDL	BDL	BDL	BDL
RCA-III crude				
Plain RCA-III	58.906	BDL	BDL	BDL
SDS treated RCA-III	76.631	25.163	BDL	BDL
CTAB treated RCA-III	63.129	BDL	BDL	BDL
TTX treated RCA-III	56.216	BDL	BDL	BDL

### 3.8 MECHANISM

It was found that some surfactants were effective in one type of crude oil while others in other types. The SDS was more effective in RCA-III crude while the CTAB and TX-100 were more effective in RCN-II crude. In terms of the distillate yield both surfactants were efficient and exhibited promising results but the efficiency of the SDS in RCA-III was better. The behavior of each dispersant can be explained in terms of the nature of the asphaltene contents of the respective oils and the polar head of the dispersant. The asphaltenes have been reported to be consisted of condensed polyaromatic rings with peripheral aliphatic chains and functional polar groups, which render asphaltenes interfacially active [85, 86]. The interaction mechanisms between asphaltenes or asphaltene model compounds in different organic solvents or aqueous media have been studied elsewhere. The interaction forces between asphaltene surfaces have been reported elsewhere to be repulsive in good solvent toluene, which gradually changed to adhesion with increasing the content of a poor alkane solvent (e.g., heptane) in the organic medium [87].

As the oils under study contained mostly paraffins and were found to be lean in aromatics like toluene, therefore, the asphaltenes gave aggregates/ droplet coalescence in distillation when used in un-dispersed/plain forms and gave high yields of residues and heavy fractions. The surfactant used in current study acted as interface-active agents and have avoided interactions between asphaltene molecules thus keeping them dispersed during distillation. A number of interface-active materials, like surfactants [88], lipids [89, 90], amphiphilic polymers [91], or bi wetting nano- and microparticles [92, 93] have been reported to create an energy barrier against droplet coalescence, stabilizing the emulsions when added to petroleum oils.

The solvation of asphaltenes by the dispersant can be explained on the basis of the ion pair formation. Electrostatic interaction between the charged head groups of the surfactant molecules

and the crude oil components, known as the ion pair formation. The solvation is further assisted by the interaction of the hydrophobic end of the dispersant (the tail of surfactant molecules) and crude oil components. Surfactants owing to a strong acid group ( $\text{SO}_3^-$ ) are capable of interacting with asphaltene molecules, in crude oils [94]. The high efficacy of the SDS in RCA-III crude oil may be due to the formation of the ion pairs between the anionic heads of the surfactant molecules and the opposite surface charges on asphaltenes like those resulted from the protonation of heteroatomic components in the asphaltenes, which are positively charged. The surfactant molecules, which progressively attach to the available sites on asphaltene molecules/aggregates, occupy the virtual totality of sites and satirically hinder the attractive interactions with other asphaltene aggregates [95].

Further, such interactions lead to multilayered coverage on asphaltene aggregates which provide steric stability, thereby preventing them from associating into larger structures. The interaction between dispersant and asphaltenes in crude oils depend on several factors including the chemical and structural properties of asphaltenes [96, 97] as well as surface charge density of the dispersant [98]. Overall, the results suggest that the asphaltenes of crude (RCA-III) have more positively charged functional groups compared to RCP-I and RCN-II crudes, so  $\text{SO}_3$  group have made the attachment with asphaltenes and have stabilized them from interaction with the neighbor molecules.

The efficiencies of CTAB was found to be excellent in RCN-II crude oil compared to RCP-I and RCA-III crudes. This suggests that asphaltenes of this oil have more negatively charged functional groups in comparison to asphaltenes of RCP-I and RCA-III crudes, so cationic groups (heads) of the dispersant have made attachment with asphaltenes to stabilize and preventing them to interact with the neighbor asphaltene molecules. The results suggest that the polar group of the

hydrocarbonic chain which causes interaction between bulk crude oil and asphaltenes were less dominant in RCN-II crude compared to other oils under study.

The efficiency of the TX-100 was also found to be excellent in RCN-II crude oil. The addition of TX-100 results in a more compact molecular arrangement and decreases interfacial forces. Further, owing to nonionic nature, the TX-100 not only accumulates at the surface of the asphaltenes but enters in to the bulk phase [99]. The other reason may be, it has branched-chain alkyl groups in its hydrophobic segment that are more soluble in non-aqueous phase liquids i.e. light non-aqueous liquid phase and dense non-aqueous liquid phase [100], compared to other surfactants used. It is well understood that the crude oil contains resins (non-ionic) which adsorbed on the asphaltene molecules enhance their size and prevent them from being coagulated or precipitated [101]. As the TX-100 is non-ionic, it may have acted like resins and prevented asphaltenes aggregation.



## CONCLUSIONS

- All of the three crude oils studied have quite similar chemical compositions in terms of various individual hydrocarbons. However, they differ in paraffinic, olefinic, naphthenic, and aromatic group types with varying carbon range distributions. The relative abundance of the saturated hydrocarbons suggests that the oils are predominantly enriched in aliphatic constituents. RCP-I is dominated by C<sub>11</sub>–C<sub>13</sub>, RCN-II by C<sub>5</sub>–C<sub>10</sub> while RCA-III also by C<sub>5</sub>–C<sub>10</sub> range hydrocarbons.
- Pre-dispersion of the oil samples with the surfactants increased the distillate products yields, which increased at the expense of the residue.
- The yields of the distillate fractions particularly that of the F1 and F2 increased in chemically–dispersed crudes compared to control. Among the chemically dispersed crudes, it was found that some surfactants were effective in case of one type while others in other types of crude oils. The SDS was more effective in the RCA-III where the yield of F1 increased significantly to 58 % and the yield of residue decreased to 6 %. The CTAB was found to be more effective in the RCN-II crude and gave significant increase in the yields of the F1 and R fractions. The F1 fraction was increased to 49 % whereas the R yield was declined to 7 %. The triton X-100 also proved to be more effective in the RCN-II and gave 48 and 6 % yields of F1 and R fractions.
- Remarkable effects of the dispersants on the boiling point range and volatility were observed which best describes their performance. The results showed an increased volatility. Hydrocarbon constituents that were less volatile (remained in the liquid phase) in the plain crudes, began to vaporize early in the dispersed samples. However, the

volatility reduced as the distillation progressed. The FBTs were not affected to a greater extent.

- The results revealed compositional continuum of the fuel components in the plain and chemically dispersed crude oil samples. The F1 as well as the F2 fractions exhibited enormous structural similarities in terms of the hydrocarbon group type and the C-number distributions.
- Fuel quality of the distillate fractions did not deteriorate and the incremental distillate yields did not affect the overall product quality. Most of the key properties found to be reasonably closer to the values and in good agreement with the ASTM standard specifications reported for the gasoline, diesel and heavy oils.

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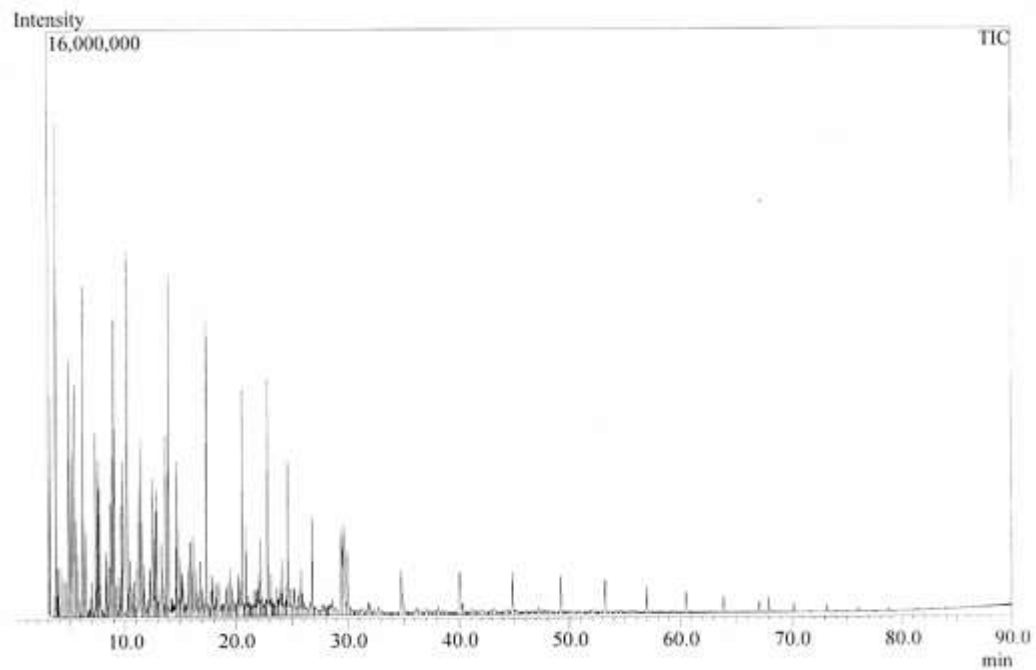
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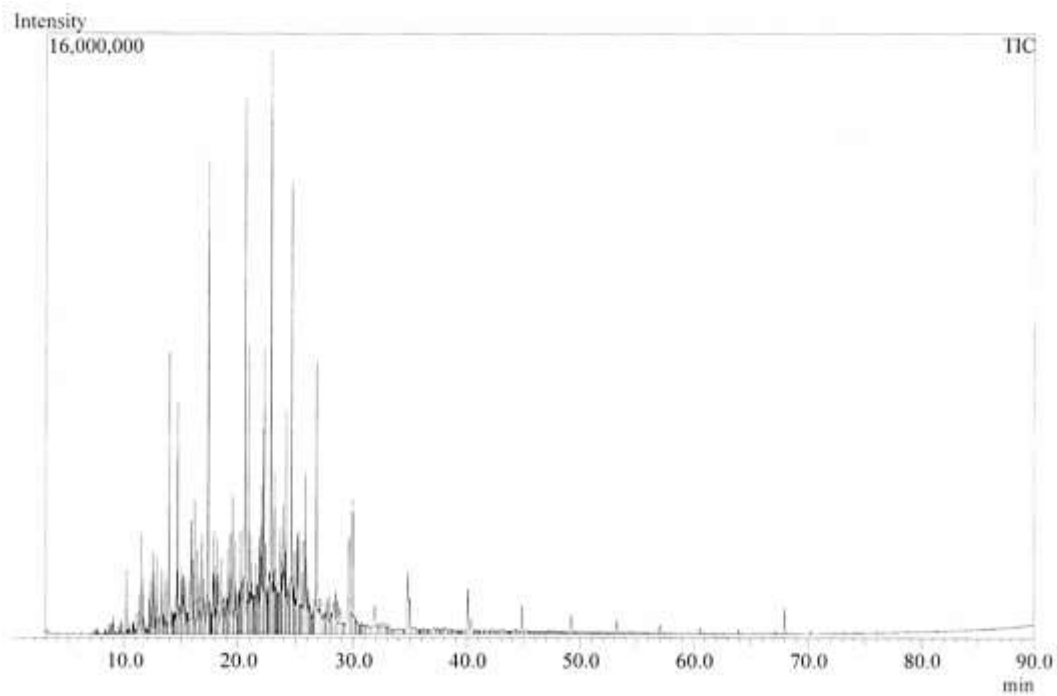
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**Appendix**  
**GC-MS Spectra**

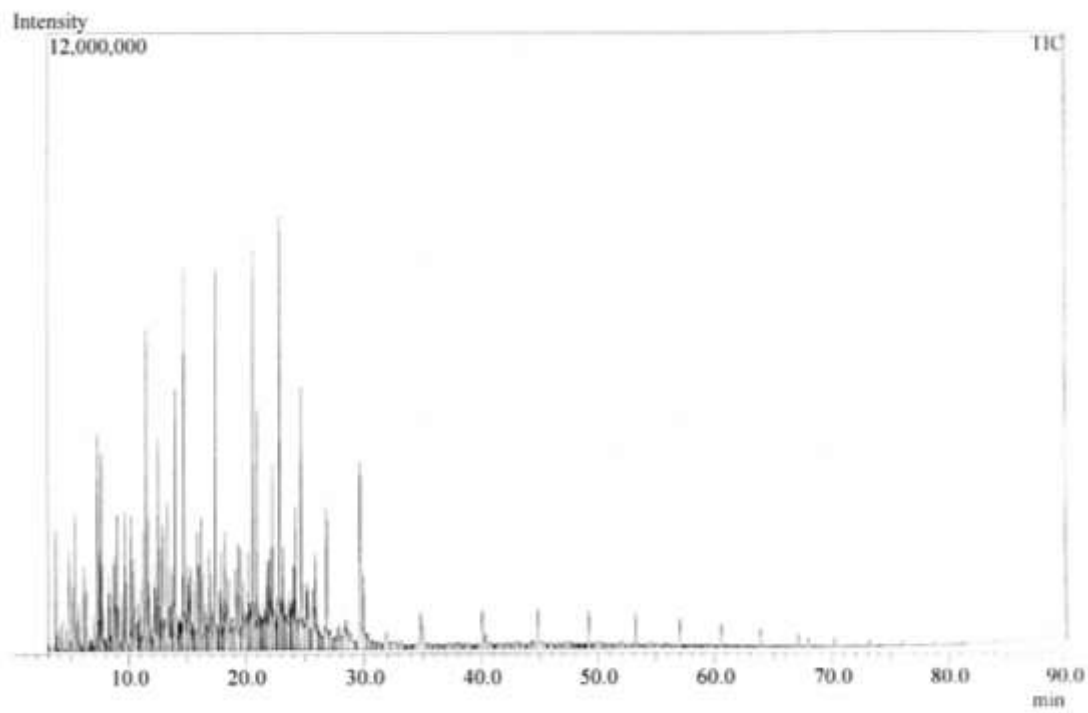
## Appendix



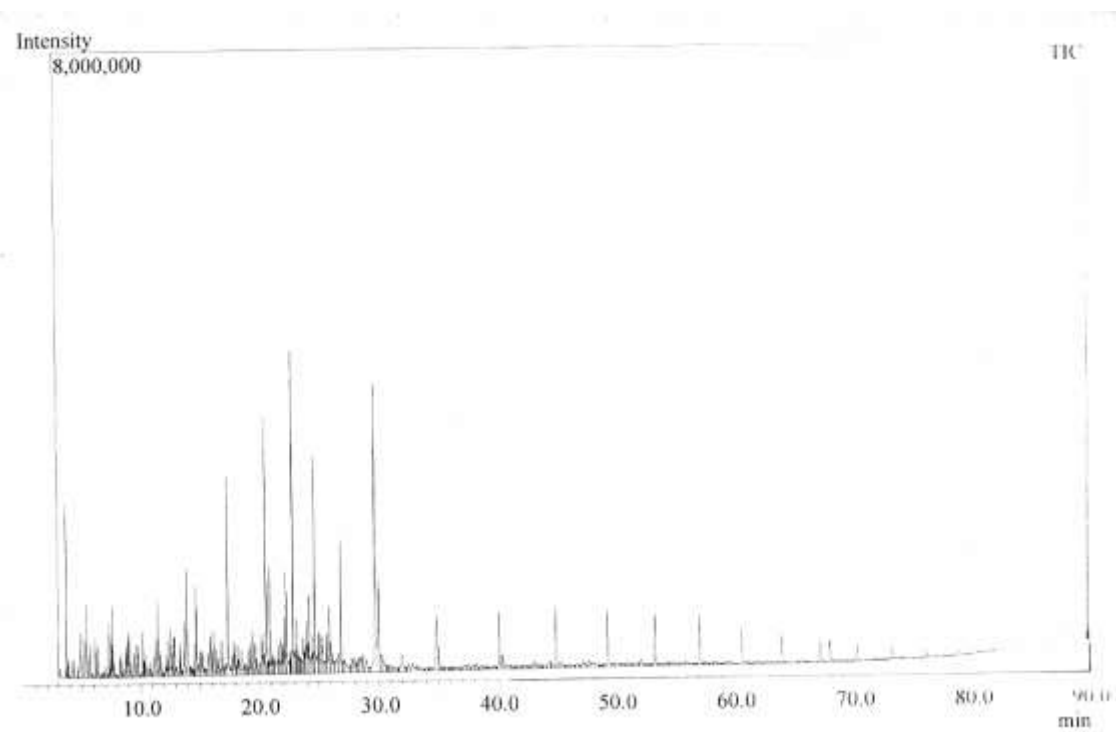
**Fig. S1 GC-MS spectrum of F1 fraction of plain RCP-I crude.**



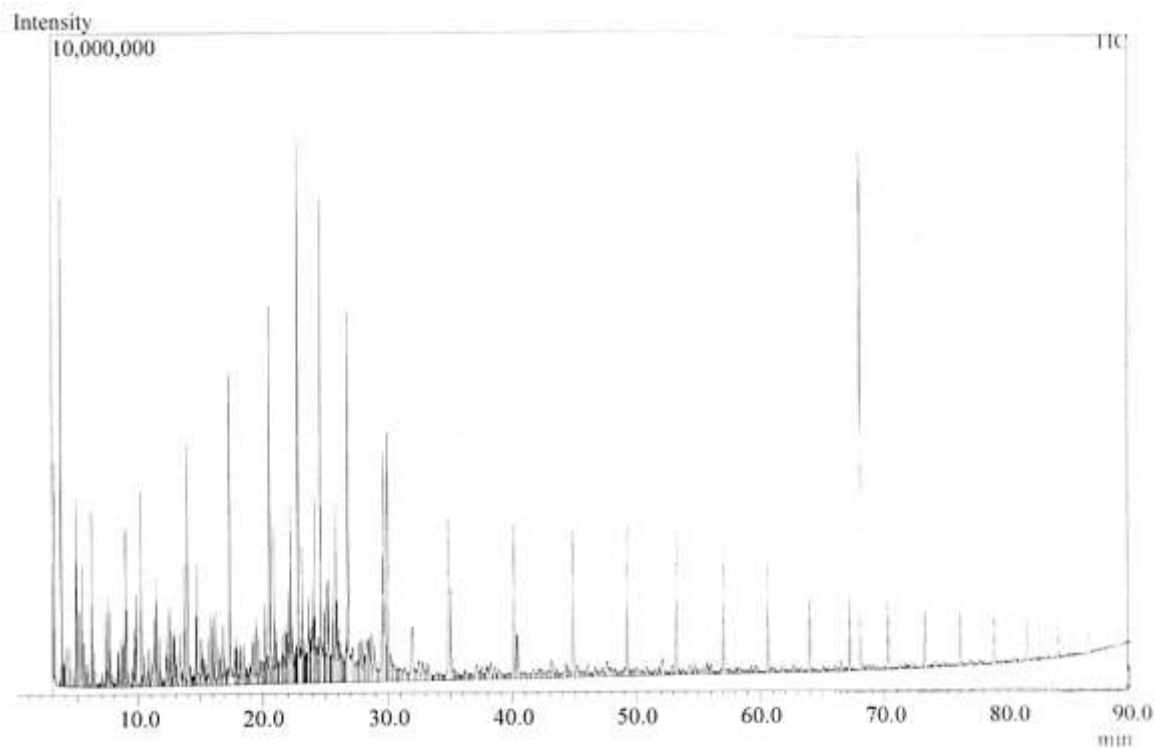
**Fig. S2 GC-MS spectrum of F1 fraction of plain RCN-II crude.**



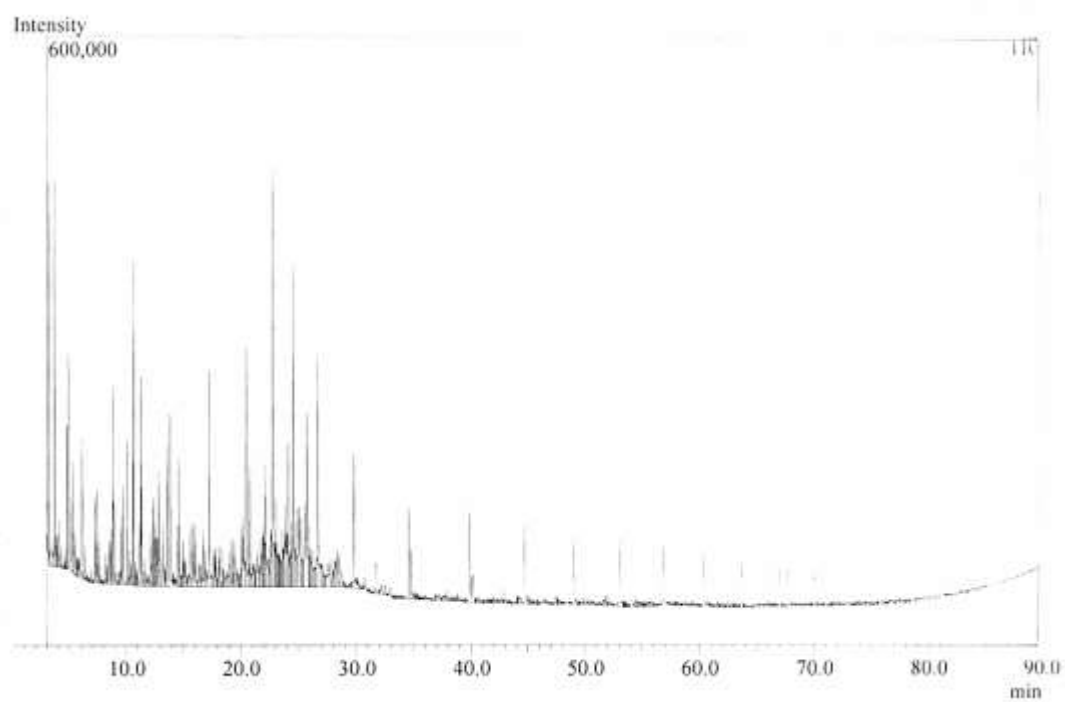
**Fig. S3 GC-MS spectrum of F1 fraction of plain RCA-III crude.**



**Fig. S4 GC-MS spectrum of F1 fraction of SDS treated RCP-I crude.**

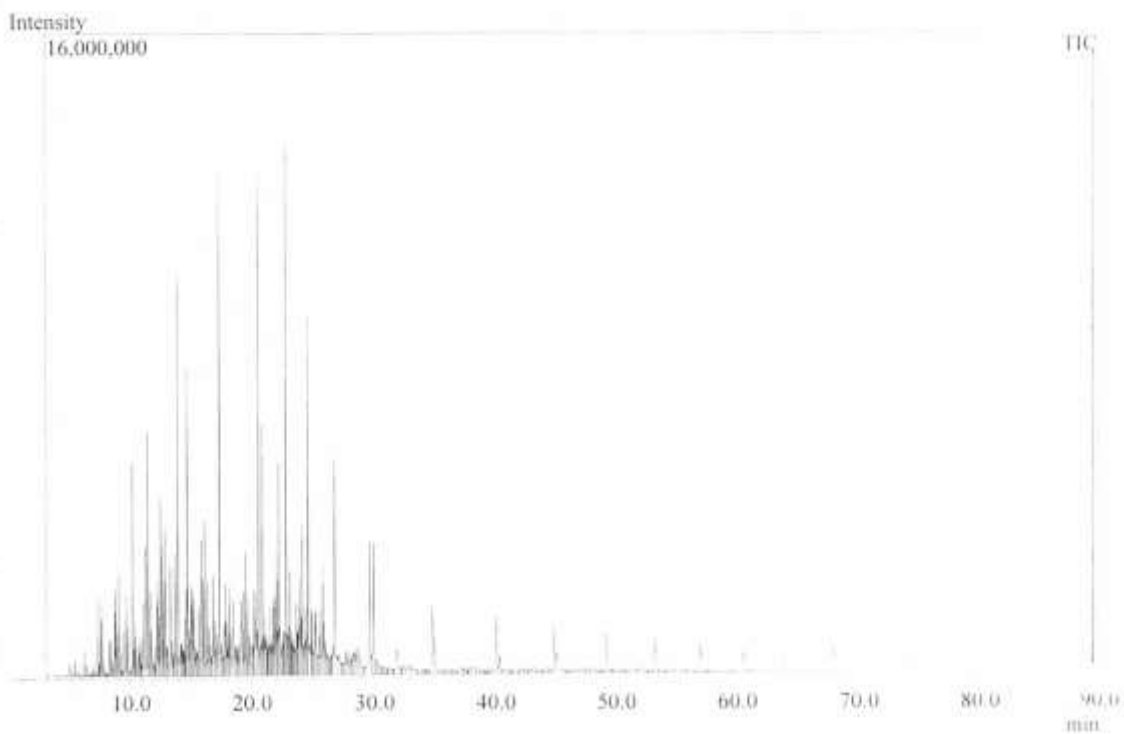


**Fig. S5 GC-MS spectrum of F1 fraction of SDS treated RCN-II crude.**

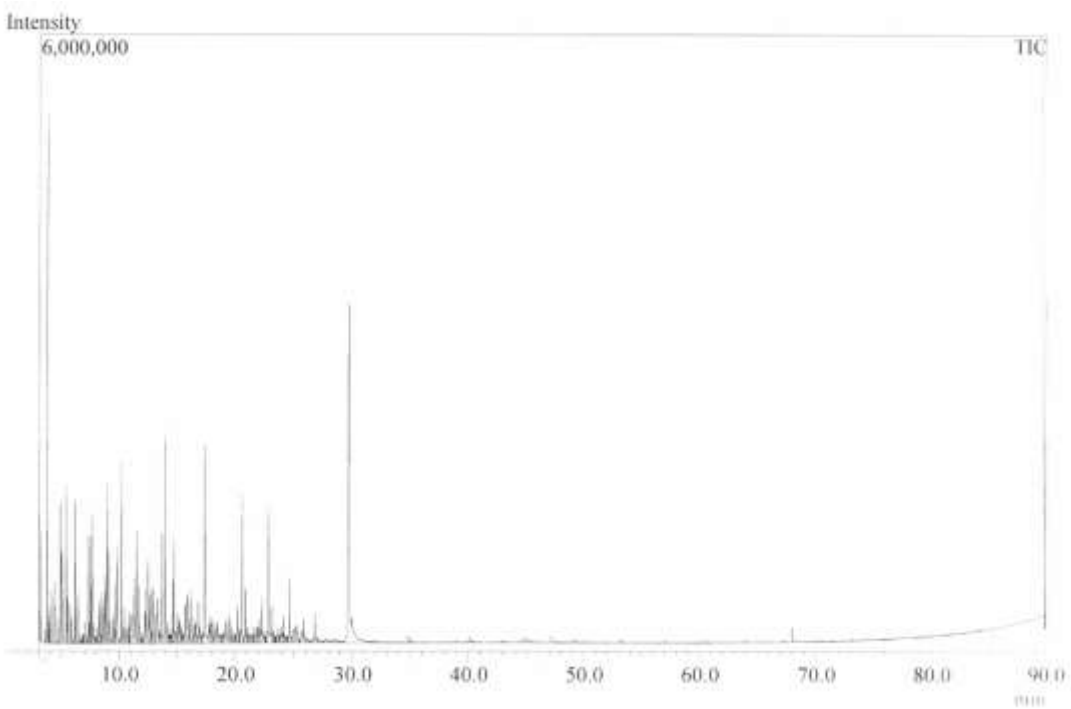


**Fig. S6 GC-MS spectrum of F1 fraction of SDS treated RCA-III crude.**

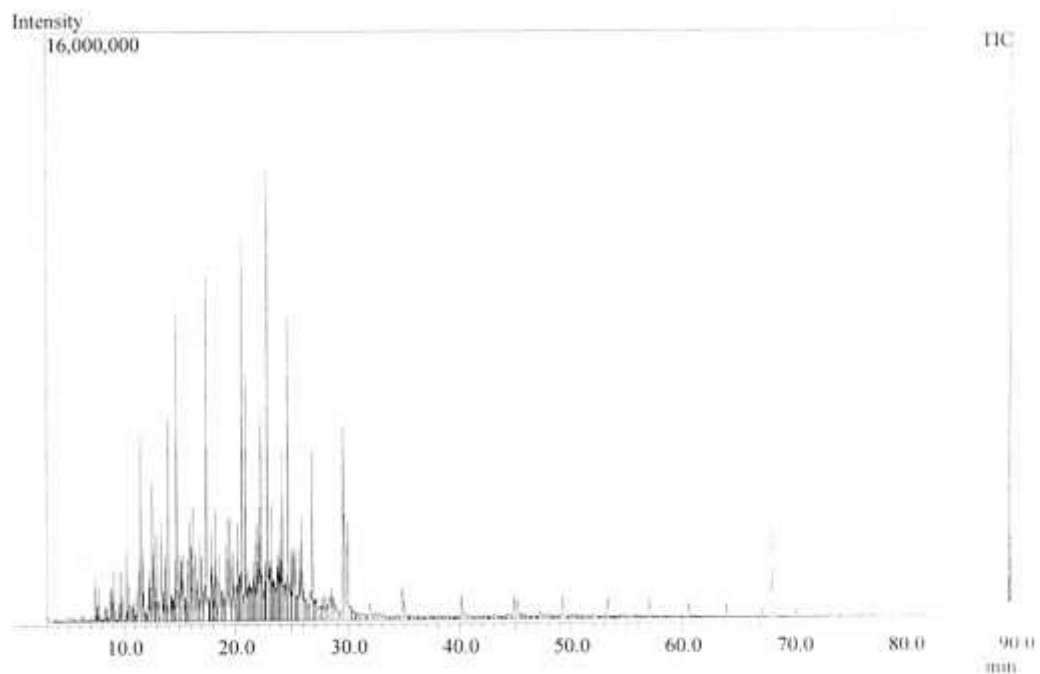




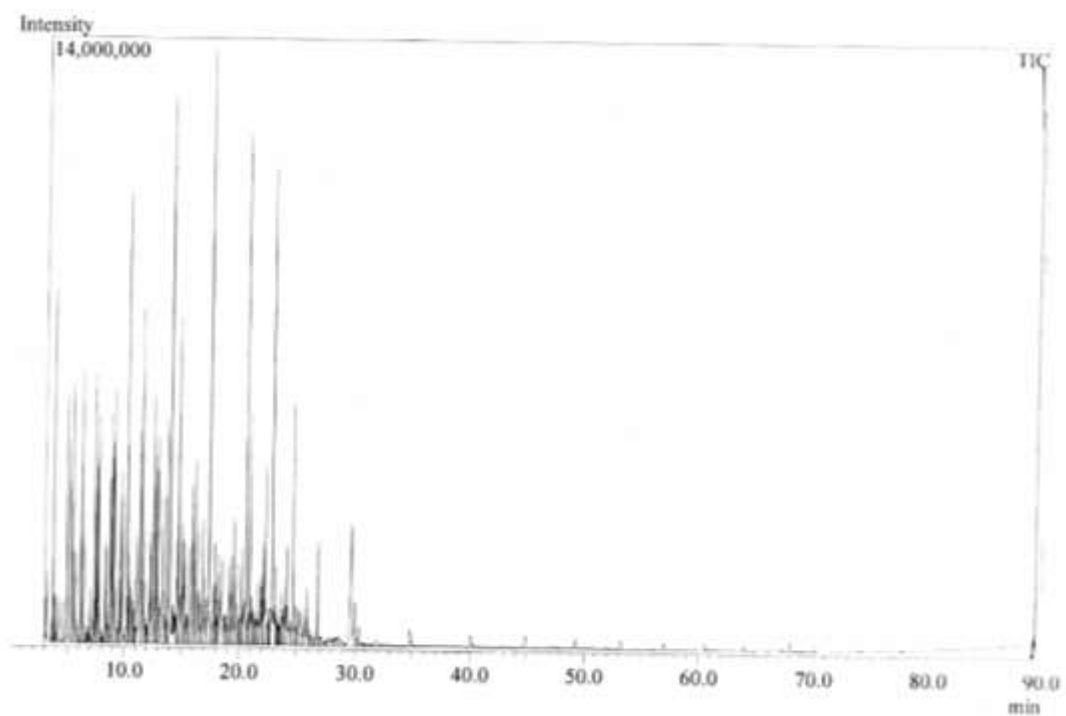
**Fig. S7 GC-MS spectrum of F1 fraction of CTAB treated RCP-I crude.**



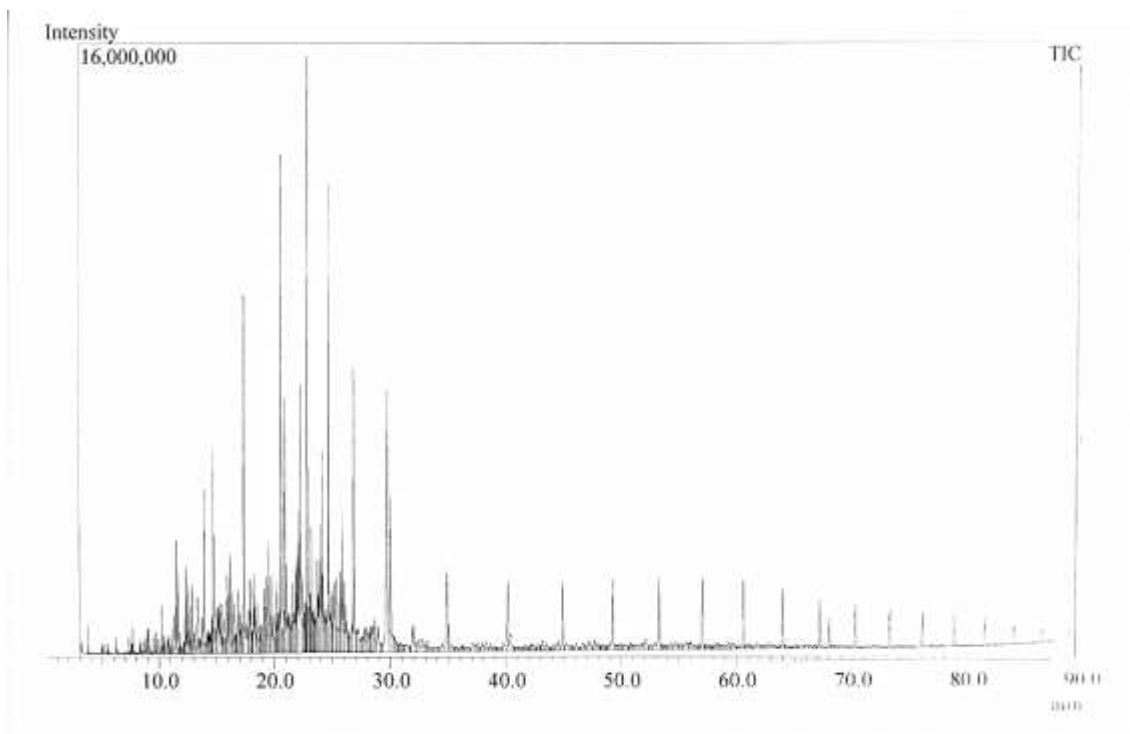
**Fig. S8 GC-MS spectrum of F1 fraction of CTAB treated RCN-II crude.**



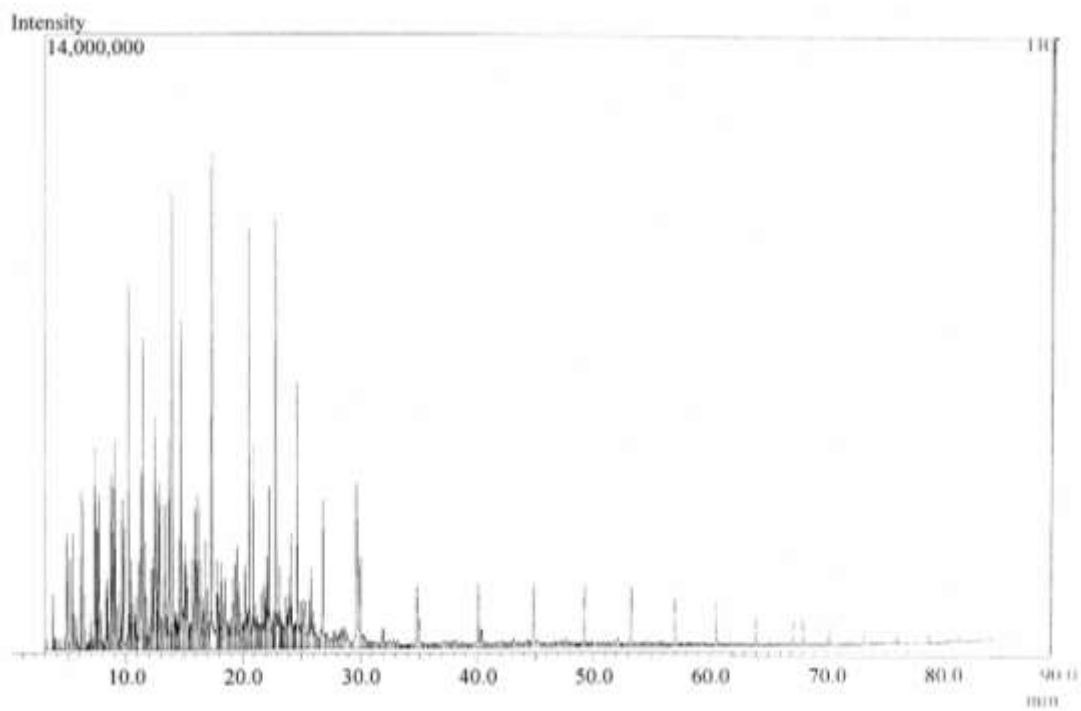
**Fig. S9 GC-MS spectrum of F1 fraction of CTAB treated RCA-III crude.**



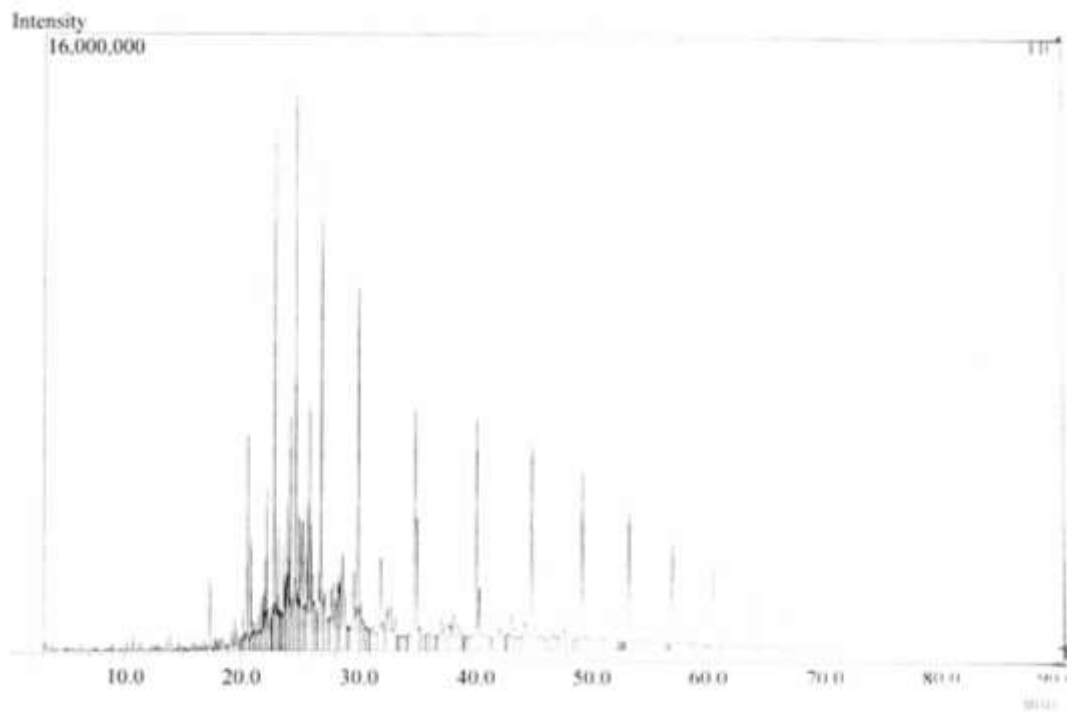
**Fig. S10 GC-MS spectrum of F1 fraction of TX-100 treated RCP-I crude.**



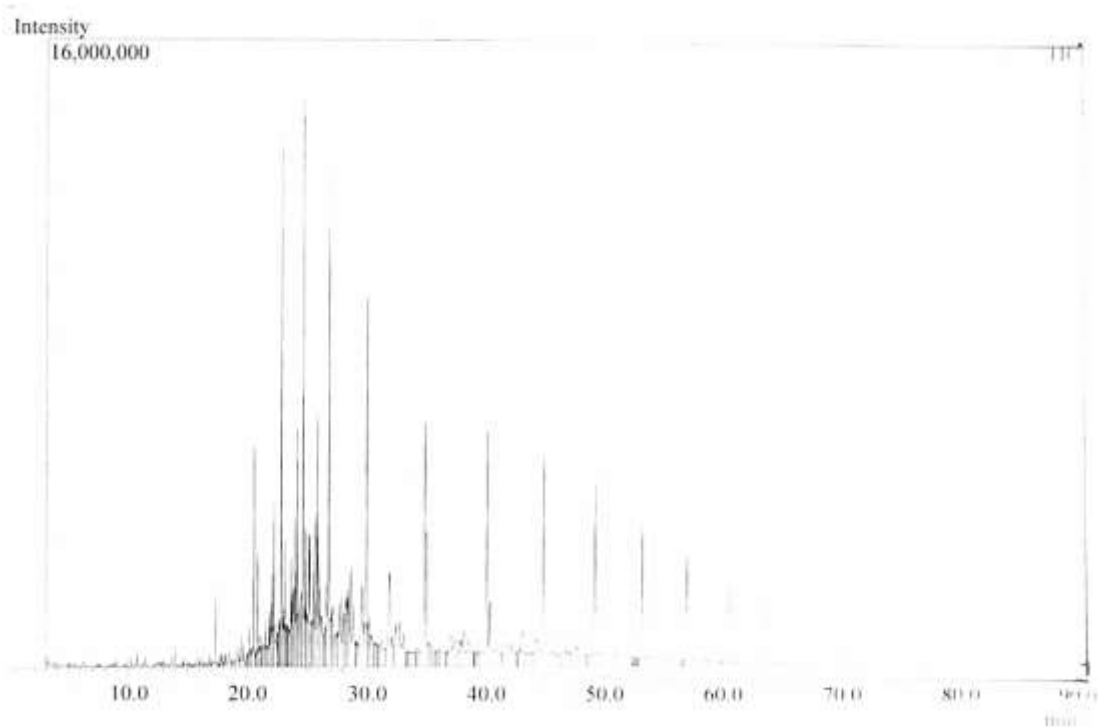
**Fig. S11 GC-MS spectrum of F1 fraction of TX-100 treated RCN-II crude.**



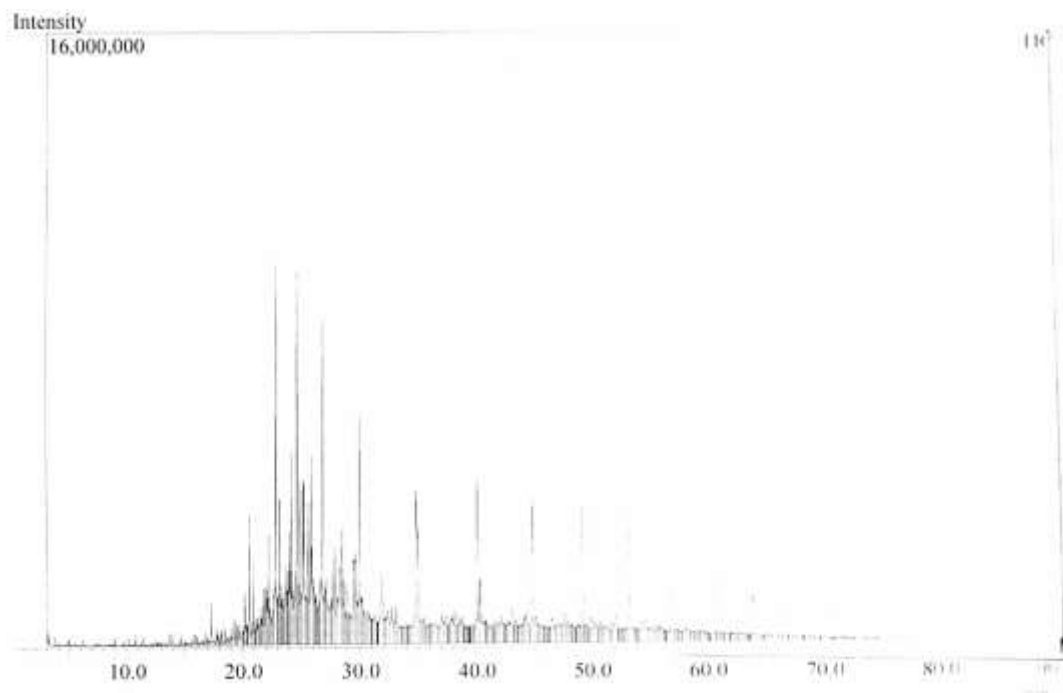
**Fig. S12 GC-MS spectrum of F1 fraction of TX-100 treated RCA-III crude.**



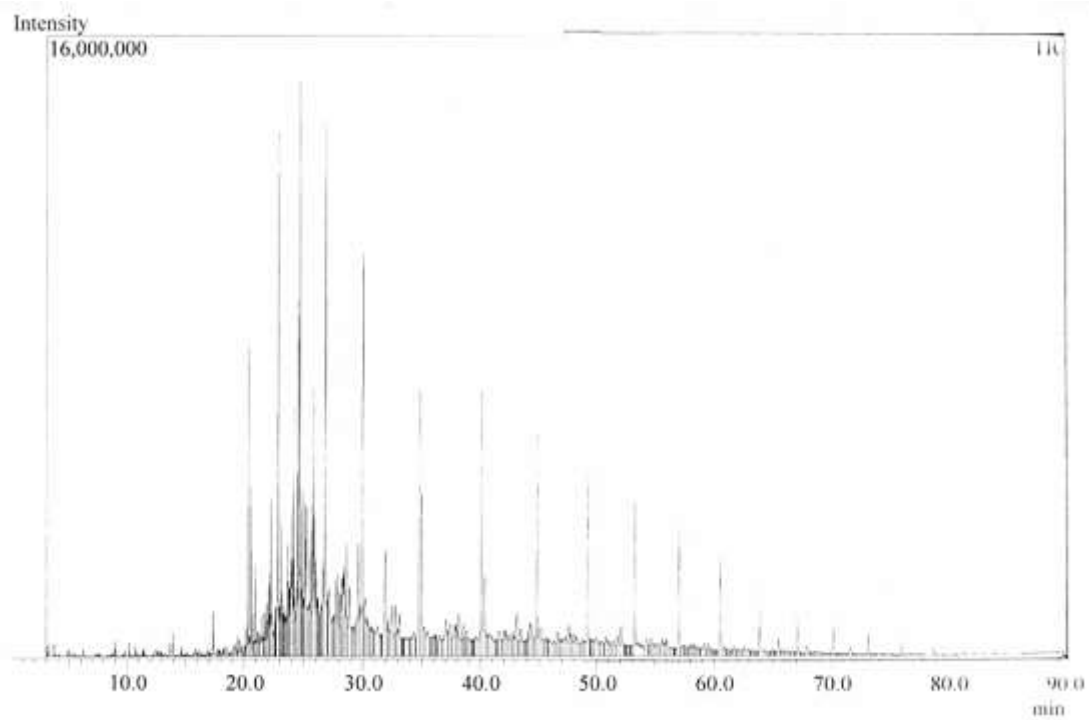
**Fig. S13 GC-MS spectrum of F2 fraction of plain RCP-I crude.**



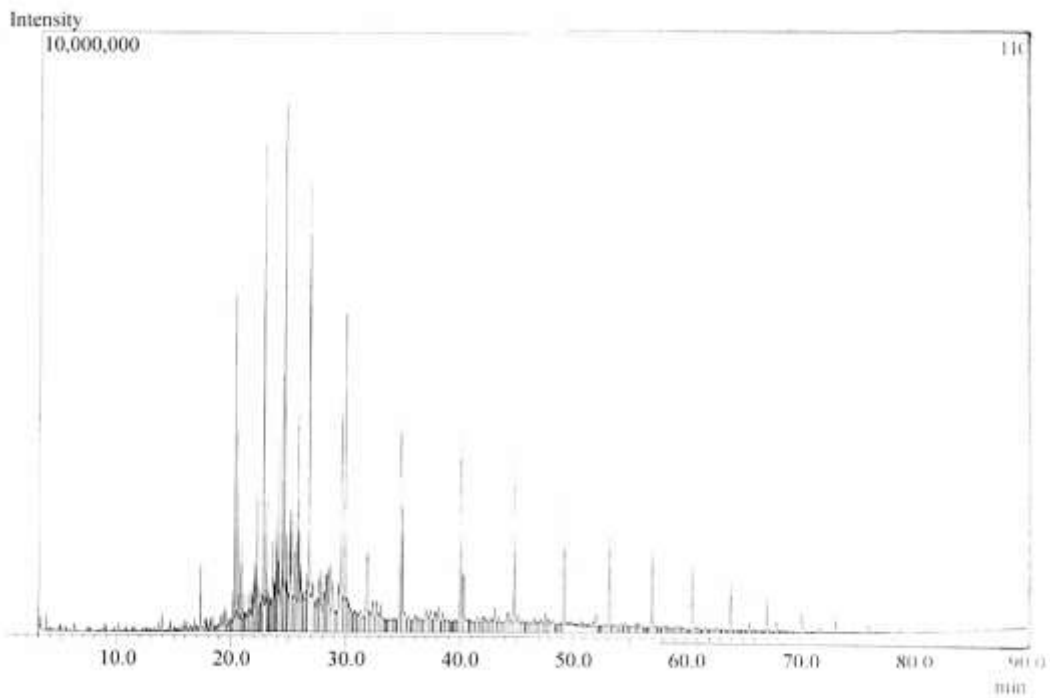
**Fig. S14 GC-MS spectrum of F2 fraction of plain RCN-II crude.**



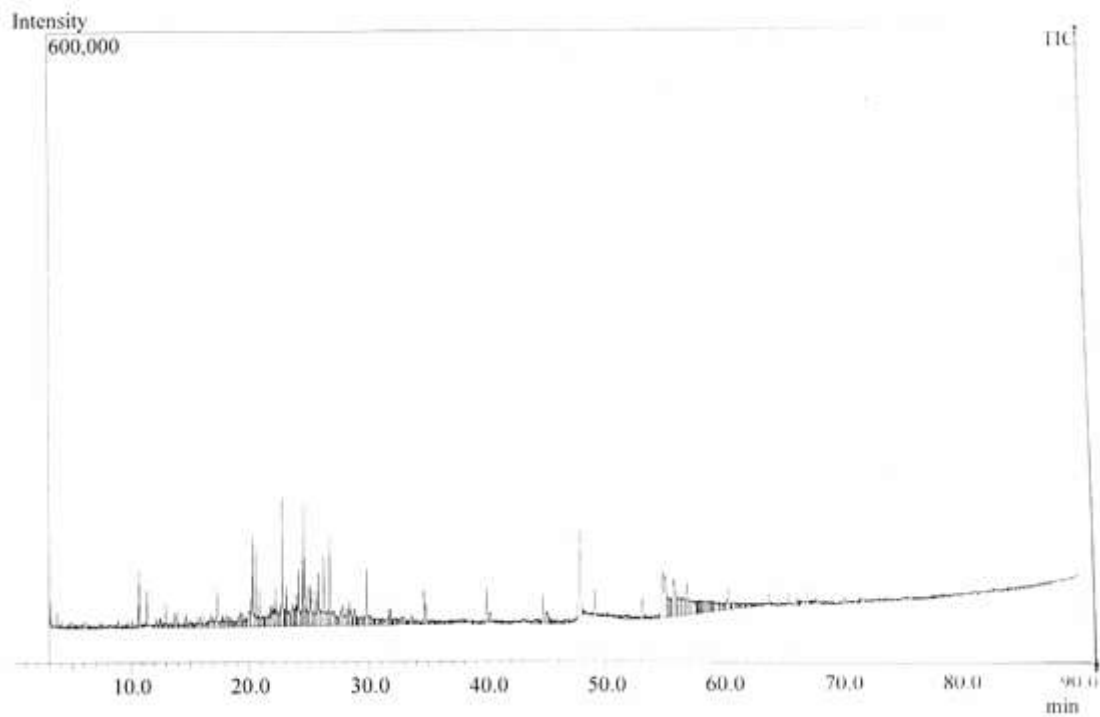
**Fig. S15 GC-MS spectrum of F2 fraction of plain RCA-III crude.**



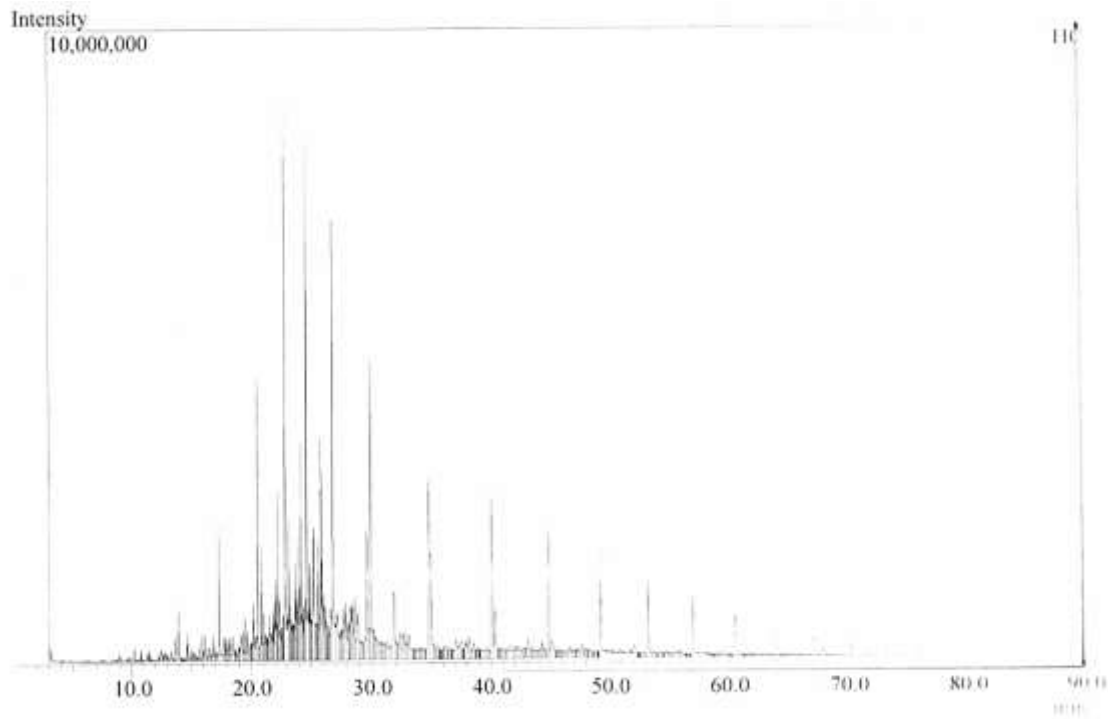
**Fig. S16 GC-MS spectrum of F2 fraction of SDS treated RCP-I crude.**



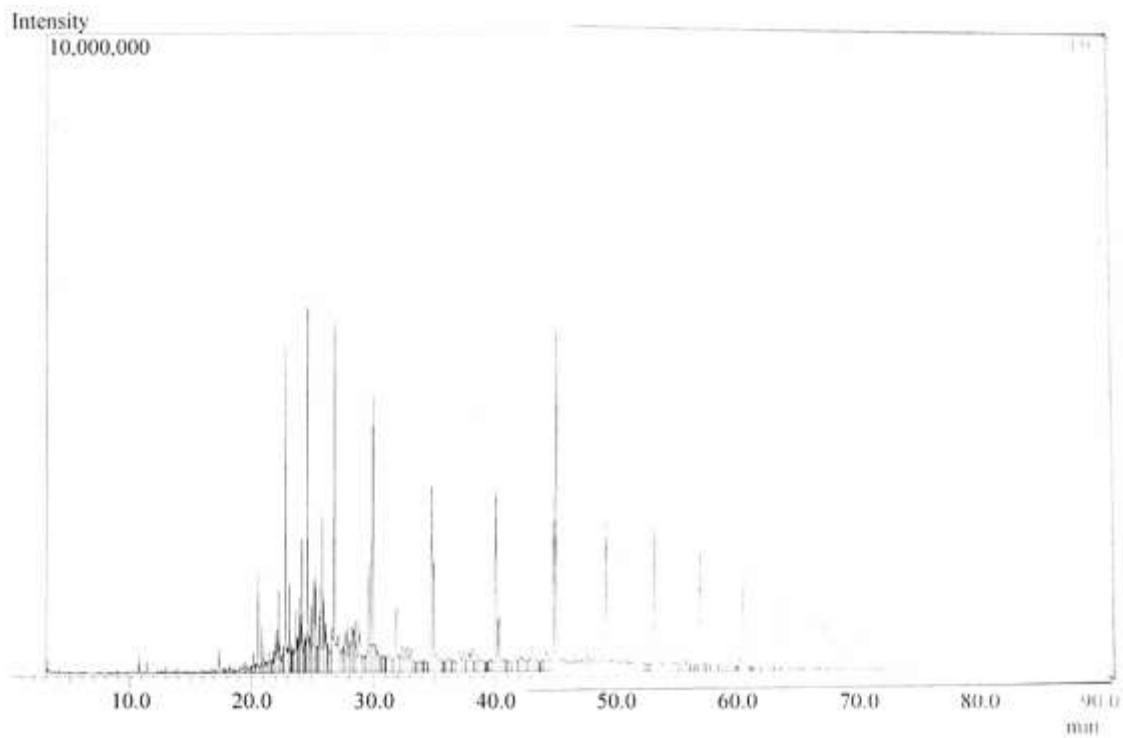
**Fig. S17 GC-MS spectrum of F2 fraction of SDS treated RCN-II crude.**



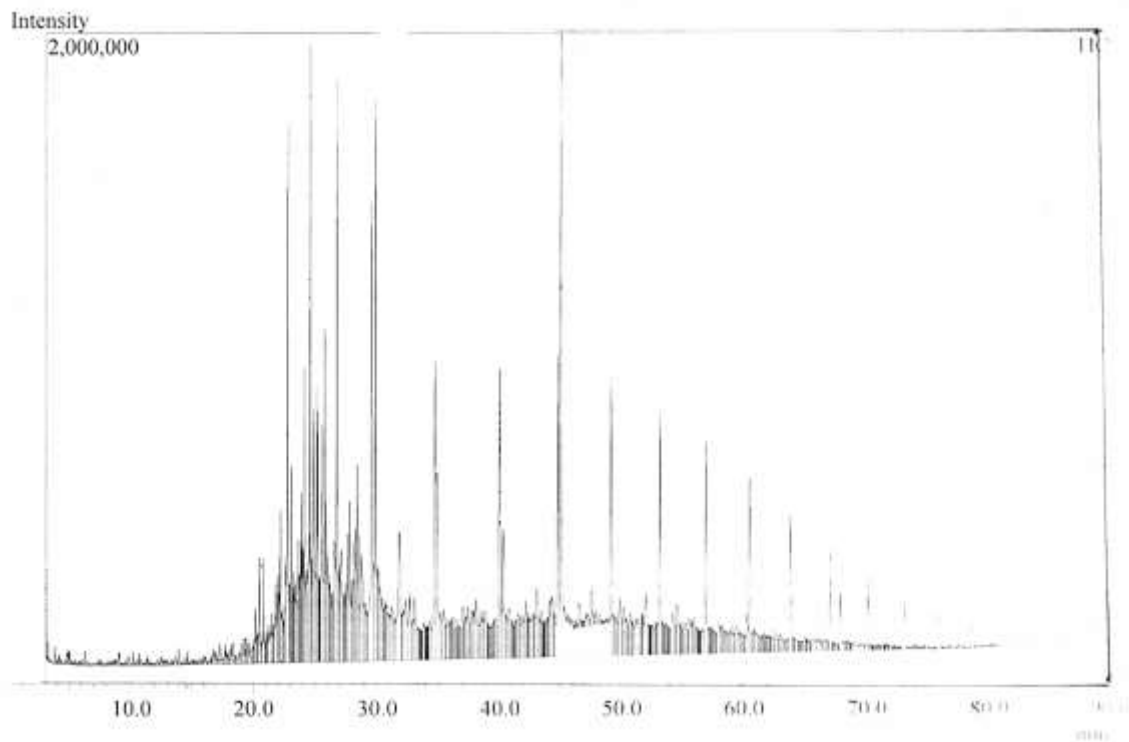
**Fig. S18 GC-MS spectrum of F2 fraction of SDS treated RCA-III crude.**



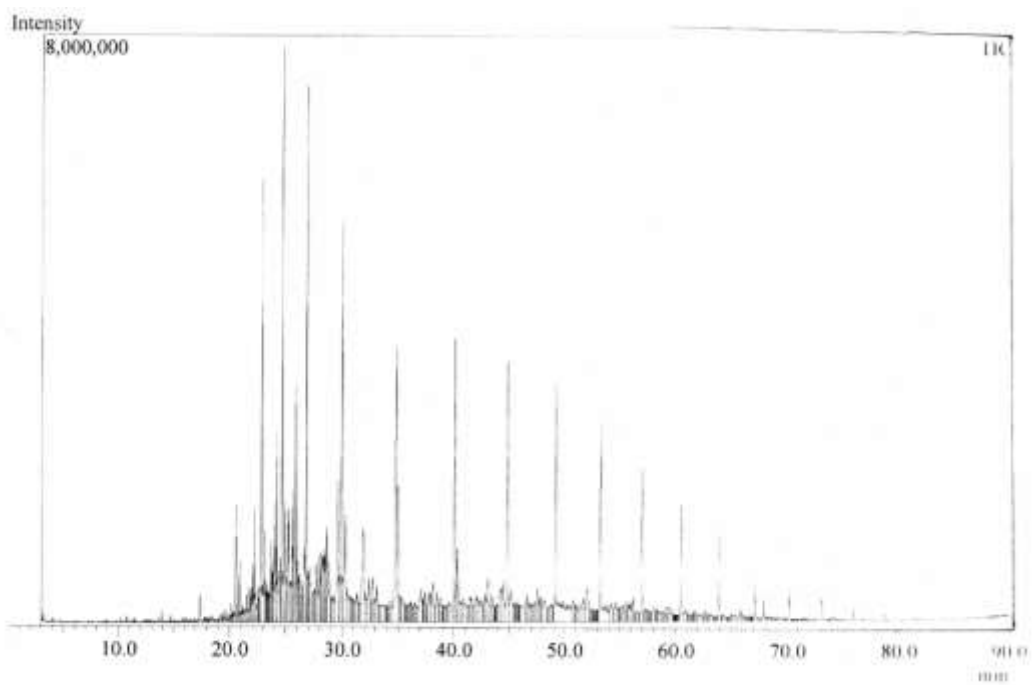
**Fig. S19 GC-MS spectrum of F2 fraction of CTAB treated RCP-I crude.**



**Fig. S20 GC-MS spectrum of F2 fraction of CTAB treated RCN-II crude.**

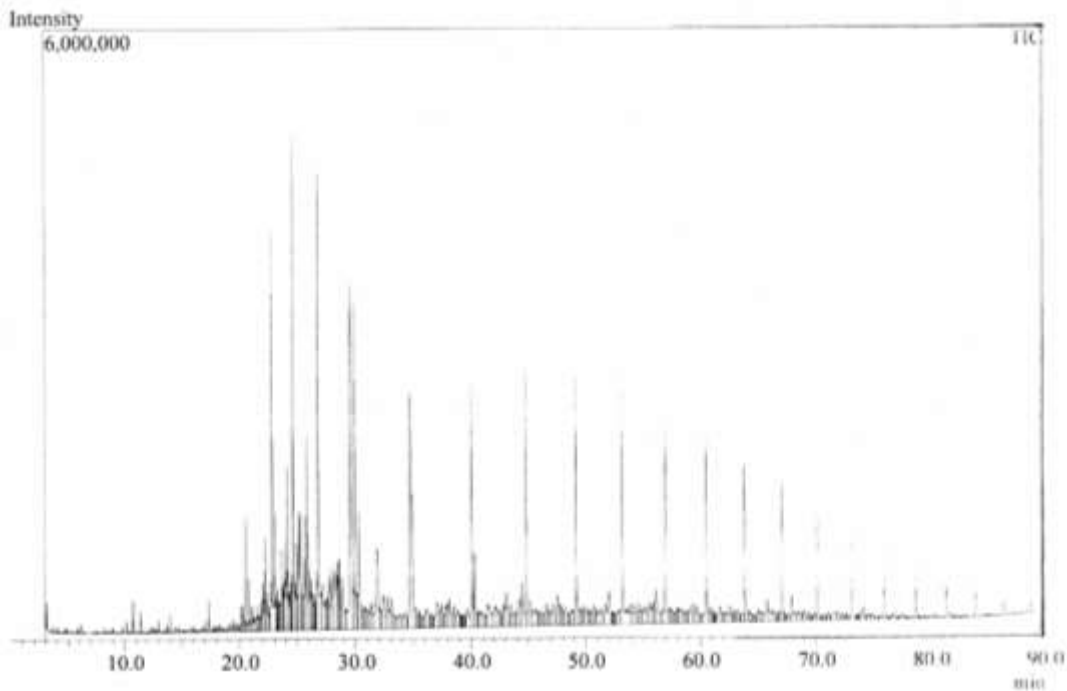


**Fig. S21 GC-MS spectrum of F2 fraction of CTAB treated RCA-III crude.**

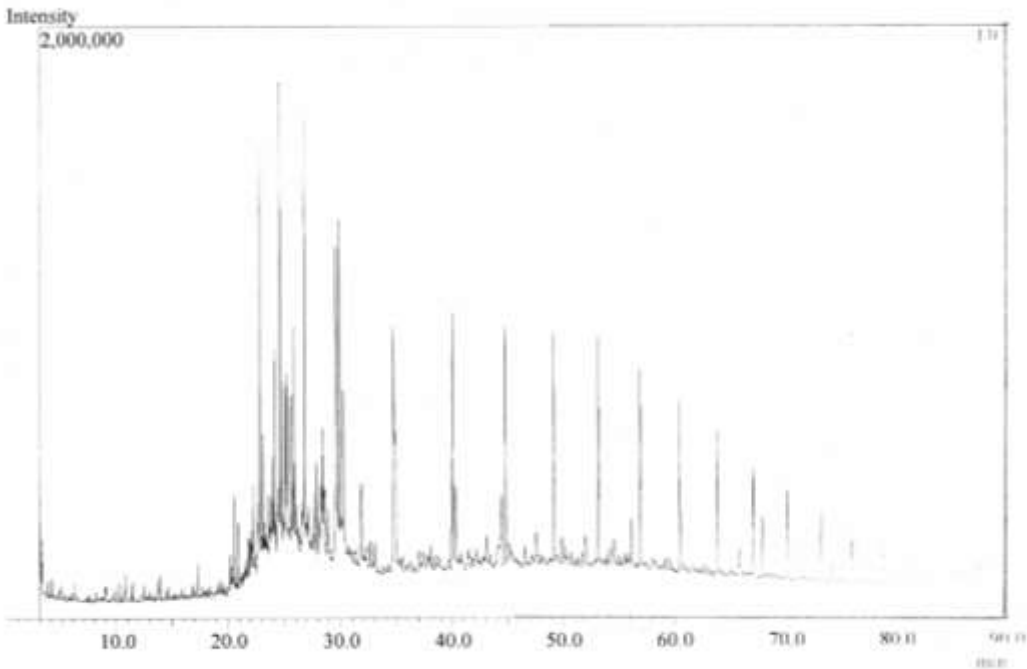


**Fig. S22 GC-MS spectrum of F2 fraction of TX-100 treated RCP-I crude.**





**Fig. S23 GC-MS spectrum of F2 fraction of TX-100 treated RCN-II crude.**



**Fig. S24 GC-MS spectrum of F2 fraction of TX-100 treated RCA-III crude.**