Sudan University of Science and Technology

College of Graduate Studies

Removal of Acids from Sudanese Heavy Crude Oil by Polar Organic Solvents

إزالة الاحماض من الخام السوداني الثقيل بواسطة المذيبات العضوية القطبية

A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

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Sudan
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إستهلال

قال تعالى:

{فَإِذَا فَرَغْتَ فَانْصَبْ (7) وَإِلَى رَبِّكَ فَارْغَبْ(8)}

صدق الله العظيم

[الشرح]

Dedication

To my lovely parents, family
Brothers and sister
In every day and every moment…
I dedicate this work………

Acknowledgement

First, I would like to express my thanks to Allah who is guides me to this success, the thanks extend to my supervisor Dr. Abdalsalam A. Daffaalla for his continuous guidance and encouragement that have been behind the completion of this work.

Second, Special thanks to the family of Petroleum Laboratories for Research and Studies for their appreciated help and valuable advices.

Finally, My gratitude to the staff members of collage of science in Sudan University of science and technology

ABSTRACT

The aim of this study was to investigate the possibility of removing acids from Sudanese heavy crude oil which is characterized by acid number more than 7 mg KOH/g by liquid-liquid extraction technique. In this work polar organic solvents (methanol and ethanol) was used. The processes were applied at different temperatures and organic solvents volumes. The optimum solvent, solvent ratio and temperature were determined. The physical and chemical properties of crude oil sample were tested before and after extraction processes to determine the effect of extraction processes in chemical and physical properties of crude oil sample.

The obtained results showed higher ratio of acids removal (31%,39% and 50%) when ethanol is used as solvent, while methanol gave less amount of removal in the same condition (24%,31% and 36%). The removal of acids was found to be increase with temperature and excess amount of solvent. The highest reduction was appeared when 20 ml of ethanol was added to 80 ml of crude oil at 50°C. The physical and chemical properties of sample after three extraction process were showed slightly decreases in pour point and API, while Gas Chromatography and Fourier Transform Infrared results showed no effects by extraction processes for crude oil sample.

المستخلص

الهدف من هذه الدراسة هو دراسة إمكانية إزالة الأحماض من النفط الخام السوداني الثقيل الذي يتميز برقم حمضي أكبر من 7 مجم KOH / جم بواسطة تقنية الاستخلاص السائل-السائل. في هذا العمل ، تم استخدام المذيبات العضوية القطبية (الميثانول والإيثانول) كما تم تطبيق الطرق في درجات حرارة وأحجام مختلفة من المذيبات العضوية. تم تحديد المذيب الأمثل ونسبة المذيب ودرجة الحرارة.

تم اختبار الخواص الفيزيائية والكيميائية لعينة الزيت الخام قبل وبعد عمليات الاستخراج لتحديد تأثير عمليات الاستخراج على الخواص الكيميائية والفيزيائية لعينة الزيت الخام.

أظهرت النتائج التي تم الحصول عليها ارتفاع معدل التخلص من الحمض (31٪ ، 39٪ و 50٪) عند استخدام الإيثانول كمذيب ، بينما أعطى الميثانول إزالة أقل تحت نفس الظروف (24٪ ، 31٪ و 36٪). وجد أن إزالة الأحماض تزداد مع زيادة درجة الحرارة والمذيب الزائد. ظهر أكبر انخفاض عند إضافة 20 مل من الإيثانول إلى 80 مل من الزيت الخام عند 50 درجة مئوية. أظهرت الخواص الفيزيائية والكيميائية للعينة بعد ثلاث عمليات استخلاص انخفاضًا طفيفًا في النقطة التدفق(الانسكاب) وكثافة API ، بينما لم تظهر نتائج تحليل كروماتوغرافيا الغاز وتحويل فورييه بالأشعة تحت الحمراء أي تأثير لعمليات الاستخلاص علي عينة النفط الخام.

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Abbreviation	**Full meaning**
ASTM	American Society s for Testing and Materials
API	American Petroleum Institute
NA	Naphthenic acids
CNPC	Chinese National Petroleum Company
TAN	TOTAL Acid Number
OSPW	Oil Sands Produced Water
COSMO-RS	Conductor-Like Screening Model for Realistic Solvents
LC-HRMS	Liquid Chromatography-High Resolution Orbitrap Mass Spectrometry
ILs	Ionic Liquids
[EMIM][EtSO4]	1-Ethyl-3-Methylimidazolium Ethyl Sulfate IL

Chapter one

1.1 Introduction

In modern societies the demand of energy increases every new day, this increase facing with many challenges some of them economical other environmental difficulties. Among these challenges Petroleum is perhaps the most important source of energy consumed in modern society new and in near future. Due to high energetic flexibility which provides raw materials for many industry sectors like transportation sector, plastic sector, electricity sector, agriculture sector industrial sector and medicine sector. So, we can conclude that the petroleum mean life for modern and poor area in the world as in Figure (1.1).

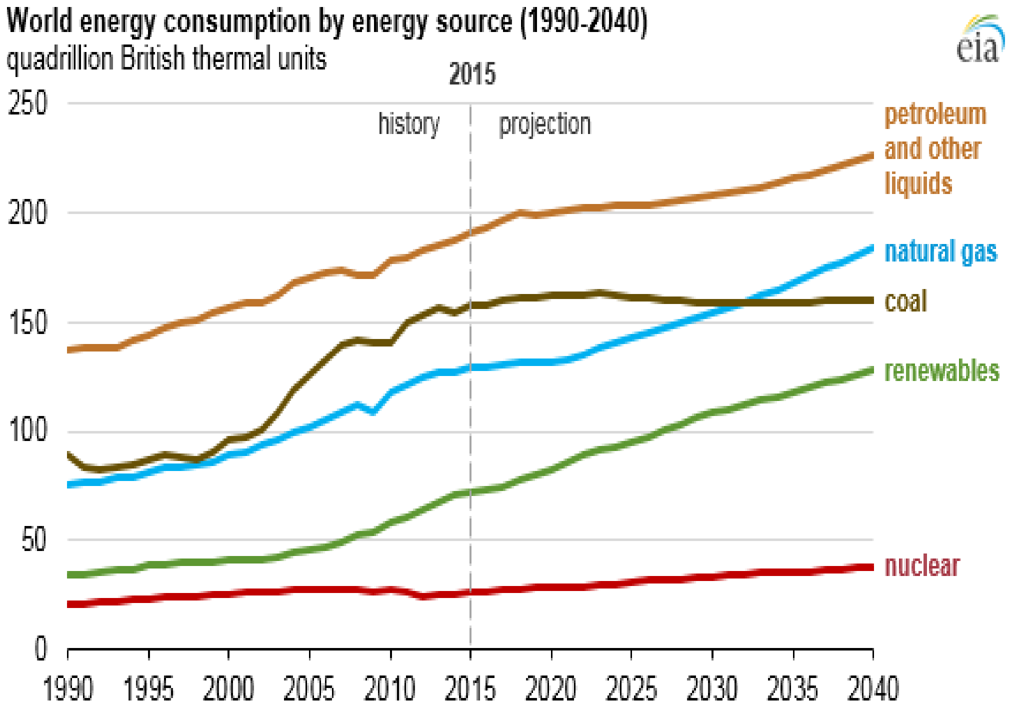
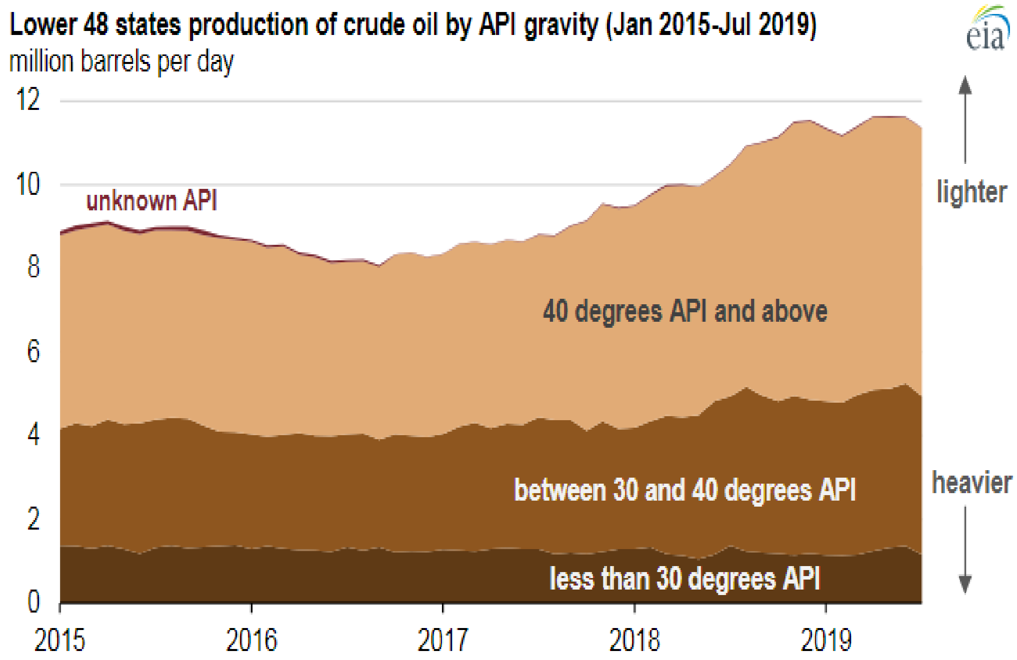


Figure No (1.1) world energy consumption per energy source

Petroleum, more properly called Crude oil, is a complex mixture of thousands (maybe millions!) of compounds. While most of these compounds are hydrocarbons. Some of these hydrocarbons contain oxygen, nitrogen, or sulfur, and there are trace amounts of metals, the naturally occurring petroleum deposits which the petroleum engineer encounters are composed of organic chemicals. Although all crude oils contain the composition described above, rarely to found two crude oils with the same characteristics. This is so because every crude oil from whatever geographical source contains different quantities of the various compounds that makes up its composition. when refer to the type of fluid in the reservoir Crude oils produced in Nigeria for example would be high in cyclic paraffin content and have a relatively low specific gravity. Crude drilled in some of the fields in Venezuela and Canada on the other hand would have a very high gravity (low API) and a low content of material boiling below 350◦C. This type of crude oil found in unconsolidated reservoir ⁽¹⁾. Crude oils can be classified in a number of ways. Chemically crude oil classified according to the type of compounds that formed the general composition of the crude oil. If the chemical mixture has high number of paraffin with the molecular formula C_nH_{2n+2} the crude can classified as paraffinic crude oil for instance, crude oil which contains a predominance of paraffinic molecules will yield very fine lubricating oils from the gas-oil fraction and paraffin wax from the residuum. If the crude oil has much numbers of aromatic compounds with molecular formula C_6H_6 can classify as aromatic crude oil while the classification also can applied to the asphaltic and naphthenic crude oil according to main composition of crude and the amount of asphaltene and naphthene compound ratio in the composition of crude oil if the larger molecules are aromatic and asphaltic, the heavier fractions of the crude oil are useful for pitch, roofing compounds, paving asphalts, and other such applications⁽²⁾. Physically the crude oil chemical mixture is composed of small molecules from (C1 to C4) it is a gas at normal temperatures and pressures, when the mixture contains larger molecules from (C5 to C16) it is a liquid at normal temperatures and pressures, more than C_{16} is consider solid form (waxy) of crude oil ⁽³⁾.

According to quality tests of crude oil we can classified the crude oil by using American Institute of Petroleum density (API) to light, moderate and heavy crude oil. Each of this classification has certain properties that can determine the quality of crude oil, treatment process required, the price, transportation procedure and even the refinery products in which the crude oil normally is separated into crude fractions according to the range of boiling points of the compounds included in each fraction to use in other types of industries . According to API crude oil can classified to light crude oil has an API gravity higher than 31.1°, medium oil has an API gravity between 22.3 and 31.1°, heavy crude oil has an API gravity below 22.3° and extra heavy oil has an API gravity below 10.0°^(4)^.



Source: U.S. Energy Information Administration, *Monthly Crude Oil and Natural Gas Production Report*

Figure No (1.2) Classification of crude oil according to API

Liquids obtained from different petroleum reservoirs have widely different characteristics. Some are black, heavy, and thick, like tar, while others are brown or nearly clear with low viscosity and low specific gravity Crude petroleum varies in appearance from a yellow or green mobile liquid to darker and often almost black syrup fluids, sometimes solidifying to a black paste. This great variety in appearance is obviously caused by differences in composition. While some crude oils consist mainly of paraffin, others may be more cycloparaffin (naphthenic) or aromatic in character. As for molecular size of the constituents, here again some oils may be particularly rich in hydrocarbons of low molecular weight, whereas others contain a high percentage of large, complicated molecule (5).

Recently new classification of crude oil discovered depend on amount of acid in crude oil determine as total acid number. If the amount of acid more than 1 mg KOH/g crude oil can classify as high acidic crude oil which called HAC crude oil. And the acid called naphthenic acid (6). In petroleum industry, high acidity crude oils are less desirable than normal oils because of the corrosion problems and high cost of the processing but, high acidity oils provide an economic opportunity, as well as a technical challenge for the petrochemical enterprises. In last year's proved reserves and annual production of high acidity crudes are increasing steadily, and they have become an important target of exploration, exploitation and utilization Consequently, it is quite necessary to study the composition and origin of high acidity crude oils. due to low cost some country have started to import heavy and high acid crude oil to process it in certain refinery which design to process these types of crude oil like Matura refinery in India and Huzhou refinery in China but still the corrosion problem caused in storage and transport, so correspondingly these oils have a relatively lower price (7).

Petroleum acids constituents in crude oils that composed from organic acids, inorganic acids and some other compounds which could influence the oil acidity such as esters, phenols, amines and pyrrole series the origin of this high acidity crude oils can be assorted into the following (8).

- Primary biodegradation type.
- Secondary biodegradation type.
- Mixed type.

Petroleum biodegradation is alteration in crude oil composition attributes to living organism in areas where there are high hydraulic head conditions (groundwater recharge areas at high altitudes), meteoric waters penetrate along high porosity/high permeability strata deeply into sedimentary basins. They are oxygenated and carry bacteria. Wherever these waters flow past petroleum accumulations, they cause biodegradation and water washing effect. Compounds which have higher solubilities in water, such as benzene and toluene, are preferentially removed. Several species of bacteria degrade and consume petroleum hydrocarbons in a very specific way.

Depending on favorable microbial growth conditions, the molecular composition of reservoir petroleum's is altered to an increasing extent and hydrocarbons are preferentially destroyed, but sulphur, oxygen and nitrogen-containing compounds can also be degraded producing new compounds such as acyclic, saturated and aromatic carboxylic acids and phenols in addition to complex variety of acidic non-hydrocarbons is generated from the aromatic heterocycles found in oil. The heterocyclic acids with multiple different heteroatoms are the main cause of corrosion problems during processing of heavy degraded oils (9). The term naphthenic acid, as commonly used in the petroleum industry, refers collectively to all of the carboxylic acids present in crude oil. Naphthenic acids are classified as monobasic carboxylic acids of the general formula RCOOH, where R represents the naphthene moiety consisting of cyclopentane and cyclohexane derivatives. Naphthenic acids are composed predominantly of alkyl-substituted cycloaliphatic carboxylic acids, with smaller amounts of acyclic aliphatic (paraffinic or fatty) acids. Aromatic, olefinic, hydroxy, and dibasic acids are considered to be minor components. Commercial naphthenic acids also contain varying amounts of unsaponifiable hydrocarbons, phenolic compounds, sulfur compounds, and water. The complex mixture of acids is derived from straight-run distillates of petroleum, mostly from kerosene and diesel fractions. Naphthenic acids have been the topic of numerous studies extending over many years. Originally recovered from the petroleum distillates to minimize corrosion of refinery equipment, they have found wide use as articles of commerce in metal naphthenates and other derivatives.

The consequences of biodegradation on the composition and physical properties of crude oil and natural gases are well known. Oxidation of oil (C_{6+} components) during biodegradation leads to a decrease in saturated hydrocarbon content (and to a smaller decrease in aromatic hydrocarbon content) and API gravity, a measure that correlates with economic value, whereas oil density, sulphur content, acidity, viscosity and metal content increase (10).

Problems associated with naphthenic acids in crude oils are of concern due to their corrosivity to refinery units (11) It is highly desirable to determine the ring-type distribution and the carbon number distribution of each ring type because the corrosivity of naphthenic acids is dependent on their size and structure. The characterization of naphthenic acids is also of interest in geochemical studies, particularly migration and biodegradation (12), and to refinery wastewater treatment for environmental.

1.2 Crude oil in Study area:

Sudan heavy crude share represents 18% of the global production (13). which holds 5,000,000,000 barrels of proven oil reserves as of 2016, ranking 23rd in the world and accounting for about 0.3% of the world's total oil reserves of 1,650,585,140,000 barrels. Sudan has proven reserves equivalent to 97.8 times its annual consumption. This means that, without Net Exports, there would be about 98 years of oil left (at current consumption levels and excluding unproven reserves) (14).

The Fula sub-basin is a fault-bounded depression located in the NE of the Muglad Basin, Sudan, and covers an area of about 3560 km2. Eleven oilfields and oil-bearing structures have been discovered in the sub-basin. The Lower Cretaceous Abu Gabra shales (Barremian–Aptian), deposited in a deep-water lacustrine environment, are major source rocks. Reservoir targets include interbedded sandstones within the Abu Gabra Formation and sandstones in the overlying Bentiu and Aradeiba Formations (Albian – Cenomanian and Turonian, respectively) (15).

Oil-source correlation indicates that crude oils in the Aradeiba and Bentiu Formations are characterized by low APIs (<22°), low sulphur contents (<0.2%), high viscosity and high Total Acid Number (TAN: >6 mg KOH/g oil on average). By contrast, API, viscosity and TAN for oils in the Abu Gabra Formation vary widely. These differences indicate that oil migration and accumulation in the Fula sub-basin is more complicated than in other parts of the Muglad Basin, probably as a result of regional transtension and inversion during the Late Cretaceous and Tertiary.

Fula crude oil was produced in Western Kordofan region in Almoglad basin; the field had an area of 38468 Sq. km. Since 1995 the Chinese National Petroleum Company (CNPC) had worked at the field and exploded some new fields in Fula North, Fula West, Mega, Hadida, Naha, Kaikan and Sifan, which contain over 60 wells that form Fula mix crude. The proposed production rate was 40,000 bpd. The expected reserve from the reservoir was 115 BPD of crude oil with a recovery factor (15-20) %. The field facilities were made to cater production rate up to 40000 bpd, for the processing unit at size up to 200000 bpd for the pipeline to Khartoum refinery. Fula crude oil in general heavy crude from geologically young formation have the highest naphthenic acids content, high calcium content made it caused fouling and scaling problems, that increase the operation and maintenance cost. Under certain conditions, the naphthenic acids present in acidic crude oil will precipitate with calcium ions (Ca^{++}) that present in co-produced water and form calcium naphthenate and, to a lesser extent form other metal naphthenates. Another property of Fula crude is high viscosity (i.e. very high temperature should be kept throughout the whole processing operation) and this is expensive from the standpoint of cost (16).

In order to improve the quality of such crude oil and to save cost, it becomes very important to remove NA compounds from it. Researchers, as well as the oil and gas industries, have been working on how to overcome this challenge, and several techniques have been developed for the removal of naphthenic acid from the crude oil. Removing of naphthenic compound from crude oils are regarded as one of the most important process in heavy oil upgrading currently industrial process are depended on dilution or quastic washing method to reduce total acid, furthermore adsorption process by using active catalyst (14).

Chapter two

2.0 Literature review:

2.1 Composition of crude oil:

larger part of crude oil consists of alkanes, cycloalkanes (naphthenes), and aromatics, with smaller amounts of polycyclic aromatics, Sulphur-containing compounds, nitrogen-containing compounds, oxygen-containing compounds, and more. The crude oil mixture is composed from many elements with high ratio of hydrogen and carbon elements as in general crude oil composed from following groups of compounds and elements:

- Hydrocarbon compounds (compounds made of carbon and hydrogen).
- Non-hydrocarbon compounds.
- Organometallic compounds and inorganic salts (metallic compounds).

These groups of elements distributed in the crude oil by different ratio according to the origin, nature and type of crude oil as table (2.1) (17):

Table No (2.1) Composition analysis of crude oil

Element	**Composition (wt%)**
Carbon	83.0-87.0
Hydrogen	10.0-14.0
Sulphur	0.05-6.0
Nitrogen	0.1-2.0
Oxygen	0.05-2.0
Ni	< 120ppm
V	< 1200ppm

Crude oils and high-boiling crude oil fractions are composed of many members of a relatively few homologous series of hydrocarbons (18). The composition of the total mixture, in terms of elementary composition, but small differences in composition can greatly affect the physical properties and the processing required producing satiable products. Petroleum is essentially a mixture of hydrocarbons, and even the non-hydrocarbon elements are generally present as components of complex molecules, predominantly hydrocarbon in character, but containing small quantities of oxygen, sulfur, nitrogen, vanadium, nickel, and chromium (19). There are three main classes of hydrocarbons. These are based on the type of carbon–carbon bonds present. These classes are (20):

- Saturated hydrocarbons contain only carbon–carbon single bonds. They are known as paraffins (or alkanes) if they are acyclic, or naphthene's (or cycloalkanes) if they are cyclic.
- Unsaturated hydrocarbons contain carbon–carbon multiple bonds (double, triple or both). These are unsaturated because they contain fewer hydrogens per carbon than paraffins. Unsaturated hydrocarbons are known as olefins. Those that contain a carbon–carbon double bond is called alkenes, while those with carbon–carbon triple bond are alkynes.
- Aromatic hydrocarbons are special class of cyclic compounds related in structure to benzene.
- In addition, in some references there is a fourth class called olefins, it was very small or neglectable in crude oil but it is formed during processing by the cracking or dehydrogenation of paraffins and naphthene

2.1.1 Paraffins:

The paraffin series of hydrocarbons is characterized by the rule that the carbon atoms are connected by a single bond, and the other bonds are saturated with hydrogen atoms. The general formula for paraffins is $C_nH_{2n+2.}$ The simplest paraffin is methane. CH_4 , followed by the homologous series of ethane; propane; normal and isobutane; and normal, iso-, and neopentane. When the number of carbon atoms in the molecule is greater than three, several hydrocarbons may exist that contain the same number of carbon and hydrogen atoms but have different structures. This is because carbon is capable not only of chain formation, but also of forming single- or double-branched chains that give rise to isomers that have significantly different properties. For example, the motor octane number of n-octane is-17 and that of isooctane (2.2,4-Erimethyl pentane) is 100.The number of possible isomers increases in geometric progression as the number of carbon atoms increases. There are two paraffin isomers of butane, 3 of pentane, and 17 strtctural isomers of octane, and by the time the number of carbon atoms has increased to 18, there are 60,533 isomers of cetane. Crude oil contains molecules with up to 70 carbon atoms, and the number of possible paraffinic hydrocarbons is very high (21).

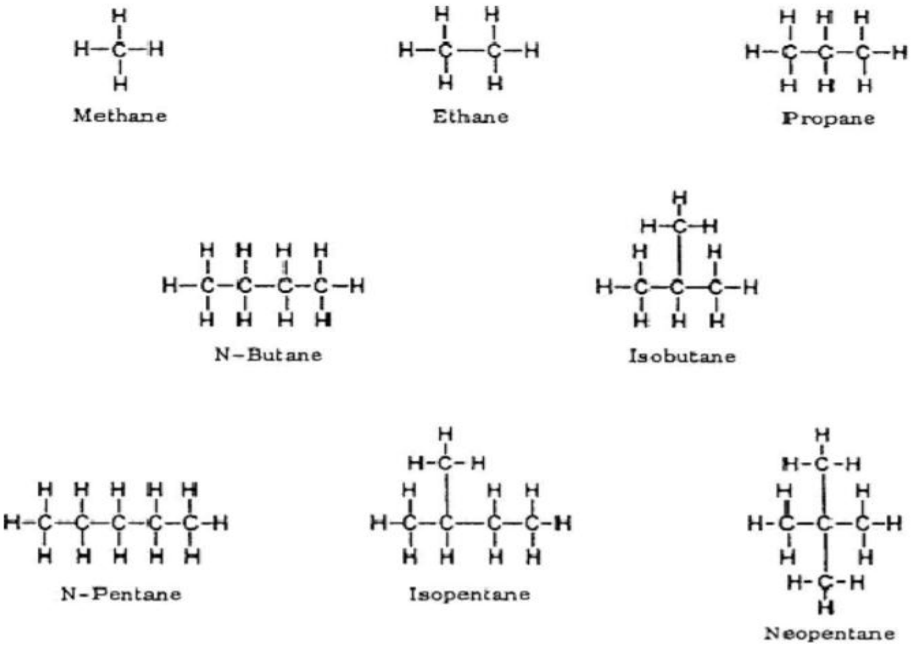
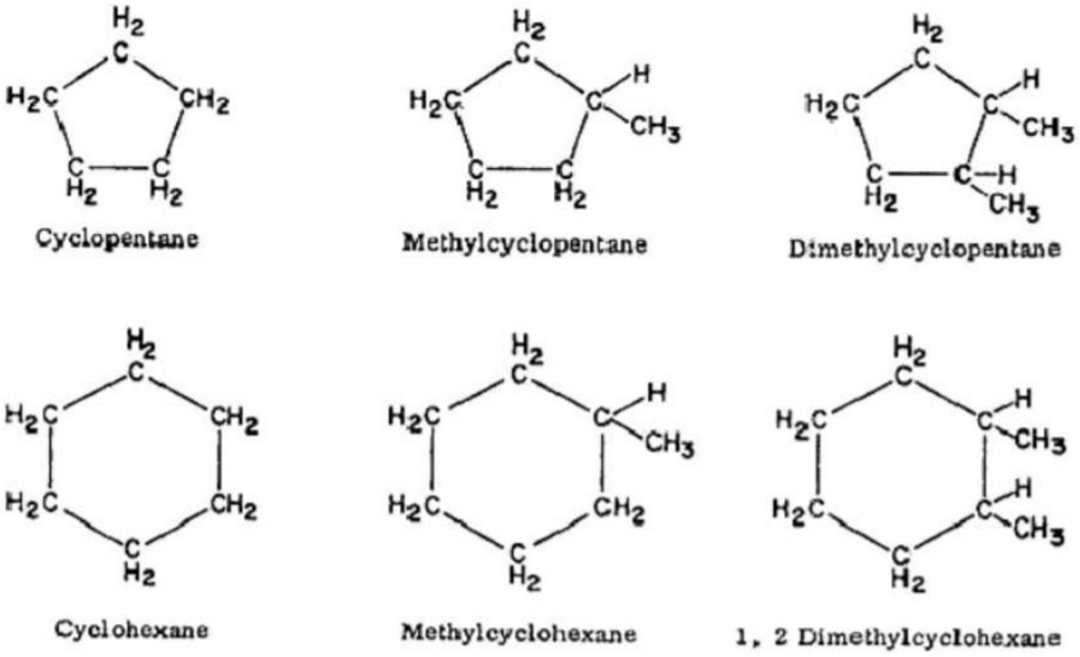


Figure No (2.1) Some paraffins compounds found in crude oil.

2.1.2 Naphthene (Cycloparaffins):

Cycloalkanes (or cycloparaffins), also called naphthenes in the petroleum industry, are saturated hydrocarbons containing structures with carbon atoms linked in a ring. There are many types of naphthenes present in crude oil, but, except for the or molecular weight compounds such as cyclopentane and cyclohexane are generally not handled as individual compounds. low-molecular-weight naphthenic acids (8–12 carbons) are compounds having either a cyclopentane or a cyclohexane ring with a carboxyalkyl side chain. These compounds are normally found in middle distillates such as kerosene and gas oil. High boiling napthenic acids from the lube oils are monocarboxylic acids, (Cl4-Cl9) with an average of 2 to 6 rings. They are classified according to boiling range and their properties determined with the help of correlation factors such as the K factor Naphthenic acids constitute about 50 wt% of the total acidic compounds in crude oils. Naphthenic-based crudes contain a higher percentage of naphthenic acids. Consequently, it is more economical to isolate these acids from naphthenic based crudes. The production of naphthenic acids from middle distillates occurs by extraction with 7–10% caustic solution (22). Some typical naphthcnic compounds are shown in Figure (2).



Cyclopentane
Methylcyclopentane
Dimethylcyclopentane
Cyclohexane
Methylcyclohexane
1, 2 Dimethylcyclohexane

Figure No (2.2) Naphthenes compound in crude oil

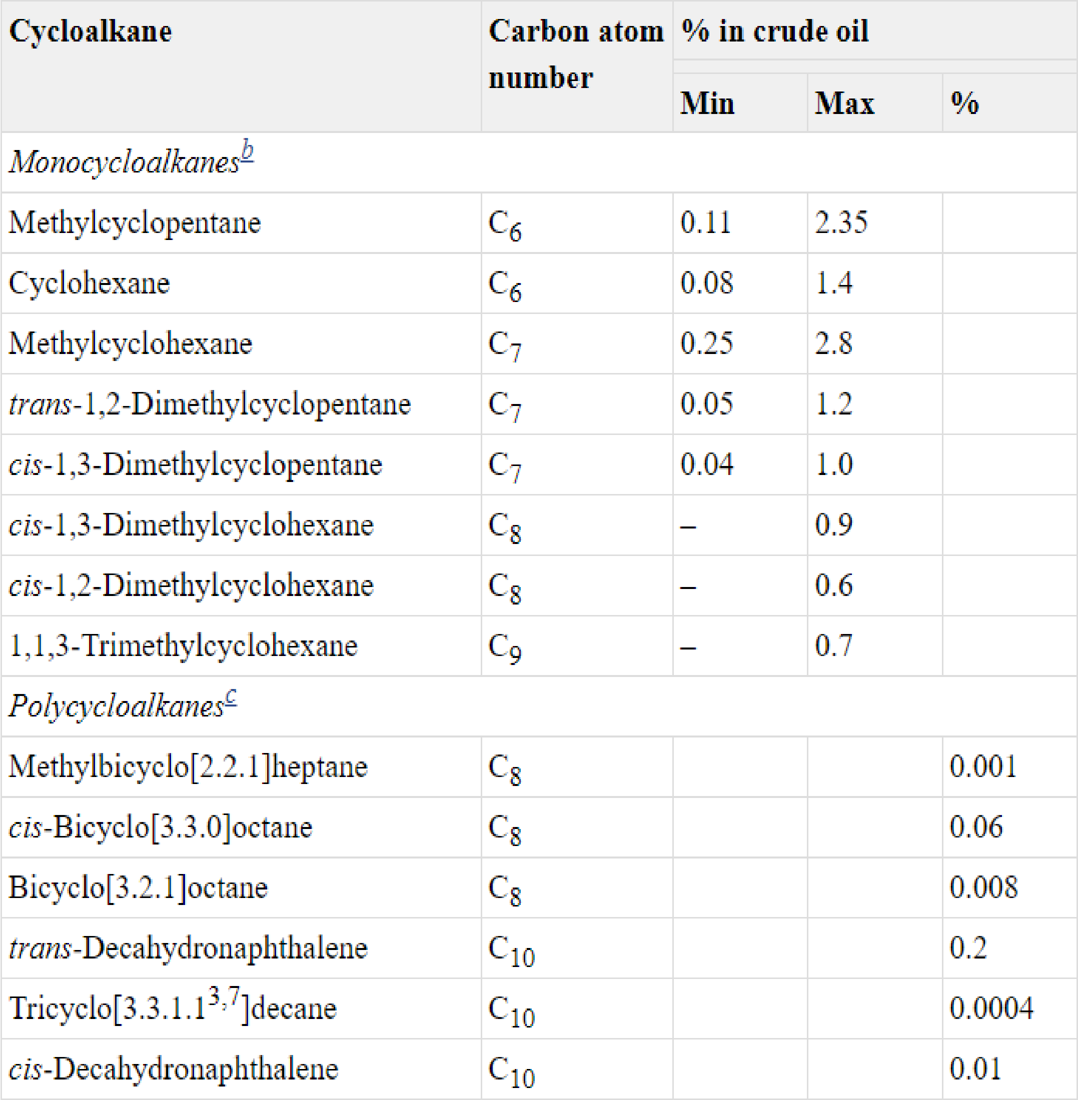
The cycloalkane composition in crude oil worldwide typically varies from 30% to 60%. The predominant monocycloalkanes in crude oil are in the cyclopentane series, having five carbon atoms in the ring, and in the cyclohexane, having a six-membered ring. Usually appear in the higher boiling fractions, such as lubricating oils, cycloalkanes with two or more rings are common, and structures containing up to ten rings have been reported. These polycyclic structures are usually composed of fused five- and six-membered rings (23).

Small number of cycloparaffin have been isolated so far, cyclohexane derivatives, cyclopentane derivatives, and decahydronaphthalene (decalin) derivatives (naphthenes) are largely represented in oil fractions. In addition, crude oil also contains polycyclic naphthenes, such as terpenes, and such molecules (often designated bridge-ring hydrocarbons) occur even in the heavy gasoline fractions (boiling point 150°C–200°C, 300°F–390°F). Naphthene rings may be built up of a varying number of carbon atoms, and among the synthesized hydrocarbons there are individual constituents with rings of the three-, four-, five-, six-, seven-, and eight-carbon atoms. It is now generally believed that crude oil fractions contain chiefly five- and six-carbon rings. Only naphthenes with five- and six-membered rings have been isolated from the lower-boiling fractions. Thermodynamic studies show that naphthene rings with five- and six-carbon atoms are the most stable. The naphthenic acids contain chiefly cycle pentane as well as cyclohexane rings (24).

cycloparaffin derivatives in petroleum varies up to 60% of the total hydrocarbons and the structure of these constituents may change within the same crude oil as a function of the molecular weight or boiling range of the individual fractions as well as from one crude oil to another.

The main structural variation of naphthenes is the number of rings present in the molecule. mono and bicyclic naphthenes are generally the major types of cycloparaffin derivatives in the lower-boiling fractions of petroleum, on the other hand when boiling point or molecular weight increased by the presence of alkyl chains like in higher-boiling fractions, such as the lubricating oils, may contain two to six rings per molecule. In the asphaltic (naphthenic) crude oils, the gas oil fraction can contain considerable amounts of naphthenic ring systems that increase even more in consideration of the molecular types in the asphaltenes. However, as the molecular weight of the fraction increases, the occurrence of condensed naphthene ring systems and alkyl-substituted naphthene ring systems increases (25).

Table No (2.2) Predominant cycloalkanes isolated from crude oil for Reference crude oil from American Petroleum Institute



Cycloalkane	**Carbon atom number**	**% in crude oil**		
		Min	**Max**	**%**
Monocycloalkanes[b]				
Methylcyclopentane	C_6	0.11	2.35	
Cyclohexane	C_6	0.08	1.4	
Methylcyclohexane	C_7	0.25	2.8	
trans-1,2-Dimethylcyclopentane	C_7	0.05	1.2	
cis-1,3-Dimethylcyclopentane	C_7	0.04	1.0	
cis-1,3-Dimethylcyclohexane	C_8	–	0.9	
cis-1,2-Dimethylcyclohexane	C_8	–	0.6	
1,1,3-Trimethylcyclohexane	C_9	–	0.7	
Polycycloalkanes[c]				
Methylbicyclo[2.2.1]heptane	C_8			0.001
cis-Bicyclo[3.3.0]octane	C_8			0.06
Bicyclo[3.2.1]octane	C_8			0.008
trans-Decahydronaphthalene	C_{10}			0.2
Tricyclo[3.3.1.1^{3,7}]decane	C_{10}			0.0004
cis-Decahydronaphthalene	C_{10}			0.01

2.1.3 AROMATICS:

The aromatic series of hydrocarbons is chemically and physically very different from the paraffins and cycloparaffins (naphthenes). Aromatic hydrocarbons contain a benzene ring, which is unsaturated but very stable, and frequently behave as saturated compounds (24). Monocyclic aromatics are valuable components in fuels, especially gasolines, because they improve their octane number. Aromatic hydrocarbons are highly stable at high temperatures, thereby leading to the desirable effect of knock-less combustion in gasoline-fueled engines. They are not desirable in fuels intended for use in spontaneous-ignition engines because they cause rough engine operation and decrease the fuel's cetane number, thus delaying spontaneous ignition (26).

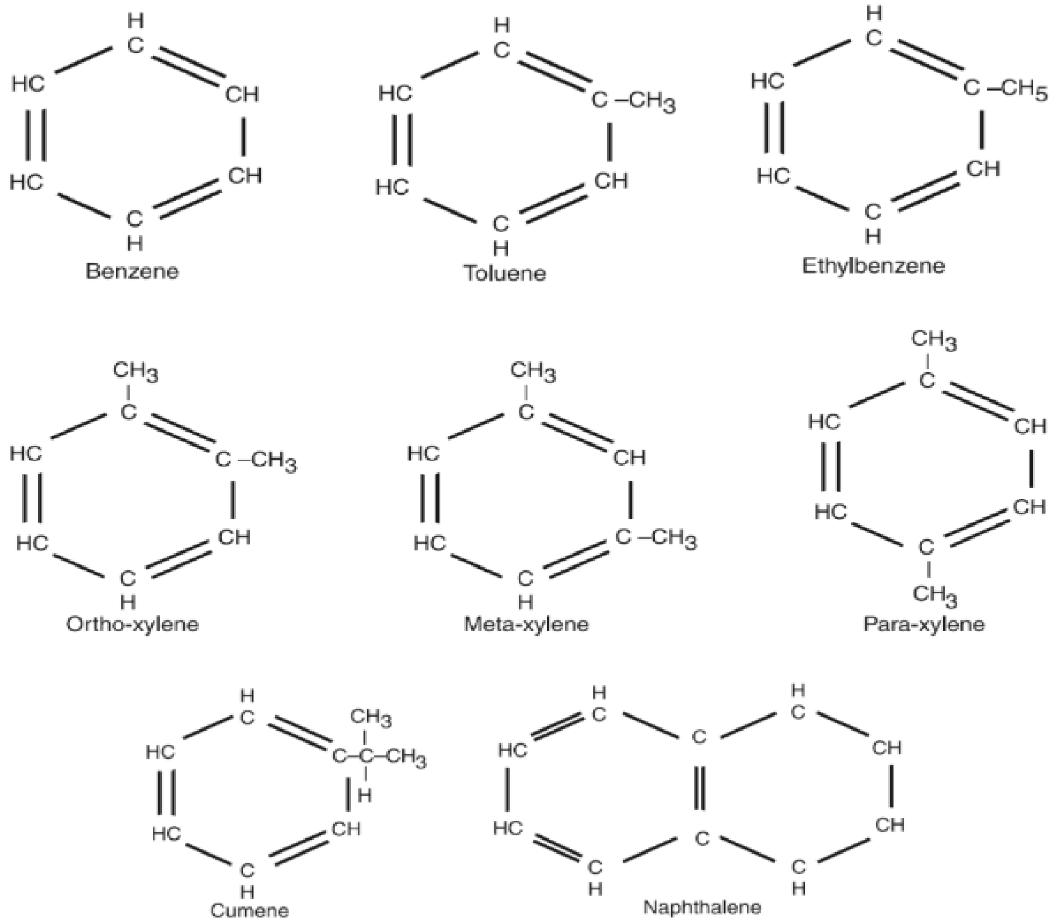


Figure (2.3) Aromatics hydrocarbons in crude oil

Generally, increase the proportion of aromatic hydrocarbons with increasing molecular weight. However, aromatic hydrocarbons without the accompanying naphthene rings or alkyl-substituted derivatives seem to be present in appreciable amounts only in the lower petroleum fractions. Thus, the limitation of instrumentation notwithstanding, it is not surprising that spectrographic identification of such compounds has been concerned with these low-boiling aromatics.

Major of aromatics are present in gasoline fractions, but the benzene content is usually low compared to the benzene homologues, such as toluene and the xylene isomer. Aromatics without naphthene rings appear to be relatively rare in the heavier fractions of petroleum (e.g., lubricating oils). In the higher-molecular-weight fractions, the rings are usually condensed together. Thus, components with two aromatic rings are presumed to be naphthalene derivatives and those with three aromatic rings may be phenanthrene derivatives(27). When Study of different types of crude oil higher-boiling petroleum fractions, many polycyclic structures occur in naphthene–aromatic systems. The naphthene–aromatic hydrocarbons, together with the naphthenic hydrocarbon series, form the major content of higher-boiling petroleum fractions. Usually, the different naphthene–aromatic components are classified according to the number of aromatic rings in their molecules.

The first to be distinguished is the series with an equal number of aromatic and naphthenic rings. The first members of the bicyclic series C9–C11 are the simplest, such as the 1-methyl-, 2-methyl, and 4-methylindanes and 2-methyl- and 7-methyltetralin. Tetralin and methyl-, dimethyl-, methyl ethyl-, and tetramethyltetralin have been found in several crude oils, particularly in the heavier, naphthenic, crude oils and there are valid reasons to believe that this increase in the number of rings and side-chain complexity continues into the heavy oil and bitumen feedstocks.

It is necessary to make a chemical classification of petroleum since chemical properties are very crucial in selecting the right method for processing the oil. There are many classifications with regard to fractions and chemical compositions of petroleum. So according to the composition of crude oil we can classified the crude oil into five classes showed in Table (2.3).

Table No (2.3) Classification of crude using 250-300°C fraction

Class	Composition of 250-300°C fraction wt.%				
	Para	Naphth.	Arom.	Wax	Asph
Paraffinic	46-61	22-32	12.0-25	1.5-10	0.6-6
Paraffinic-Naphthenic	42-45	38-39	16-20	01-6.0	6
Naphthenic	15-26	61-76	8.0-2013	trace	0.6-6
Par -Naphc- Aro	27-35	36-47	26-33	0.5-1	0-10
Aromatic	0-8	57-78	20-25	0-0.5	0-20

2.1.4 Olefins:

Olefins are unsaturated compounds with a formula of C_nH_{2n}. They are very similar in structure to paraffin's, but at least two of the carbon atoms are joined by double bonds. Compared to paraffins, olefins are unstable and can react with themselves or with other compounds such as oxygen and bromine solution.

Olefins do not occur naturally in crude oil. However, show up in the FCC feed as a result of preprocessing the feeds elsewhere. These processes include thermal cracking and other catalytic cracking operations (22). Olefins arc generally undesirable in finished products because the double bonds are reactive and the compounds are more easily oxidized and polymerized to form gums and varnishes. it gasoline boiling-range fractions, some olefins are desirable because olefins have higher octane numbers than paraffin compounds with the same number of carbon atoms. Olefins containing five carbon atoms have high reaction rates with compounds in the atmosphere that form pollutants and, even though they have high research octane numbers, are considered generally undesirable. Some diolefins (containing two double bonds) are also formed during processing, but they react very rapidly with olefins to form high molecular weight polymers consisting of many simple unsaturated molecules joined together as in Figure (2.4). Diolefins are very undesirable in products because they are so reactive, they polymerize and form filter- and equipment plugging compounds (28).

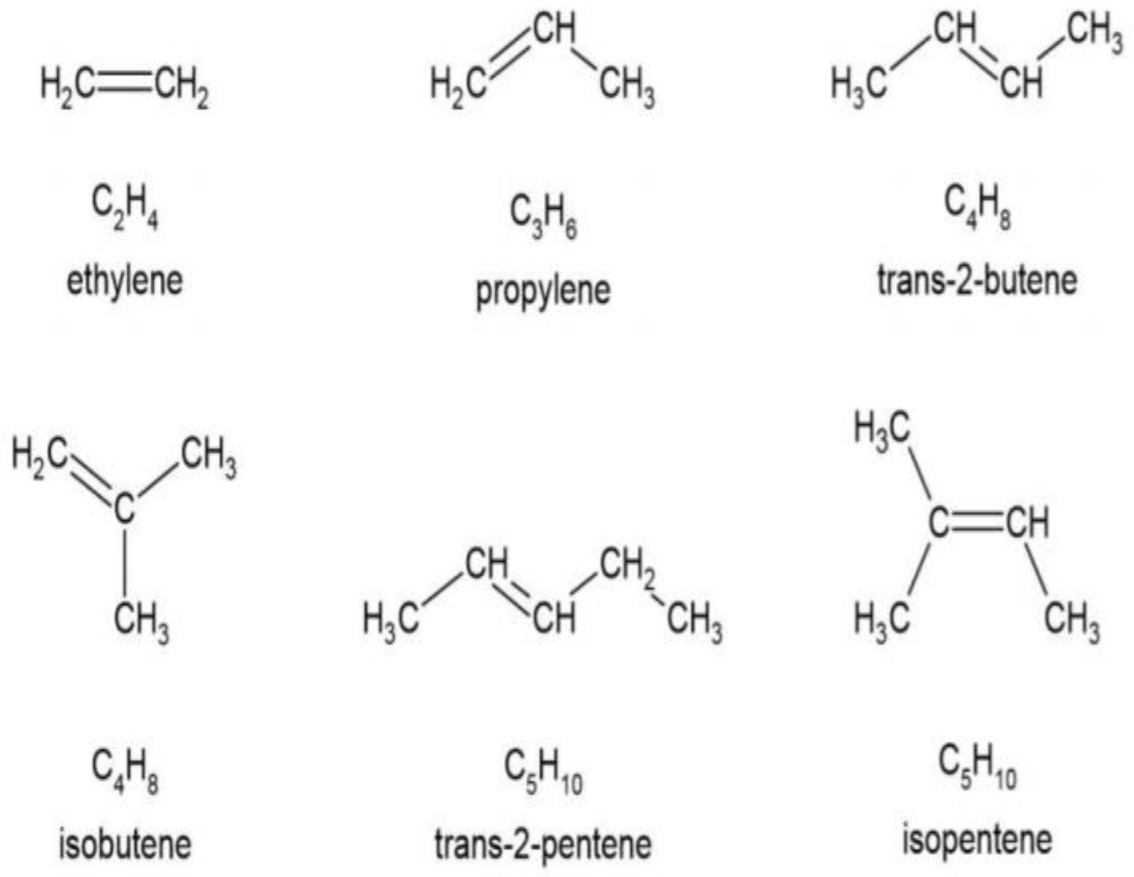


Figure No (2.4) Olefin compounds formed during crude oil process

2.1.5 Nonhydrocarbons:

2.1.5.1 Sulfur Compounds:

In addition to carbon and hydrogen, sulfur is the most abundant chemical element in petroleum, occurring at concentrations of over 10 wt.% in some heavy oils. Sulfur in crude oil comes generally from by two theories one of them is the decomposition of organic matter, depending on the time factor, which gradually settling into strata, the sulfur segregates from crude oil in the form of hydrogen sulfide that appears in the associated gas, some portion of sulfur stays with the liquid. Another theory behind origin of sulfur compounds is the reduction of sulfates by hydrogen by bacterial action of the type desulforibrio desulfuricans:

$$4H_2 + SO_4^{=(bacteria)} \rightarrow H_2S + 2OH^- + 2H_2O$$

Hydrogen comes from the reservoir fluid and the sulfate ions are kept in the reservoir rock, as a result hydrogen sulfide is generated. The H2S formed then react with the sulfates or rock to form sulfur that remains in composition of crude as in the case of oil from Goldsmith, Texas, USA. In addition, under pressure, temperature and period of formation of the reservoir conditions H2S can react with the hydrocarbons to give sulfur compounds as (28):

$$3H_2S + SO_4 \rightarrow 4S + 2OH^- + 2H_2O$$

The sulfur content of petroleum ranges from some hundredths of a percent to 8%. 3-S In rare cases, the sulfur content may reach 9.6%6 and even 14% this contributes to petroleum geochemistry, has potential utility in predicting the geological distribution of oils with high or low sulfur contents, and also has important implications for enhanced oil recovery and refining operations involving sulfur-rich crude oils (29). On other hand Increased use of sulfur-rich crude oils and increased appreciation of the environmental impact of sulfur compounds in crude oils and their products have led to consider much attention to desulphurization in the recent years to protect the environment (30)

Although each crude oil has different amounts and types of sulfur compounds the highest sulfur compound contents are observed in oils occurring at a depth of 1.5-2 km. Oils from smaller depths display a lower sulfur compound content. With increasing depth temperature and pressure increase, the catagenic processes become more intense and the petroleum undergoes gradual desulfurization. The sulfur compound destruction is accompanied by hydrogen sulfide evolution (31). Sulfur compounds in petroleum may take one of the following compound forms as hydrogen sulfide (H_2S), mercaptans, sulfides, disulfides, thiophenes, etc. or as elemental sulfur. but as a rule, the proportion, stability, and complexity of the compounds are greater in heavier crude-oil fractions.

Sulfur causes acid rain and combines with hydrogen to form hydrogen sulfide which is a major air pollutant. Sulfur compounds also causes corrosion in pipelines and downstream and contributor to corrosion in refinery processing units (32). Moreover, the corrosive sulfur compounds have an obnoxious odor.

Pyrophoric iron sulfide results from the corrosive action of sulfur compounds on the iron and steel used in refinery process equipment, piping, and tanks. The combustion of petroleum products containing sulfur compounds produces undesirables such as sulfuric acid and sulfur dioxide. Catalytic hydrotreating processes such as hydrodesulfurization remove sulfur compounds from refinery product streams. Sweetening processes either remove the obnoxious sulfur compounds or convert them to odorless disulfides, as in the case of mercaptans (33). Compounds that contain aliphatic sulfur (sulfides and thiols) have been found easier to remove than compounds containing aromatic sulfur (thiophenic compounds), which are present in higher proportions in heavy crude oils (34). Sulfur compounds have subclass depended on the chemical form which found in it inside the crude oil for examples:

- Free Elemental Sulfur S: Free sulfur is rarely present in crude oils, but it can be found in suspension or dissolved in the liquid. The crude from Goldsmith (Texas, USA.) is richest in free sulfur (1% by weight for a total sulfur content of 2.17%). It could be produced by compounds in the reservoir rock by sulfate reduction
- Hydrogen Sulfide H_2S: H_2S is found in the reservoir gas and dissolved in the crude < 50 ppm wt.%, also formed during refining operations such as catalytic cracking, hydrodesulphurization, and thermal cracking or by thermal decomposition of sulfur—containing hydrocarbons during distillation (35).

In the 1950's, scantiest classified crude oils were either corrosive (sour), or non-corrosive (sweet). Crudes containing more than 6 ppm of dissolved H_2S were classed as sour because, beyond this limit, corrosion was observed on the walls at storage tanks by formation of scales of pyrophoric iron sulfides. At this point in time, the total sulfur content of crudes was not taken into consideration, since most of them were produced and refined in the United-States and contained less than 1%, and only the gasoline coming from corrosive crudes needed sweetening (elimination of thiols) for them to meet the specifications then in force. Today all crudes containing inure than one per cent sulfur are said to be “corrosive”. Thiols: Thiols are a class of organic compounds that contain a sulfhydryl group (SH), also known as a thiol group, also known as mercaptans are acidic in behavior owing to their S - H functional group; they are corrosive and malodorous. This molecular structure in which composed of a sulfur atom and a hydrogen atom attached to a carbon atom is what distinguishes thiols from other organic chemical compounds with an oxygen-to carbon bond configuration, such as phenols and alcohols. It’s also what gives many high volatility thiols a persistent and highly unpleasant odor that is reminiscent of rotten eggs. Their concentration in crude oils is very low if not zero, but they are created from other sulfur compounds during refining operations and show up 10 the light cuts (36). as illustrated in Table (2.4):

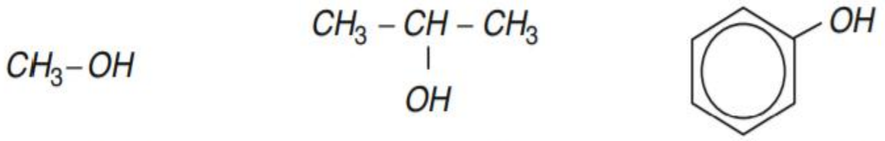
Table (2.4) sulfur compounds during the refinery process

Nature of cut (temperature interval, °C	Mercaptan %	Total sulfur, %	Mercaptan sulfur%
Crude petroleum	0.11	1.8	0.6
Butane	0.0228	0.0228	100
Light gasoline (20-70 °C)	0.0196	0.024	82
Heavy gasoline(70-150°C)	0.0162	0.026	62
Naphtha (150-190°C)	0.0084	0.059	14
Kerosene (190-250°C)	0.0015	0.17	0.9
Gas oil (250-370 °C)	0.0015	1.4	<0.1
Residue (370+ °C)	0.0000	3.17	0

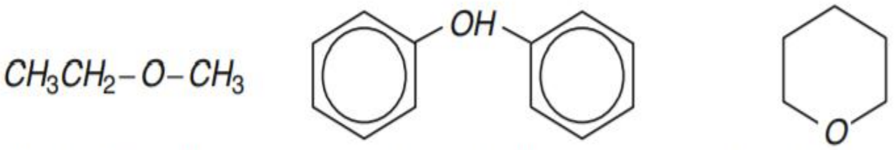
2.1.5.2 Oxygenate Compounds:

The oxygen content considers one of the important properties of crude oil although it found by small amount usually less than 2 wt.% but has sever effect on the crude oil. A phenomenally high oxygen content indicates that the oil has suffered prolonged exposure to the atmosphere. Oxygen in crude oil can occur in a variety of forms. These include alcohols, ethers, carboxylic acids, phenolic compounds, ketones, esters and anhydrides. The presence of such compounds causes the crude to be acidic with consequent processing problems such as corrosion.

Alcohols have the general formula R–OH and are structurally similar to water but with one of the hydrogen atoms replaced by an alkyl group. In phenols, one of the hydrogen atoms in the aromatic ring is replaced with a hydroxyl group (–OH). Ethers have two organic groups connected to a single oxygen atom (R–O–R) (37). Examples of alcohols, phenols and ethers are acid may find in crude oil in Figure (2.5):



methyl alcohol (methanol) isopropyl alcohol (2-propanol) phenyl alcohol (phenol)



ethyl methyl ether diphenyl ether tetrahydropyran (cyclic ether) pentamethylene oxide

Figure No (2.5) Alcohol and ether compound form in crude oil.

other form of oxygen compound in crude oil is carboxylic acids have a carboxyl group as their functional group (–COOH), which found either aliphatic or aromatic shape and their general formula can be written as:

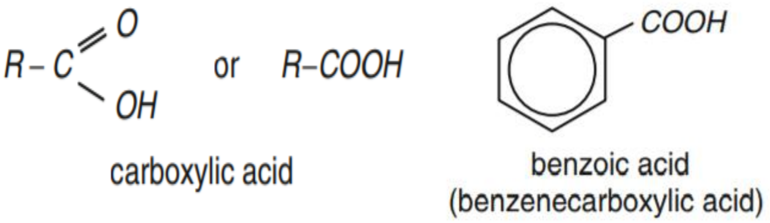


Figure No (2.6) Aliphatic and aromatic carboxylic acid in crude oil.

2.1.5.3 **Nitrogen Compounds**:

Despite their smaller concentrations, these nitrogen and oxygen compounds play an important role in the science of petroleum. Their greater reactivity compared with that of the hydrocarbons makes them more sensitive indicators of the physicochemical environment of petroleum during its long storage in the ground. Similarly, their greater structural complexity provides more stringent checks on proposed relationships between petroleum components and past or present plant constituents. Nitrogen compounds poison many refining catalysts and cause undesirable deposits in finished products such as gasoline and jet fuel. A knowledge of the nature of these nitrogen compounds should prove useful in the development of processes for their removal and of additives for their control. Nitrogen is found in lighter fractions of crude oil as basic compounds, and more often in heavier fractions of crude oil as nonbasic compounds that may also include trace metals such as copper, vanadium, and/or nickel. Nitrogen oxides can form in process furnaces. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion (38).

2.1.5.4 **Carbon Dioxide:**

Carbon dioxide may result from the decomposition of bicarbonates present in or added to crude, or from steam used in the distillation process.

2.1.5.5 **Trace Metals**:

Crude oils contain apart from the well-known metals, including nickel, iron, and vanadium are often found in small quantities and are removed during the refining process for environmental and prolonging the lives of catalysts during processes. The origin of the metals in crude oils varies some of metal origin in the crude itself (e.g. nickel); some are added conversion process for crude oils world-wide, is during production (e.g. barium) and transportation. Burning heavy fuel oils in refinery furnaces and boilers can leave deposits of vanadium oxide and nickel oxide in furnace boxes, ducts, and tubes. It is also desirable to remove trace amounts of arsenic, vanadium, and nickel prior to processing as they can poison certain catalysts. (39).

2.1.5.6 Salts:

Salts in crude oil are mainly in the form of magnesium, calcium, and sodium chlorides, sodium chloride being the most abundant. These salts can be found in two forms: dissolved in emulsified water droplets in the crude oil, as a water-in-oil emulsion, or crystallized and suspended solids.

The negative effect of these salts in downstream processes as salt deposit formation as scales where water-to-steam phase change takes place and corrosion by hydrochloric acid formation. Hydrochloric acid is formed by magnesium and calcium chlorides' decomposition at high temperatures (about 350 °C) (40) as:

$$CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl$$

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

Hydrogen chloride may also combine with ammonia to form ammonium chloride (NH_4Cl), which causes fouling and corrosion. Chloride element also can react with carboxylic acid to form acid chloride. So, in present of alcohol this organic acid can convert to in organic acid (HCl).

2.2 Crude oil quality:

Quality of the petroleum products is playing the major role of consumer satisfaction and speaks about the performance of the refineries. To identify and predict the behavior of the crude oil and finished petroleum products in particular circumstances, it is necessary to measure Physicochemical properties

(41) and to compare the measured values with International Standards. The typical nature of crude oil from different sources is different or less identical. The same is true for crude oil also; the individual oil even from the same well at different time of extraction is differing in the characteristics in term of chemical composition (42).

2.2.1 Light and heavy crude oil:

Density of crude oils is used to expressed the quality of crude oil and classified it to four group according API (American Petroleum Institute) gravity as light, medium, heavy and extra heavy crudes. The units of API gravity are API° and can be calculated from specific gravity by the following Equation:

$$API = \frac{141.5}{SG} - 131.5$$

In this Equation specific gravity refer to the weight per unit volume at 60F (15.6C°) for sample as compared to water weight per unit volume at 60F. Crude oil API gravity may range from less than 10 API° to over 50 API°, but most crudes fall in the 20 to 45 API° range. API gravity always refers to the liquid sample at 60F (15.6C°). API gravities are not linear and, therefore, cannot be averaged. For example, a gallon of 30 API° gravity hydrocarbons when mixed with a gallon of 40 API° hydrocarbons will not yield 2 gal of 35 API° hydrocarbons, but will give 2 gal of hydrocarbons with an API gravity different from 35 API°. Specific gravities can be averaged. In practice, however, API gravities are frequently averaged because the error is usually small.

Table No (2.5) classification of crude oil according to API (43)

API Range (Degree 0)	Description	Rheology	Color	Main Components
0.0 – 22.0	Heavy	Highly Viscous	Dark	Asphalt
<33.0 & >22.0	Medium	Moderately Viscous	Brown	Gasoline & Diesels
> 33	Light	Very fluid	Light yellow	Condensate / Gasoline

Density consider important properties to determine the quality of crude oil in purchase process. Moreover, use to determine another quality parameter for petroleum such as determine the chemical type of crude oil (paraffinic, naphthenic, aromatic or asphaltic) by using API gravity and viscosity to determine the characterization factor (K).

2.2.2 Sulfur in crude oil:

Depending on the amount of total sulfur present crude oil can be classified as sweet, sour sweet/sour crude oil. When the total sulfur level in the oil is less than 0.5 wt.% the oil is called sweet and if it is more than that the oil is called sour and, in some references, when the value is 0.5 is sweet/sour. Due to environmental issues Sweet crude oil is more preferred by refineries as it contains valuable chemicals which is needed to produce the light distillates and high-quality feed stocks. Historically, early prospectors tasted the crude oil to determine its quality. Crude petroleum had a sweet taste and pleasant smell if the content of sulfur was low. For this reason, sweet crude is a low sulfur crude oil (44).

In addition, sweet crude is easier to refine and safer to extract and transport than sour crude. Because sulfur is corrosive, light crude also causes less damage to refineries and thus results in lower maintenance costs over time.

Major locations where sweet crude is found include the Appalachian Basin in Eastern North America, Western Texas, the Bakken Formation of North Dakota and Saskatchewan, the North Sea of Europe, North Africa, Australia, and the Far East including Indonesia (45). On other hand sour crude with high sulfur content and low price because the sulfur compounds in the crude oils are generally harmful impurities, they are toxic, have an unpleasant odor, contribute to the deposition of resin and in combination with water causes intense corrosion (46). Even though it does not restrains the production of inconvenient crude and the data shows that from 1995 to 2011 medium sour and sour crude has been the major hydrocarbon produced in the world taking about

55 to 60% of whole crude production in North America (Alberta (Canada), United States' portion of the Gulf of Mexico, and Mexico), South America (Venezuela, Colombia, and Ecuador), Middle East (Saudi Arabia, Iraq, Kuwait, Iran, Syria, and Egypt) (47).

2.2.3 Acidity in crude oil:

Petroleum acids occur widely in crude oils, and have become one of the most concerned chemical species by researchers and refiners. Generally, acidic constituents in crude oils consist of organic acids, inorganic acids and some other compounds which could influence the oil acidity such as esters, phenols, amines and pyrrole series (48).

The acidity of a crude oil is expressed as number of milligrams of KOH needed to neutralize the acidity in one gram of oil. This number know as total acid number (TAN) and determined by non-aqueous titration (ASTM D 664-1989) if oils has TAN value higher than 0.5 mg KOH/g the crude oil consider as high acidity crude oils.

2.2.3.1 Origin of acid in crude oil:

As we mention in introduction the mechanisms for formation of oil accumulations has direct relation with the origin of acidity in crude oils which can be assorted into the primary type, the secondary biodegradation type and the mixed type.

In primary biodegradation type the biodegradation cannot effect on the crude oil in general, the TAN value of this type of crudes is below 2.0 mg KOH/g and aliphatic acids usually account for above 15% of total acid.

Most crude oils in the world have been affected by secondary alteration or biodegradation in reservoirs. and it was a process that occurs where temperature remained below around 75—80 ℃, resulting in a gradual increase in density, sulfur content, acidity and viscosity of crude oils. Meanwhile, over the geologic age, the microorganisms could selectively remove alkanes, branched alkanes, and cycloalkanes, and might also attack aromatics.

According to the order of ring number (smaller rings degraded first). Mixed type oils are formed from mixing of high or ultrahigh acidity crude oils which have accumulated and suffered the effect of biodegradation and water washing in the early stage, followed by being recharged later with oils of normal acidity. After being mixed, the TAN value of these oils is still greater than 0.5 mg KOH/g. The geochemistry characteristics of this type are intact in terms of the distribution of n-alkanes and the existence of 25-norhopane in oils. For example, crude oil from the Palogue field in Sudan ranges from 3.0 to 10.6 mg KOH/g, and their preservation of n-alkanes is relatively complete, with the pristane/n-C17 ratio being equal to 0.17—0.29, and the phytane/n-C18 ratio equating to 0.05—0.21. The GC-MS (m/z 177) data of the Palogue crude indicated the existence of 25-norhopane, with its biodegradation level being up to 6. So, the oil from the Palogue field is a typical mixed type of high acidity crude oil (49).

2.2.3.2 **Chemical Structure of naphthenic acid:**

The name naphthenic acid is derived from the early discovery of monobasic carboxylic acids in petroleum, with these acids being based on a saturated single ring structure. The low molecular weight naphthenic acids contain alkylated cyclopentane carboxylic acids, with smaller amounts of cyclohexane derivatives occurring. The carboxyl group is usually attached to a side chain rather than directly attached to the cycloalkane. The simplest naphthenic acid is cyclopentane acetic acid, (1, n ¼ 1).

Naphthenic acids are represented by a general formula CnH2n-z O2, where n indicates the carbon number and z specifies a homologous series. The z is equal to 0 for saturated, acyclic acids and increases to 2 in monocyclic naphthenic acids, to 4 in bicyclic naphthenic acids, to 6 in tricyclic acids, and to 8 in tetracyclic acids. Typical structures for the homologues of naphthenic acids are shown in Figure 1. Naphthenic acids in the range of C-7 to C-12 consist mainly of monocyclic acids. The more complex acids contain larger proportions of multicyclic condensed compounds (50).

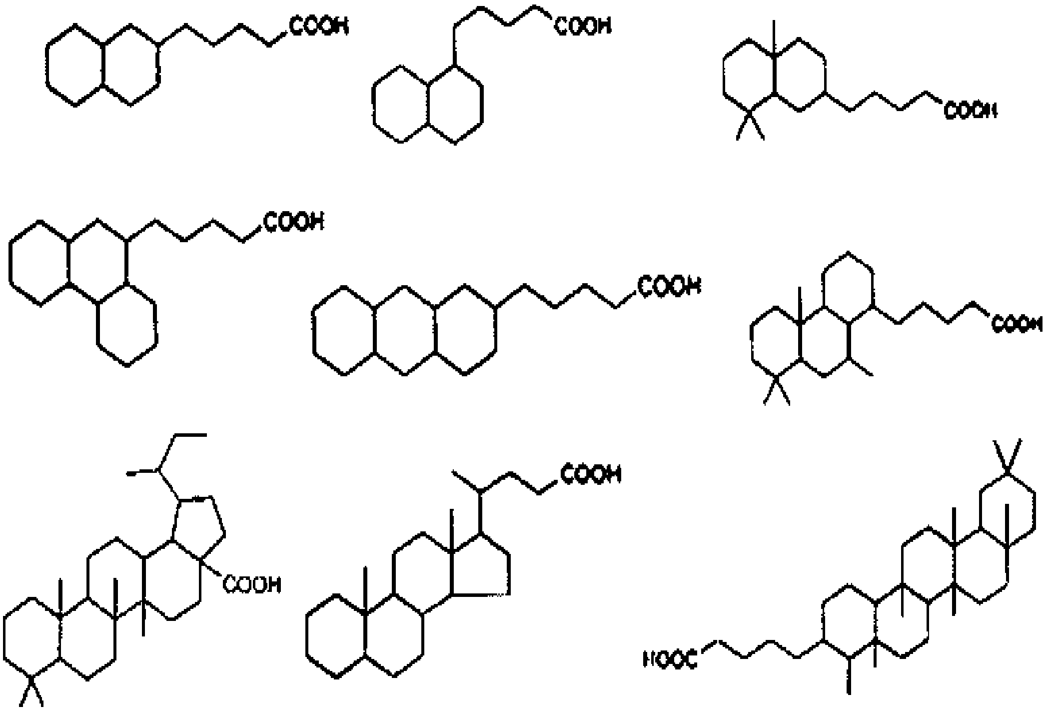


Figure No (2.7) Chemical structure of some naphthenic acid

2.2.3.3 High acid crud in the world:

Recently high acid crude takes part in the international crude oil market lead to increase of the production in world in excess of 5 million barrels per day of Atlantic basin, crudes have high acid numbers and are sold at a discount to marker crudes that can be substantial (51).

High acid crude become plentiful in most global regions and are increasing their proportion of the total crude supply especially in South America which consider as a net exporter of high acid crude and high acid crude blends. North West Europe which has traditionally been a net exporter of high acid crudes is now started to construct a new expansion refinery capacity for high acid crudes, and the crudes are exported to the US East Coast, the US Gulf Coast, the Mediterranean area, and even to the Far East.

West African high acid crude production is rapidly increasing and being exported out of the region. Total global supply of high acid crudes is in excess of 9 million barrels per day (52)(53). While North Sea overall production will decline, the UK and Norway will experience increases in the output of high acid crudes. Most acidic crude production, such as the Grane crude with an acid number of 2.3 mg KOH/g oil (54). On the other hand, the output of high acid crudes in Latin America will have an increasing impact on the Asia Pacific crude oil slate.

Venezuelan crude oils will continue to appeal to the Chinese and Brazilian for increased sales of high acid crudes. West African producers have added a number of new HAC since 2004 and overall output of high acid crudes will continue to grow. Angola and Sudan are the main producers of HACs. Sudan will expand substantially the output and reservoirs of high acid crude, particularly for the very acidic Fula crude oil (55).

A lack of refining capacity and, in some cases, operational issues, in most of these African countries make it to continue export of high acid crudes.

Table No (2.6) Country export high acid crude oil by high ratio.

Source	Crude	Source	Crude
North West Europe	Alba	South America	Marlim
	Captain		Roncador
	Clair		Venezuelan blends
	Grane		
	Gryphon	West Africa	Ceiba
	Harding		Benguela
	Heidrun		heavy Dalia
	Leadon		Kome Kuito
	Troll blend		Lokele Rosalita

2.2.3.4 High acid crude processing:

Processing acidic crudes mean corrosion issues to processing unit and refinery equipment which requires special and expensive technical solutions like blending, inhibition, material upgrading, and process control. Some, but not all, refineries are presently able to refine high acid crudes without suffering serious corrosion problems by blend high acid crudes with other crudes before refining like Matura refinery in India.

Given that crude is purchased in large parcel sizes, the need to blend one such parcel with multiple parcels of low acid crudes is costly and worthwhile only if there is a substantial discount available for the high acid crude. In the United States, most of the facilities which process heavy sour crude oils and crude oils having a high TAN from Venezuela, Brazil, and Mexico are located on the Gulf Coast. Most of the lighter lower sulfur feedstocks (synthetic crudes) are expected to be shipped to the low- to medium-sulfur refineries in the Mid-Continent, Midwest, and Great Lakes regions of the United States (56). The refineries which can process high acid crudes are then able to benefit from the existence of the price discount.

The high acid crude processing been with high profit if the buyers owning refineries with specialized metallurgy, large refineries that can dilute acidic crude through blending or large refineries buying discounted acidic crude with the plan to use the residue as feedstock for a catalytic cracking unit. So that Refiners can handle acidic crudes safely through three main methods dilution (i.e., blending with nonacidic crude), chemical injection, to neutralize acidity, and through the selection and use of specialized materials for the refinery, particularly special alloy steels.

2.2.3.5 Use of naphthenic acids:

Originally the NAs were recovered from crude oil distillates to mini mize refinery equipment corrosion, but they have now found a wide use as commercial articles. However, not all crudes contain enough usable acids to make recovery an economic process (57). Naphthenic acids, NA esters and NA metal salts are a highly marketable product because they have many areas of application; they are used as emulsifiers, textile and wood preservatives, paint, driers, surfactants, and adhesion promoters in tire manufacture. They improve water resistance and adhesion of concrete; increase high pressure resistance of drilling oils; prevent foaming in jet fuel; prevent fungus growth in wood; preserve and act as a flame retardant in fabric; increase insecticide solubility by acting as emulsifier; catalyze rubber vulcanization; stabilize vinyl resins; and catalyze production of alkyl and polyester resins. The use of copper and zinc naphthenates has replaced creosote as a wood preservative (58). NAs that are commercially derived from crude oil are a complex mixture. The NA product quality is determined by the refining processes and the crude oil source used. This makes large compositional variations among commercial supplies of NAs. Traditionally the TAN number has been used as an indicator of the product quality. Since the TAN value also measures other acid components in the oil, such as several compound classes of carboxylic acids, naphtheno aromatic acids and fatty acids, some supplies with high enough TAN values contain only small amounts of NAs (59).

2.2.3.6 High acid corrosion:

Corrosion is a natural irreversible interfacial reaction deterioration of a material environment by chemical or electrochemical means as a result of its interaction of the material with the surroundings (60). which results in its consumption or dissolution into the material of a component of the environment.

The most common current measures of the corrosive potential of a crude oil are the neutralization number or total acid number. These are total acidity measurements determined by base titration. Commercial experience reveals that while such tests may be sufficient for providing an indication of whether any given crude may be corrosive, the tests are poor quantitative indicators of the severity of corrosion for the same TAN, molecular size and structure of the acid also have an important influence (61). However, the TAN is expressed in terms of milligrams of potassium hydroxide per gram (mg KOH/g) and is not specific to a particular acid but refers to all possible acidic components in the crude, and is defined by the amount of potassium hydroxide required to neutralize the acids in one gram of oil.

When naphthenic acid containing crude oils are processed in refineries, corrosion may occur, this type of attack is called “naphthenic acid corrosion”. This type of corrosion is a well-known problem and a major concern in crude oil processing. NAs present in crude oils are considered only to be a part of the problem and simple measures of corrosivity based on the TAN are insufficient. The fundamental problem is the complexity of the factors affecting corrosiveness. The role of crude oil composition, temperature, fluid velocity, turbulence, physical state (vapor or liquid), pressure and materials of construction may also contribute to the extent of oxidation.

Steel alloys that are resistant to corrosion by sulphide-containing compounds can be corroded by NAs. This “naphthenic acid corrosion” involves the reversible binding of the metal ion by the carboxylate with the formation of hydrogen gas (chelation). High throughput rates and operating temperatures between 220 and 400 ºC favor corrosion. Temperatures above 400 ºC decompose NAs, forming a film of coke that protects the alloy (62). The nature and extent of corrosion can also be influenced by sulphur species and chlorides, but unlike naphthenic corrosion, sulphuric corrosion increase in severity with increasing temperature. NA corrosion is associated with TAN, temperature, and fluid rate. When the crude oil has a TAN of more than 0.5, the NA corrosion is generally high, but the TAN value is a poor quantitative measure of the severity of the corrosive behavior of the oil (63).

It has been observed that the corrosive behavior of oils with fairly low TANs was comparable to others with high TANs, whereas other oils with high TANs have been observed to be less corrosive than their TANs might indicate (64). The extent of corrosion by NAs does not only depend on NA content, but also on the chemical structure of the NA, the availability of the carboxylic acid group to adsorb on the metal surface and to form metal complexes. It is well known that an increase in the number of $(CH2)_n$ groups in C chains, up to n = 3 to 4, increases the adsorb ability in a given reaction series of organic compounds. After that, the steric hindrances between organic molecules causes a decrease in adsorb ability(65).

The sulphur content in a crude oil is an important factor in NA corrosion, mainly due to a competition between the two kinds of processes, naphthenic attack and hydrogen sulphide attack according to the following equations:

$$Fe + 2RCOOH \rightarrow Fe\,(RCOO)_2 + H_2 \qquad (1)$$

$$Fe + H_2S \rightarrow FeS + H_2 \qquad (2)$$

$$Fe\,(RCOO)_2 + H2S \rightarrow FeS + 2RCOOH \qquad (3)$$

Equation (1) illustrates the NAs direct attack iron (carbon steel). Here the NAs are transported towards the metal surface which adsorbs the NA molecules. Active sites on the metal surface react with the NAs and generate corrosion products. Eq. (2) illustrates the corrosion by hydrogen sulphide (66). The difference lies in the corrosion product, iron naphthenate, which is very soluble in oil, and iron sulphide, which tends to form a protective film on the metal. Eq. (3) illustrates the reaction between hydrogen sulphide and the soluble iron naphthenate that produces iron sulphide, precipitate d in the oil (67). By this reaction the NAs are regenerated. Crude oils with 2-3 % sulphur content form a protective layer, whose stability is dependent on flow, particularly wall shear stress, and temperature e. This is why a crude oil with a high NA content and low sulphur content seems to be more corrosive at high temperatures than a crude oil with the same NA content and high sulphur content.

2.2.3.7 Removing of acid from crude oil:

Several deacidification removal techniques have been reported in the literature. These include catalytic destructive methods, non-catalytic destructive methods, and non-catalytic non-destructive methods (68).

Thermal decomposition, which is an example of non-catalytic destructive methods, has shown to be ineffective in the reduction of acidity in heavy crude oil (69). High temperature, which is higher than 400°C, is often used. This offers thermal cracking of the heavy crude oil, which then resulted in coke formation.

Catalytic decarboxylation process (70) has been used as an alternative to the non-catalytic destructive methods for naphthenic acids (NAs) removal from heavy crude oil. Polymeric compounds exhibiting basicity characteristics, on the other hand, can be used to neutralize NAs. Although, expensive neutralizing agents, which are difficult to recover from deacidified products, are needed in this method.

Extractive separation is another method used in the removal of NAs from heavy crude oils. Using this method, valuable hydrocarbons are usually removed and this makes the process expensive. Extractive separation method requires multistage wash using different types of solvents. A single NA compound or their derivatives such as salt and water-oil emulsion can also be used (69). It has been reported that solutions of metal oxides, such as those of aluminum and magnesium, exhibit high adsorption capacity and are able to remove more than 95% of the NAs present in a liquid hydrocarbon feedstock at temperatures between 30 and 80°C (71).

Adsorption process of NA removal from heavy crude oil can be used under low temperature condition for distillate fractions. Strong bases, such as alkali metal hydroxides (MOH), are often used as pre-treatment of the heavy oil prior to the adsorption process. The metal hydroxides, however, does not only provide an alkaline environment, but it neutralizes the acidic components of NAs in the heavy crude oil. The major challenge associated with this technique is its environmental challenge as disposal of MOHs into the environment creates nuisance to the environment (71). Oxides and carboxylates of metals have been successfully applied in NAs removal from heavy crude oils using the esterification method at reaction temperatures between 250 and 350°C (72).

2.2.4 Removal of acids from high acid crude oils:

A very significant amount of literature, both patents and publications, exists that deal with organic acid removal by extraction, conversion, decomposition or absorption. For example, many aqueous materials can be added to crudes or crude fractions to convert the naphthenic acids to some other material, e.g., salts that can either be removed or are less corrosive. Other methods for naphthenic acid removal are also well-known including absorption, on zeolites, for example. Additionally, one common practice for overcoming naphthenic acid problems is the use of expensive alloy materials in refinery or producer equipment that will encounter relatively high naphthenic acid concentrations. Another common practice involves blending off crudes with high total acid numbers (TAN) with crudes of lower TAN, the latter, however, being significantly more costly than the former. Saul et al studied naphthenic acid decomposition of topped crudes or distillates, affected at atmospheric pressure between 600° F. and 750° F. However, it only recognizes CO_2 as the sole gaseous non-hydrocarbon, naphthenic acid decomposition product and makes no provision for conducting the reaction with a continuous inert gas sweep to avoid build-up of reaction inhibitors.

In their process for reducing the total acid number (TAN) of whole crude or crude fraction feeds which comprises thermally treating the feed in a treatment zone at a temperature of at least 400° F. and a pressure between 0.1 and 100 atmospheres for a period of time sufficient to substantially reduce the TAN , removing water vapor which would inhibit TAN reduction, simultaneously during thermal treating with a sweep gas rate in the range of 1-2000 standard cubic feet per barrel of feed. Nevertheless, there remains a need for eliminating or least substantially reducing petroleum acid concentration in crudes or fractions thereof that is low cost and refinery friendly, particularly crudes or fractions thereof where the total acid number (TAN) is above about 2 mg KOH/gm oil, as determined by ASTM method D-664(73).

Anda Lucia (74) studied extraction of naphthenic acid from Indonesian crude with TAN concentration more than 0.5 mg KOH/g oils, by methanol-ammonium solution the presence of naphthenic acid tends to increase the value of TAN. Extraction process is done by mixing solvent and crude oil in a separating funnel of 500 ml and then shaken for five minutes. Thereafter, the separating funnel is kept for sixteen hours at room temperature. Two layers are formed in the funnel. Water soluble phase, the bottom layer, is removed through the spout. Then the top layer which is the crude oil is extracted with solvent again. The extraction process is carried out four times.

The layer of water that has been obtained from the extraction and centrifuge is inserted into the rotary evaporator with rotation at 30 per minute and temperature of 60-80°C for 1-2 hours. After evaporation with a rotary evaporator there will be a solution of ammonia in the container and naphthenic acid stick to the flask wall. The result of extraction of naphthenic acid from crude B shows quite high results of that is equal to 65.47% with a purity level of 96.6%. while acid in sample reduce by (49.06%) and C by (21.01%).

Syed Nasir Sha. et al (74), were working in extraction of naphthenic acid from highly acidic oil using hydroxide-based ionic liquids by neutralization of the model oil t by mixing 10 g of dodecane with a set amount of ionic liquids in a round-bottom flask with a hot plate, reflux condenser, and magnetic stirrer. The stirring rate was kept at 500 rpm, and the reaction time was 1 h. Several temperature settings were used for the reaction to optimize the process temperature. The reaction mixture was then transferred to a separation funnel and kept for 1 h to enable a clear separation between the ionic liquids and the model oil. A total of 5 g of oil was withdrawn from the top of the separation funnel, and the TAN was measured (74).

They found that, hydroxide-anion-based tetraalkylammonium and tetraalkylphosphonium ionic liquids are very effective in the complete deacidification of high TAN model oil. Only a very low ionic liquids / oil ratio is necessary for the complete extraction of naphthenic acid. When the alkyl spacer length on the cation increases, the extraction performance of the hydroxide-based ILs decreases. The plausible mechanism of extraction is the formation of naphthalenate salt of the tetraalkylammonium or tetraalkylphosphonium cation, resulting from the reaction between naphthenic acid and the hydroxide anion of ILs. The extracted naphthenic acid can be regenerated by the addition of an aqueous solution of a mineral acid. The hydroxide IL can be used several times for the extraction process without losing its activity. The results revealed that this method has the potential to extract and regenerate naphthenic acids from high TAN crude oil(74).

Shohaimi and et al(75), tried to produce new method of treatment of acidic petroleum crude oil utilizing catalytic neutralization technique of magnesium oxide catalyst, first they studied magnesium-based catalyst with dopant of Nickel and Copper. The ratio of based-dopant used were 10(dopant):90(based) and 30(dopant):70(based). Various calcination temperatures used were 400°C, 700°C and 1000°C. The metal precursors used in this research are nitrate salt. The magnesium loading used was 90 wt%. Then, the solutions were mixed together and stirred continuously by magnetic bar for 30 minutes at room temperature to homogenize the mixture. In Mg based catalyst, Al_2O_3 is the most widely used support material. The support was immersed into the catalysts solution for 1 hour and transferred the supported catalysts onto evaporating dish with glass wool on it. It was then aging inside an oven at 80-90°C for 24 hours to remove water and allow good coating of the metal on the surface of the supported catalysts. It was then followed by calcination in the furnace at 400°C for 5 hours using a ramp rate of 5°C/min to eliminate all the metal precursor and excess of water or impurities. The feedstock used in this study was light and heavy crude obtain from Petronas Penapisan Melaka. Ammonia solution in ethylene glycol was prepared to be used as the base chemical in the acid base neutralization process. The concentrations of ammonia solution in ethylene glycol use were 100 mg/L, 500 mg/L and 1000 mg/L. prepared as 400 µL of ammonia solution was added into 99.6 mL of ethylene glycol and stirred for about 15 min. The solution was stirring vigorously for 1 hour and stored in the dark place to avoid sunlight's penetration. The solution was then ready to be blend with the crude oil samples.

The results showed that, Crude A is a heavy crude oil, the total acid number (TAN) in the crude oil was 4.21. But, after treatment with 100 mg/L of ammonia solution, the number was reduced to 3.18. The number was further decreased to 2.33 and 1.78 after added with 500 and 1000 mg/L of ammonia solution respectively. Initially, without addition of ammonia solution of ethylene glycol, the total acid number (TAN) in the crude B which is light crude oil was 2.52. But, with addition of 100 mg/L of ammonia solution, the TAN was lowered to 2.05. TAN was decrease as the amount of ammonia solution is increase; this has been shown when the number of acids in crude B was decreased to 1.77 and 1.49 for 500 and 1000 mg/L of ammonia solution. It can be concluded that only 57.72 percent of acid number in the crude A and 40.87 percent of crude B were reduced when treated with ammonia solution of ethylene glycol due to insufficient amount concentration added. Thus, in order to completely reduce the number of acids in both crude oils, the concentration of the ammonia solution must be greater than 1100 mg/L or by addition of catalysts(75).

Chun Yang, et al (76) studied Characterization of naphthenic acids in crude oils and refined petroleum products in a number of crude oils and refined petroleum products including light and mid-range distillate fuels, heavy fuels, and lubricating oils collected from various sources, as well as oil sands produced water (OSPW) samples. A solid phase extraction method was used to effectively isolate NAFCs from other petroleum components, by liquid chromatography-high resolution Orbitrap mass spectrometry LC-HRMS was applied in the identification and quantitation of these compounds with unsaturated degree of z −0 to z −24 and carbon number ranging from 6 up to 60.

They found naphthenic acids in conventional light crude oils are usually at low concentrations, while relatively higher in heavier crudes and oil sands bitumen. For most of studied oils acids are dominant by ≥ C22 up to C60 congeners (referred to β-NAs), which make up to about 70% of total NAs. In addition, these NAs are dominated by z = −2∼−6 species. NA series from z −0 to z −12 series totally account for about 90% of NAs in Alberta oil sand bitumen, and z −14 to z −24 accounting for about 10% of total NAs.

In their study also conclude that acids are rarely found in the lightest distillation fractions and tend to be concentrated in heavier petroleum fractions. 90% of the NAs in Alaska North Slope crude oil were collected in the 287–481 °C (equivalent to ∼n-C17 to n-C34) during distillation fraction. However, intermediate fuel oil, Bunker C and lubricating oils contain relatively low concentration of NAs since these substances are removed during the manufactures of these petroleum products in order to improve their performance characteristics and storage properties (76).

Syed Nasir Shah, et al (77) tried to deacidification of crude oil using four different imidazolium based ionic liquids were chemically tethered to silica. These adsorbents can selectively extract naphthenic acid from model oil and it could able to avoid the leaching of ionic liquids to the model oil layer because of the strong chemical bonding of imidazolium moiety to the silica surface. The recovery of the naphthenic acid and the purity of the recovered naphthenic acid were also studied. The extraction study was modeled via conductor-like Screening model for Realistic Solvents (COSMO-RS) to evaluate the extraction capability of solid supported ionic liquids. The COSMO-RS predicted results were compared with the experimental results. The ionic liquids had a good potential to deacidify extremely highly acidic crude oil (TAN 2.93 mg KOH/g of oil) with very small ionic liquids to oil ratio. The purity of the recovered naphthenic acid was found to be more than 80%. The experimental extraction efficiency trend and the COSMO-RS predicted extraction efficiency are in good agreement. The regeneration of the extracted naphthenic acid was achieved by simple washing of the supported ionic liquid phases with diethyl ether (77).

Baudilio Coto, et al (78) worked to investigate the extraction ability of 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO4]) IL for the removal of acid compounds from a synthetic mixture representing a crude oil (SC) is investigated in order to reduce the TAN value. The mixture was formed by four components (n-heptane+ cyclohexane+ toluene+ dodecanoic acid) but experimental determination was focused on acid content. Experimental conditions analyzed were temperature and IL/mixture ratio. Simulation of the TAN reduction was carried out by considering phase equilibria conditions, extraction of the acid compound and thermodynamic models for activity coefficient determination. The use of thermodynamic models as NRTL or UNIQUAC requires a big interaction parameter matrix for systems with 5 compounds, on the opposite most UNIFAC group interaction parameters are available for considered system.

Two different calculation procedures were considered for COSMORS and COSMO-SAC models. Procedure (C + A) refers to the consideration of cation and anion as separate species and computed separately while procedure (CA) refers to the situation where cation and anion are placed in a relative position and computed together.

Temperature increase improves the extraction of acid components but in a reduced extent, being the best results obtained at 50 °C. IL to oil ratio is a main variable whose increment always lead to better TAN reductions. Best TAN reduction values were around 25% for the highest IL/oil ratios studied. In order to obtain higher reductions, the IL to oil ratio should be increased.

Liquid-liquid equilibrium equations were used with activity coefficient models as UNIFAC, COSMO-RS and COSMO-SAC, and they adequately described the extraction of the acid components and subsequent TAN reduction. UNIFAC model required the fitting of the parameter for the ILCOOH interaction not previously available and given accurate description of the phase fraction and the TAN values for both the organic and the IL phases. Results obtained by means of COSMO models were less accurate, with an overestimation of the TAN reduction for the organic phase due to the description of the interaction between IL and acid compound stronger than expected. Such results improved when profile for the IL is computed considering both the cation and anion together in a certain relative position where the basic behavior of the anion is partially shielded by the cation (78).

2.3 Objectives of the study:

Despite the number of studies that have been done to assess the reduction or removal of naphthenic acid present in crude oil, there is little information available about the mechanism of the removal in low temperature without using a catalyst. So, the objective of this study is:

- To study the possibility of removing acids from heavy Sudanese crude oil by polar organic solvents.
- To determine optimum solvent volume and operations temperature.
- To study the effect of extraction process on physical and chemical properties of crude oil sample.

Chapter three

3.1 Materials:

3.1.1 Sample collection

- Crude oil sample was collected from west Kordofan Moga heavy FPF in 40 Liters IATA Cans in good condition and no damage or leakage was noted to the containers.
- The sample observed to be heavy and in liquid form at room temperature. And did not have any peculiar odor of Hydrogen Sulphide.
- The sample container was heated to 55°C to facilitate easy transfer and homogenization.

3.1.2 Chemicals:

- Methanol use as solvent by the following properties: supragradient HPLC grade M = 32,04 g/mol, density: 0,792 g/cm3, soluble in water: (20 °C): miscible, melting point: -98 °C, Boiling point: 65°C, flash pt. 10 °C, Ignition temp.: 455 °C, vapour pressure: (20°C) 128 hPa, refraction index: (n 20 °C/D) 1,3288, dielectric const.: (25 °C) 32,6.
- Ethyl alcohol, use as solvent by the following properties: M = 46,07 g/mol, density: 0,79 g/cm3, soluble in water: (20 °C): miscible, melting point: -114,5 °C, boiling point: 78,3°C, flash pt. 12°C, ignition temp.: 425°C, vapors pressure: (20 °C) 59 hPa - dielectric const.: (25 °C) 24,3.
- Titration alcoholic mixture solvent prepare according to ASTM D664/D974: toluene: 500 ml isopropyl alcohol: 495 ml water: 5 ml free acid (as C_2H_5COOH): max. 0,001 % iron (Fe): max. 0,0001 % heavy metals (as Pb): max. 0,0002.

3.2 Instrumentations:

3.2.1 Varian CP3800 gas chromatograph:

The Varian CP-3800 GC meets all your analytical requirements with practical solutions for simple and complex applications. In a standard configuration, the CP-3800 accommodates up to three injectors and three detectors, all operating simultaneously. In addition, the CP-3800 is easily configured to perform on-line analyses for monitoring critical gas and liquid process streams. The CP-3800's flexible platform which start with a basic configuration and add a wide variety of options in the field. Options include additional channels, gas and liquid sampling valves, and external sampling devices.

The primary components of CP3800 includes:

- Injection port.
- The column and oven.
- A detector (FID)
- Recorder.
- Carrier and detector gases.
- Flow controllers or valve.

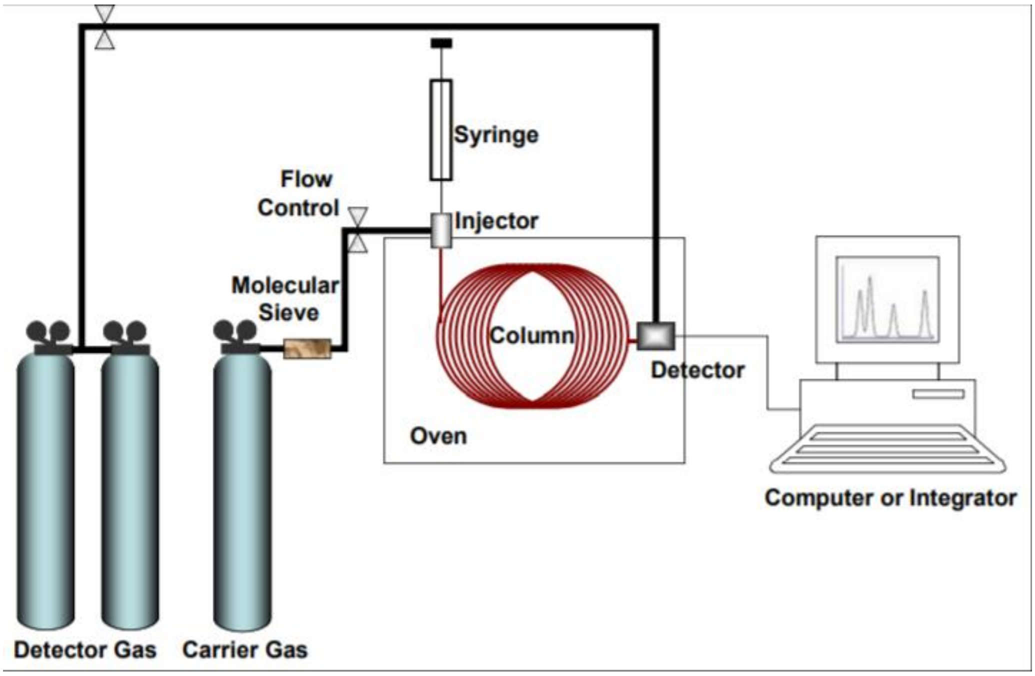


Figure No (3.1) scheme diagram of GC

Varian 3800 GC Software Overview is controlled using the Workstation v. 5.51 software. This software is used to develop and control methods, run single or multiple samples, and view and modify run results.

3.2.2 A Thermo Nicolet Nexus 370 Fourier Transform Infrared Spectroscopy:

A Thermo Nicolet Nexus 370 instrument (Madison, WI, USA) equipped with a deuterated triglycine sulphate (DTGS) detector and KBr beam splitter was used to measure the FTIR spectra of oil samples. A common FTIR spectrometer consists of a source, interferometer, sample compartment, detector, amplifier, A/D convertor, and a computer.

The source generates radiation which passes the sample through the interferometer and reaches the detector. Then the signal is amplified and converted to digital signal by the amplifier and analog-to-digital converter, respectively. Eventually, the signal is transferred to a computer in which Fourier transform is carried out.

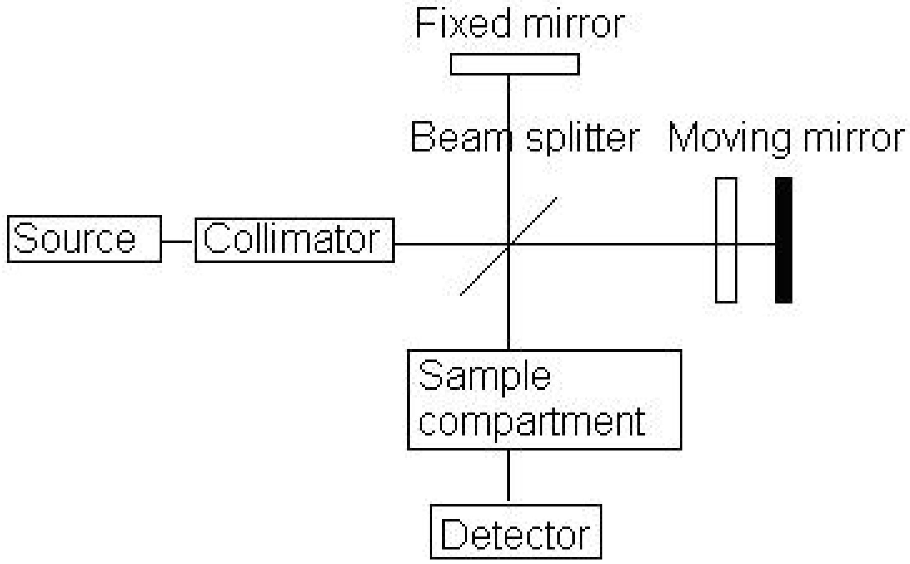


Figure (3.2) Block diagram of an FTIR spectrometer

3.3 Methods of analysis:

3.3.1 Extraction of acids and acidic behavior compounds:

- Crude oil sample was kept overnight in oven at 60 °C.
- Known volume (100, 90 and 80 ml) of crude oil was added to the separating funnel.

- Known volume of polar solvent (methanol or ethanol) was added to the funnel hence the total volume of material in the funnel equal 100 ml**.**
- The content of the funnel shakes vigorously by hand for 10 minutes then kept in required temperature (Room, 40 or 50°C) for 16 hours.
- After 16 hours the crude oil was separated and the total acid number was determined.
- The process was repeated again to the remain crude oil with fresh amount of solvent till we reached to three extraction.

3.3.2 Determination of total acid number:

Total Acid Number (TAN) is the amount of potassium hydroxide in milligrams that’s needed to neutralize the acid in one gram of oil. Crude with TAN 1.0 mg KOH/g conventionally labeled as high TAN. Most high TAN oil tends to be heavy.

A weighed quantity of sample was introduced into a 250-mL beaker as recommended in Table (3.1) and add 125 mL of titration solvent. The electrodes were prepared (beaker was placed on the titration stand and its position was adjusted so that the electrodes are about half immersed). Stirrer was started, and stir throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution.

Table No (3.1) Recommended weight of samples (ASTM D664)

Acid Number	Mass of Test Portion, g	Accuracy of Weighing, g
0.05 – < 1.0	20.0 ± 2.0	0.10
1.0 – < 5.0	5.0 ± 0.5	0.02
5 – < 20	1.0 ± 0.1	0.005
20 – < 100	0.25 ± 0.02	0.001
100 – < 260	0.1 ± 0.01	0.0005

The meter readings are plotted manually or automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained, end points are taken at meter readings corresponding to those found for aqueous acidic and basic buffer solutions. (79)

Determination of TAN in crude oil is based on standard method ASTM D664 and the formula is calculated using equation:

$$TAN\left(mg\frac{KOH}{g}\right)=\frac{(A-B)*M*56.106}{Wt}$$

Where:

A: volume of KOH solution used to titrate sample, ml B: volume corresponding to A for blank titration, ml N: concentration of KOH solution, mol/L W: sample mass, g.

Determination of the percentage of acid-removal using the equation:

$$Acid\ removal\ \% = \frac{TAN(before)-TAN(After)}{TAN(before)}*100\%$$

3.3.3 Determination of Density, specific gravity and API:

Density is mass per unit volume at a specified temperature. while elative density (SG): the ratio of the density of a material at a stated temperature to the density of water at a stated temperature and API is abbreviation to American Petroleum Institute consider as ratio related to specific gravity of sample equal:

$$API=\frac{141.5}{SG}-131.5$$

According to ASTM D5002 approximately 0.7 ml of crude oil sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample (80).

3.3.4 Determination of pour point:

Using ASTM D5853 method to determine pour point of crude oils is an important parameter from a processing point of view; its lowest temperature at which movement of specimen can be observed, essentially, define the temperature that is required to pump the crude. Since crude oil is a complex mixture of compounds, it does not congeal at specific temperature, but different compounds crystallize out of solution at different temperatures. Heating crude to 45-65 C° re dissolves some of the paraffinic seed crystals, therapy lowering the pour point, while heating it to 100C° would again raise the pour point due to loss of light materials by evaporation. In practice pour point is determined after preheating to 45-48C°.

After preliminary hearing, the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point(81) .

3.3.5 Determination Kinematic viscosity:

The viscosity of crude mainly influences pumping cost, because it determines the pressure drop in pipelines and refinery units. The viscosity temperature relationship depends on the crude composition, with paraffinic crudes showing a rapid increase in viscosity decrease temperature, while naphthenic crude has a more gradual decrease. Viscosity of crude oils varies over a wide range, having values of less than 10 to more 5000cSt.

Time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity (determined value) is the product of the measured flow time and the calibration constant of the viscometer. Two such determinations are needed from which to calculate a kinematic viscosity result that is the average of two acceptable determined values (82).

3.3.6 Determination Carbon Residue (Micro Method):

A weighed quantity of sample is placed in a glass vial and heated to 500°C under an inert (nitrogen) atmosphere in a controlled manner for a specific time. The sample undergoes coking reactions, and volatiles formed are swept away by the nitrogen. The carbonaceous-type residue remaining is reported as a percent of the original sample as “carbon residue (micro).” When the test result is expected to be below 0.10 % (m/m), the sample can be distilled to produce a 10 % (V/V) bottoms, prior to performing the test.(83)

3.3.7 Determination of Water in Crude Oil by Distillation:

Known amount of sample (depend on amount of water in sample) is heated under reflux. conditions with a water immiscible solvent (toluene or xylene) which co-distills with the water in the sample.

Condensed solvent and water are continuously separated in a trap the water settles in the graduated section of the trap, and the solvent returns to the distillation flask.(84)

3.3.8 Fourier Transform Infrared Spectroscopy analysis:

Drops of oil samples were placed on a multi bounce plate ZnSe of horizontal attenuated total reflectance (HATR) crystal. Measurements were taken at 64 scans and at a resolution of 4 cm^{-1} with strong apodization. The background of air was collected before every sample was measured. After each measurement, the plate was carefully cleaned from any previous residues by wiping using acetone and hexane and dried with a soft tissue before filling in with the next sample. The software used for FTIR data collection was Nicolet Omnic (version 7.0, Madison, WI, USA). All spectra were recorded from 4000 to 650 cm−1 and read as absorbance in triplicate.

3.3.9 Gas chromatograph analysis steps:

- The Desired method was activated using file activate method.
- Hydrogen and air cylinders valves were opened (each cylinder must have more than 200 psi total pressure and have enough gas to complete the desired analyses). The cylinder delivery pressures should already be set as: hydrogen 40 psi, air: 60 psi and helium: 80 psi.

- While the instrument is equilibrating, sample list was created and all sample parameters were sited.
- The sample was Loaded into the autosampler tray.
- Sample run was started.

Chapter four

4.1 Results and Discussion:

To determine kind of crude oil collected sample was analysis in which physical and chemical properties were tested before extraction processes.

4.1.1 Physical and chemical properties of collected crude oil sample:

Table No (4.1) properties of original crude oil sample

Test Name	Test Method	Unit	Result
Density @15°C	ASTM D5002	g/cm^3	0.9271
API	ASTM D5002		20.99
S.G	ASTM D5002		0.928
TAN	ASTM D664	mgKOH/g	7.69
Pour point	ASTM D5853	^{0}C	15
Kinematic Viscosity @50°C	ASTM D445	cSt	326
MCR	ASTMD4530	Wt%	5.5
Water content by distillation	ASTM D4006	%V	0.05

From the Table (4.1) we can classify the crude oil sample as heavy with low API, high acid crude oil, low pour point and high carbon residue. This classification confirmed when acid distribution result appeared in Table (4.2) showed most acid distribute in higher cuts this distribution increased with temperature till 375+ after that acid decomposed due to high temperature (555+).

Table No (4.2) Acid distribution in distillation cuts

BP ranges ° C	C5 – 165	165 – 240	240– 315	315 – 360	360--375	375+ Res	555+ Res
Wt. %	1.29	2.16	5.7	5.67	1.78	83.4	51
Vol%	1.55	2.34	5.94	5.81	1.8	82.56	49.92
TAN mg KOH/g	0.02	0.05	0.47	2.66	4.88	6.37	2.28

Fourier transform infrared scan for collected crude oil sample showed saturated (-C-H) stretching peaks, pending peak of methylene group (-C-H$_2$) and bending peak of the methyl group) FTIR for original crude oil sample while gas chromatogram for crude oil sample its clear the sample is heavy crude oil because first peak is C6 (no light paraffins) in the chromatogram.

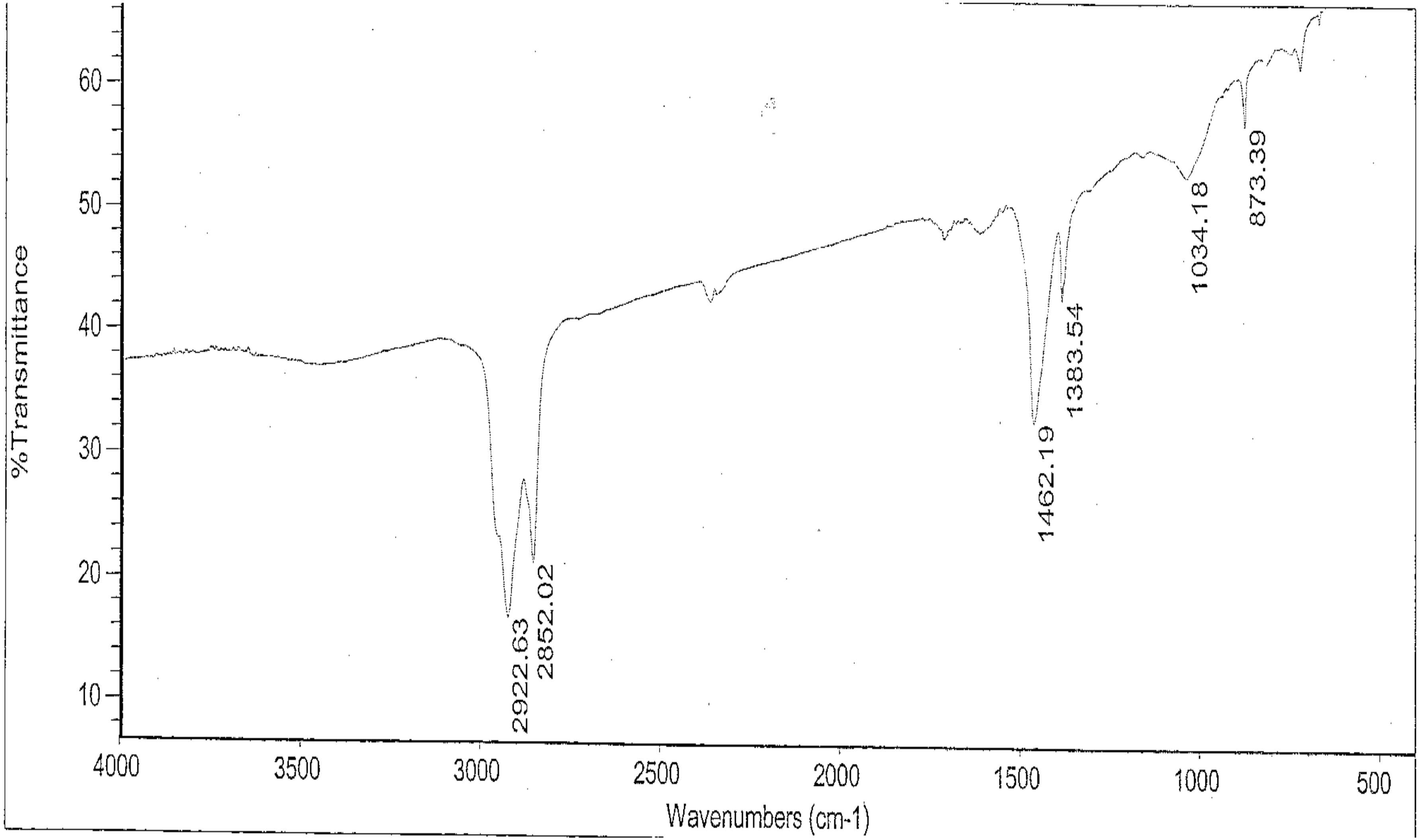


Figure No (4.1) FTIR for collected crude oil sample

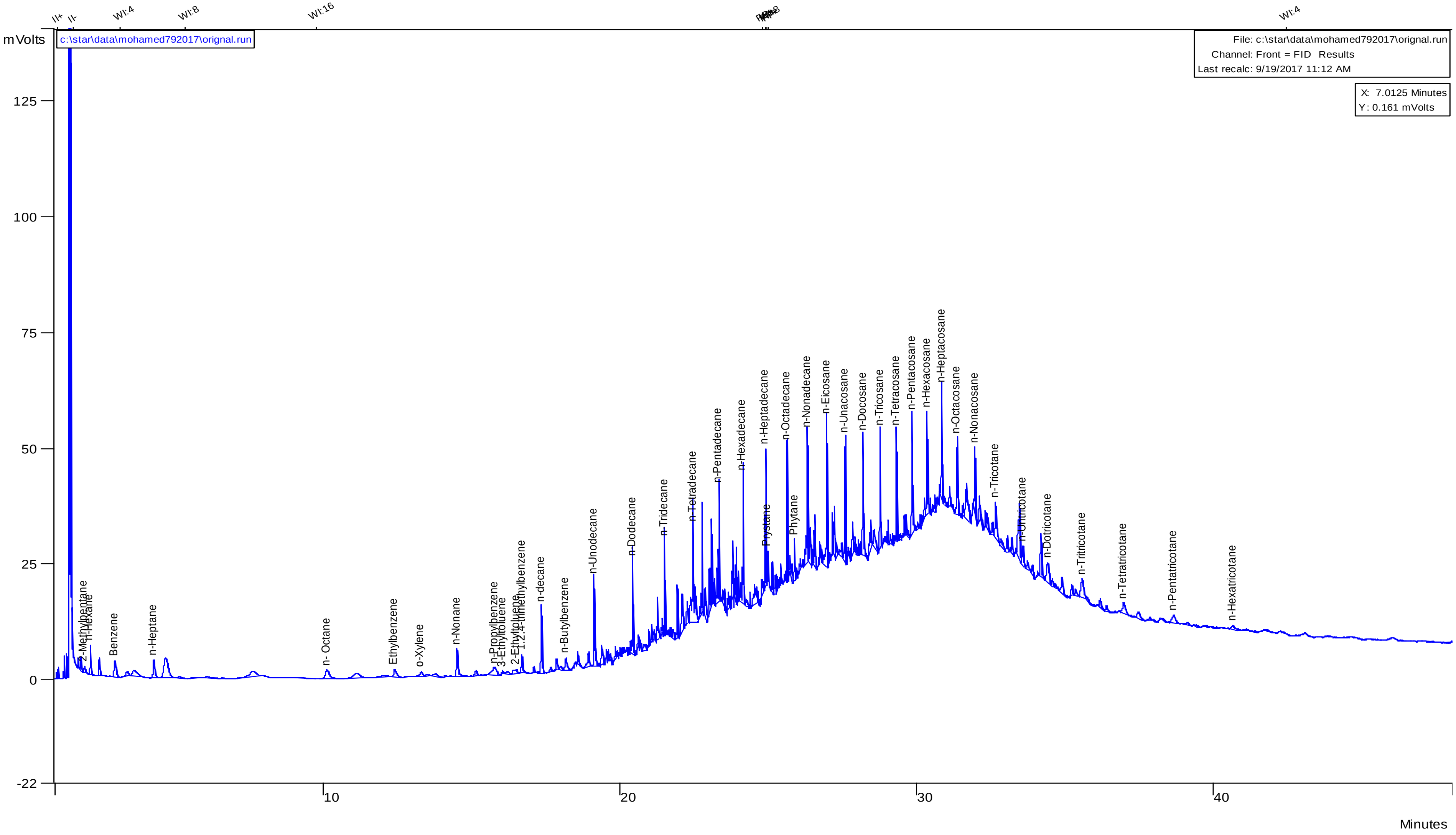


Figure No (4.2) GC for original crude oil sample

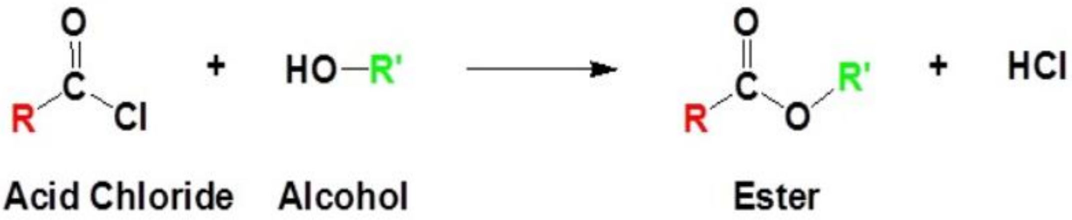
4.1.2 Extraction of acid at room temperature:

Separation of naphthenic acid from crude oil was carried out liquid-liquid extraction method using two kinds of solvent. Extraction for three times at room temperature without catalyst showed differences in acid removal. Results of the third crude oil extraction with methanol and ethanol showed in Tables (4.3) & (4.4).

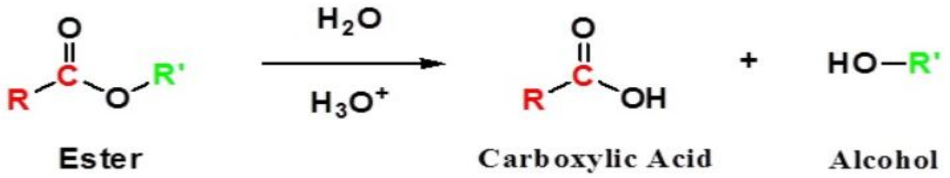
Table No (4.3) Extraction of acid at room temperature by 10% methanol

Sample Name	TAN mg KOH/g	Removal%
Collected crude oil	7.69	17.30
After first extraction	6.36	17.30
After second extraction	5.43	14.62
After third extraction	6.15	-13.26
total removal after two extraction	Optimum	20.99

The optimum number of extractions using methanol at room temperature were two extraction which remove about 2.26 mg KOH/g equivalent to 20 % of acid. According to some literature these acid or acidic behavior compound are classified as light acid compounds (saturated acid). In the third extraction the acid amount in crude oil increased more than 1.2 mg KOH/g. This increase may be due to the conversion of alcoholic compounds to carboxylic acids i.e. an unstable form of ester may be formed during the extraction last step or formation of HCL when acid chloride reacts with alcohol.



Another suggestion for the increasing the acidity of crude in the third extraction is that, esters can be cleaved back into a carboxylic acid and alcohol by reaction with water and a catalytic amount of acid as:



Alcoholic compound like phenol and their derivatives also have strong acidic behavior but did not appeared in FTIR of collected sample or after extraction as in Figure (4.3). Same peaks in range of 2500 – 3300 cm^{-1} is appeared and classified as -CH, although acid extracted from the sample of crude oil the FTIR. The probability of acidic compounds increased by appearing C=O peak in range of 1705 to 1720 cm^{-1}.

To optimize the extraction process from solvent point of view extraction process had been done by less polarity solvent ethanol and showed the following result as in Table (4.4).

Table No (4.4) Extraction of acid at room temperature by 10% ethanol

Sample	TAN mg KOH/g	Removal%
Collected crude oil	7.69	0.00
After first extraction	6.88	10.53
After second extraction	6.85	0.44
After third extraction	6.72	1.90
Total removal after three extraction	Optimum	12.61

Ethanol has same effect for extraction of acid from the crude oil but by low magnitude. Ethanol less polarity (0.654) compare with methanol (0.762). In room temperature when compare the extraction ratio we found methanol has high extraction ratio 38.1% (i.e. 25.9% more than ethanol).

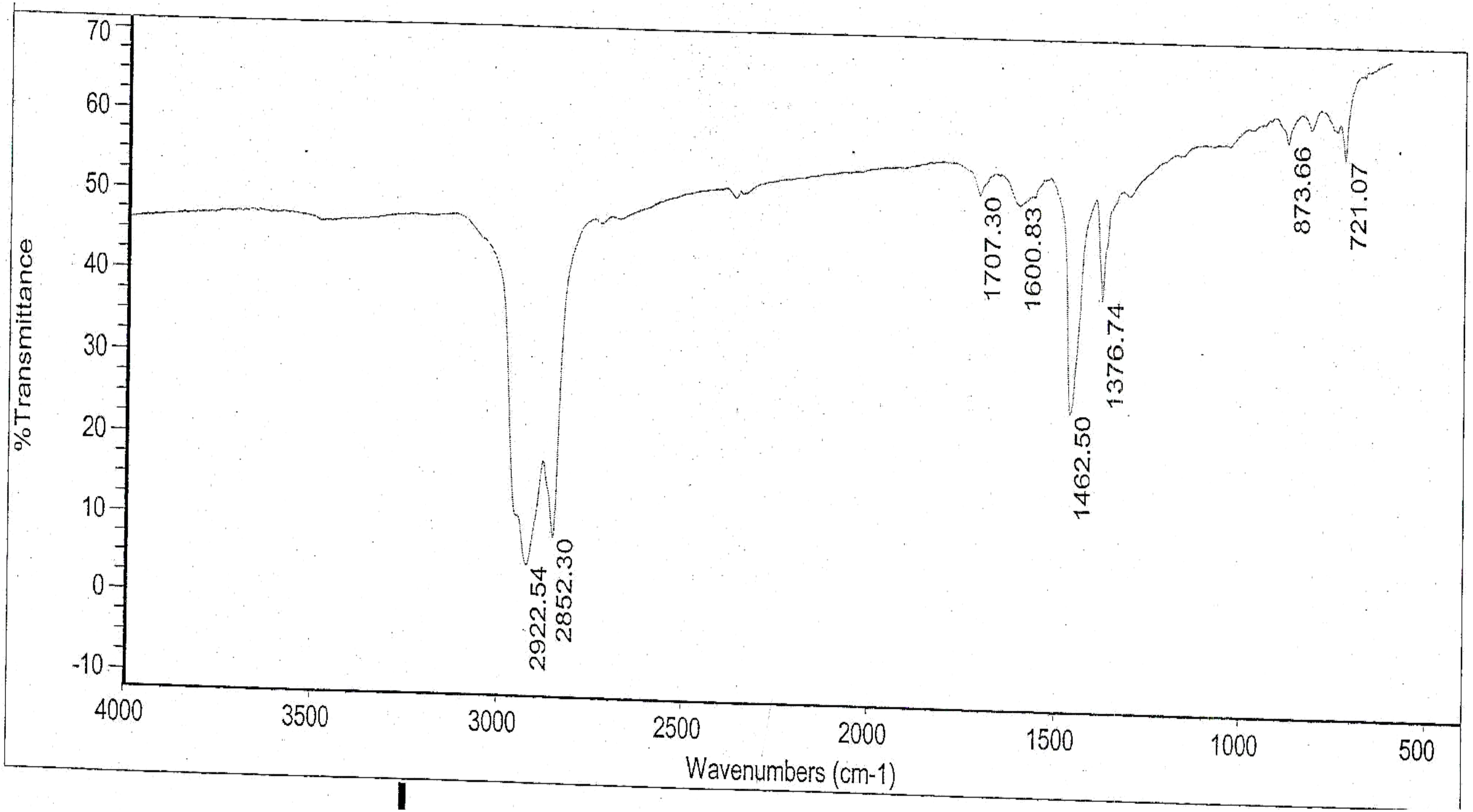


Figure No (4.3) FTIR for crude oil sample after extraction by 10% methanol.

4.1.3 **Extraction of acid at 40 °C:**

Separation processes were continuing with 40 °C to examine the effect of temperature in the process the following Tables (4.5) and (4.6) showed extraction with 10% of methanol and ethanol respectively at 40°C.

Table No (4.5) Extraction of acid at 40 °C by 10% methanol

Sample	TAN mg KOH/g	Removal%
Collected crude oil	7.69	0.00
After first extraction	6.59	14.30
After second extraction	6.18	6.22
After third extraction	5.82	5.83
Total removal after three extraction	Optimum	24.32

When the temperature increased the efficiency of methanol solvent was increased hence one extraction process gave 1.1 mg KOH/g of acid removal equivalents to 24 % of total acid in sample. the extraction process in this step was more effective when compared with different solvent (methanol). The general paraffinic Skelton of crude oil doesn't change as showed in GC in Figure (4.4). So, the extraction process has no effect on the other compound.

Extraction by ethanol results in Table (4.6) showed higher extraction percentage when compare with methanol at same extraction condition (temperature 40°C and solvent volume 10 ml) and also at room temperature extraction processes. First extraction had lower percentage of removal when compare with second extraction processes. So, second extraction consider as optimum because has high extraction percentage of removal (28%) and TAN removed by 2.70 g KOH/mg.

When we compared extraction process from stability point of view, we found ethanol is most stable than methanol as in third extraction at 40°C the back reaction appeared but the acid increase by low amount (5%) from acid extracted while using of methanol extraction process at room temperature (13%).

Table No (4.6) Extraction of acid at 40°C by 10% ethanol

Sample	TAN mg KOH/g	Removal%
Collected crude oil	7.69	0.00
After first extraction	7.00	8.97
After second extraction	4.99	28.71
After third extraction	5.26	-5.41
Total removal after two extraction	Optimum	31.60

Gas chromatograph showed similarity in peaks which started from C_6 carbon number in both solvent extraction process. Also when compared the gas chromatograph results with the collected crude oil sample chromatograph we can observed same peaks which mean the extraction process had no effect upon the composition of collected crude oil sample i.e. the composition of paraffinic and aromatic of crude oil doesn’t affected by extraction process and the crude oil still consider as heavy crude oil as showed in Figures (4.4) and (4.5).

Although extraction processes showed removing of some acidic compounds from crude oil sample but still the crude oil has classified as high acid crude oil.

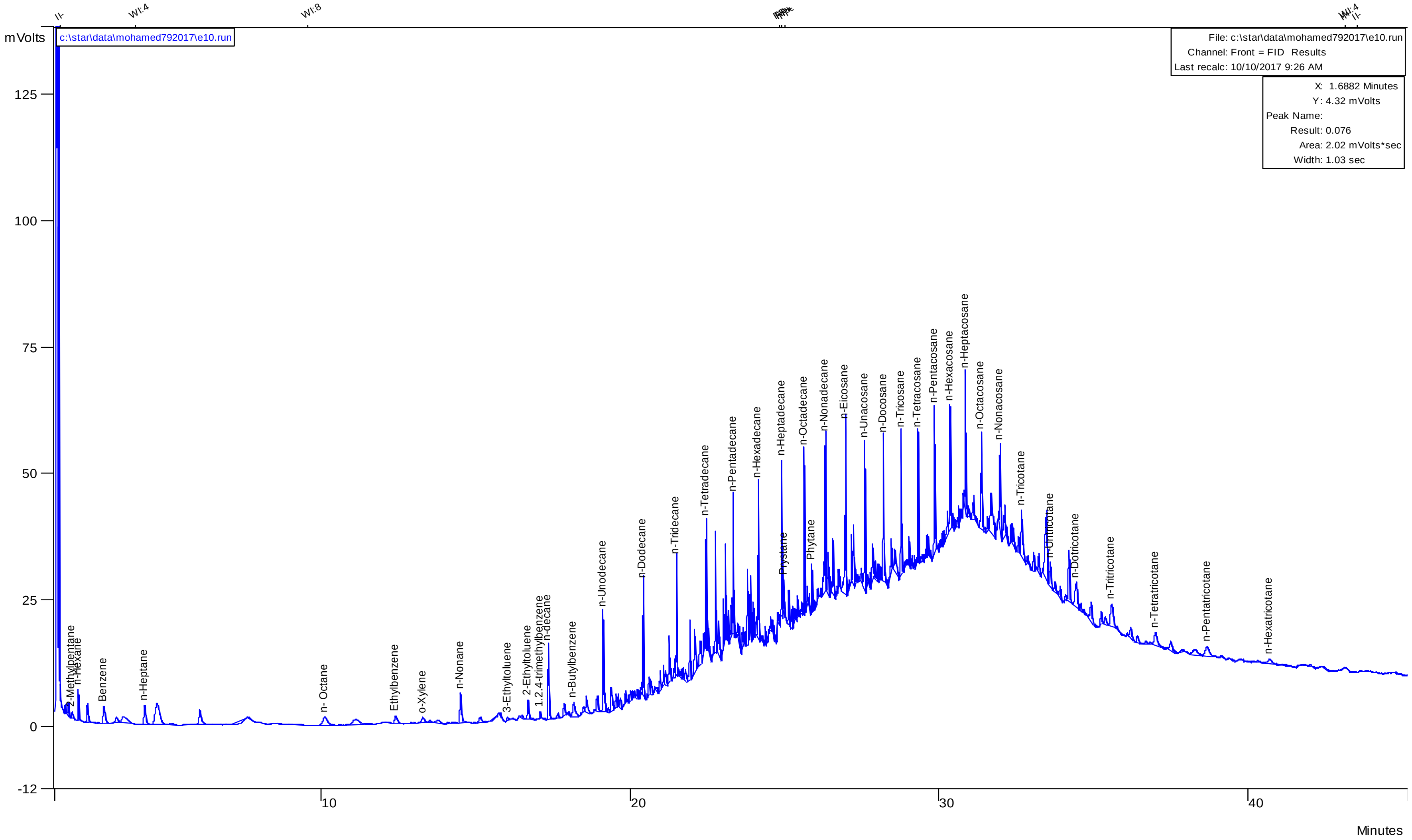


Figure No (4.4) GC for crude oil extracted by 10% of methanol at 40°C

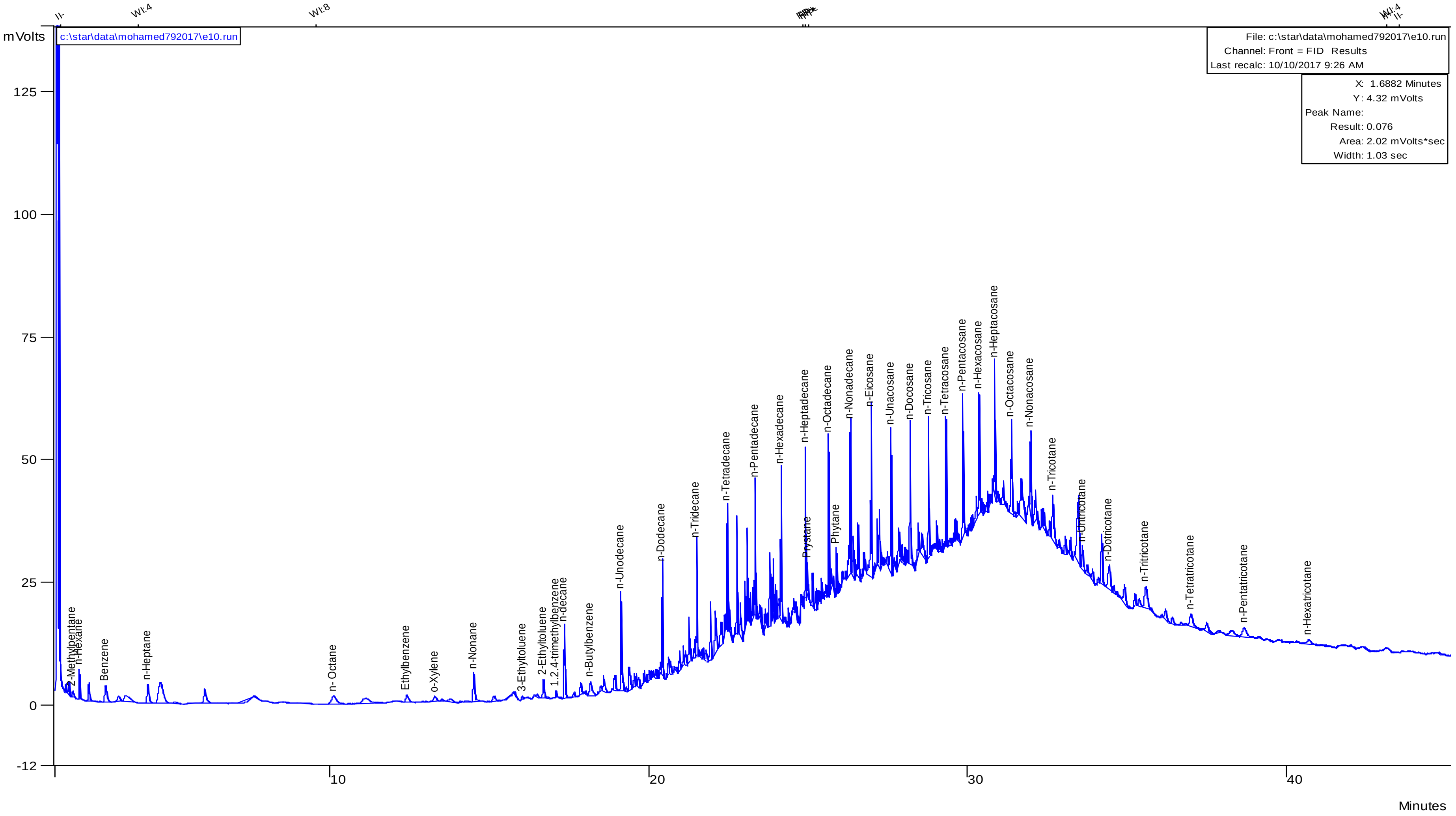


Figure No (4.5) GC of crude oil extracted by 10% of ethanol at 40°C

4.1.4 Extraction of acid in excess of solvent at 40 °C:

To optimize the extraction process. the extraction solvents (methanol and ethanol) were increased by 100% and the extraction effect was study under the same temperature which showed the results as in Tables (4.7) and (4.8).

Table No (4.7) Extraction of acid at 40 °C by 20% methanol

Sample	TAN mg KOH/g	Removal%
Collected crude oil	7.69	0.00
After first extraction	5.82	24.32
After second extraction	5.9	-1.37
After third extraction	6.49	-10.00
Total removal after one extraction	Optimum	24.32

Frist extraction process consider as optimum with high amount of acid removal with acid decreasing by 1.87 mg KOH/g which equivalents 24%. Second and third extraction process showed instability of solvent toward removal processes, hence showed increasing in backward reaction and formation of acids.

The overall extraction ratio same as that showed when using 10% methanol at 40°C. GC and FTIR showed same result as appeared in previous samples as crude oil composition kept as in original sample.

Table No (4.8) Extraction of acid at 40 °C by 20% ethanol

Sample	TAN mg KOH/g	Removal%
Collected crude oil	7.69	0.00
After first extraction	5.39	29.91
After second extraction	5.72	-6.12
After third extraction	4.68	18.18
Total removal after three extraction	Optimum	39%

First extraction removed most acid content from crude oil. Although acid increased in second extraction by (6%) third extraction again removed this acid formed in second extraction to reduce the TAN to 4.68 by (39%). When compare the extraction process with that at room temperature and pervious result with 10% of ethanol at 40°C extraction process with excess amount of ethanol consider the highest.

The result of GC give chromatogram same as original sample even for aromatic compounds like xylene and benzene derivatives.

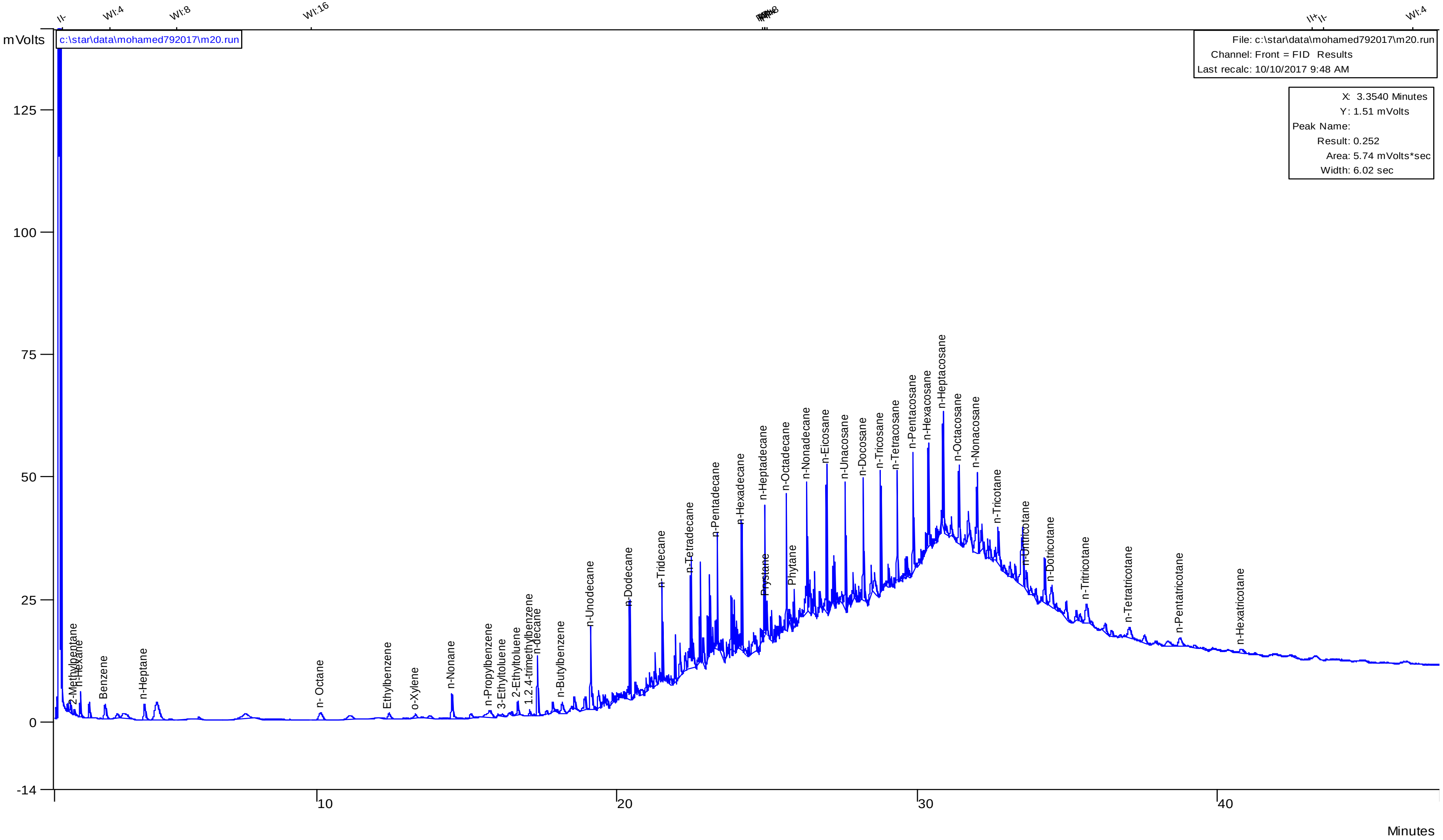


Figure No (4.6) GC of crude oil extracted by 20% of methanol at 40°C

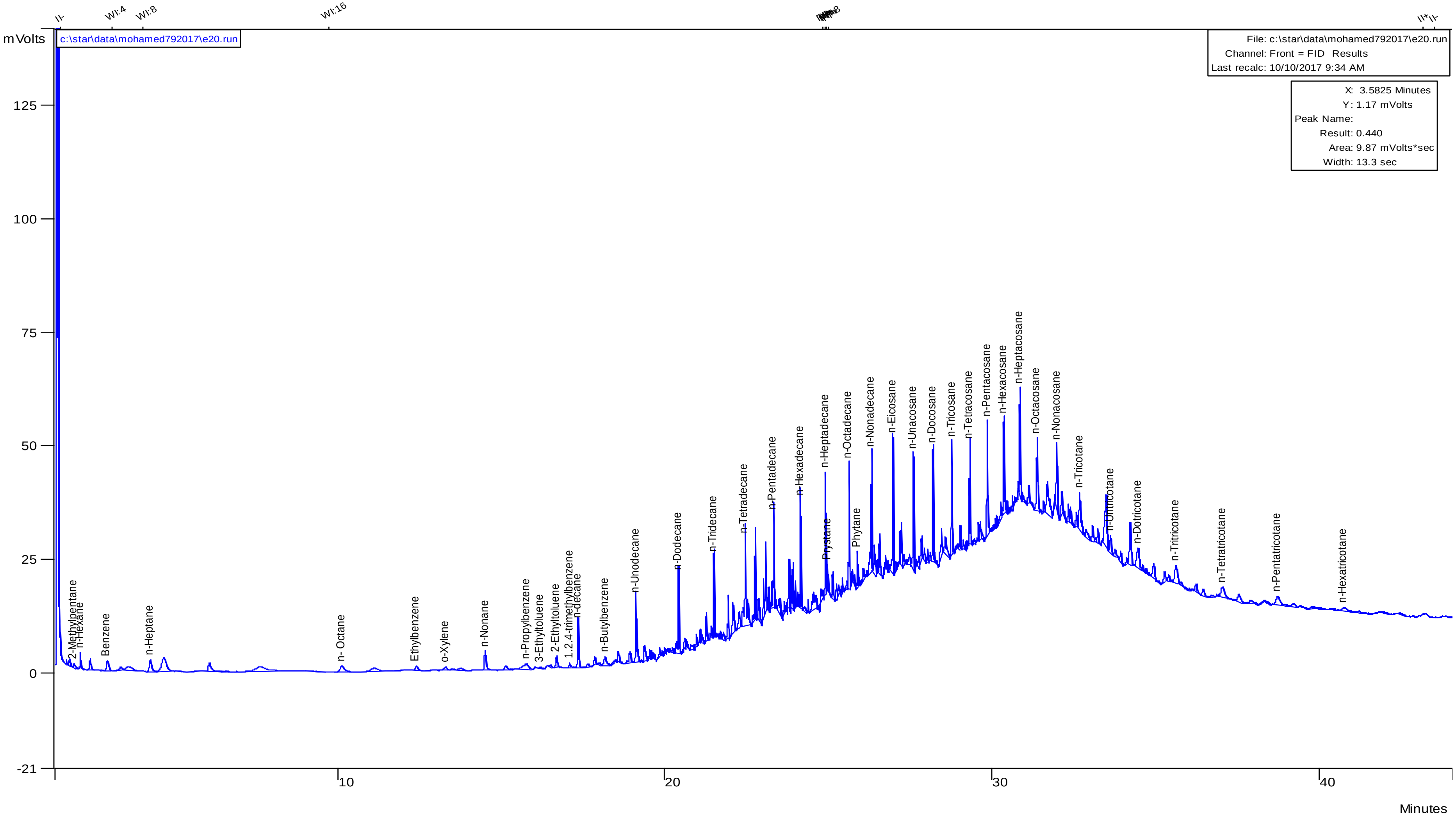


Figure No (4.7) GC of crude oil after extraction by 20% of ethanol at 40°C

4.1.5 **Extraction of acid at 50°C:**

These extraction processes were done at 50°C to optimize the effect of temperature in the removal process which gave the following results in Table (4.9).

Table No (4.9) Extraction of acid at 50°C by 10% methanol

Sample	TAN mg KOH/g	Removal%
Collected crude oil	7.69	0.00
After first extraction	7.25	5.72
After second extraction	5.1	29.66
After third extraction	5.23	-2.55
Total removal after two extraction	Optimum	31%

Second extraction (29%) was optimum when compare with first and third also consider higher than all pervious extraction with same solvent. third extraction showed increased in acidity of crude oil sample like extraction at room temperature and with excess amount of solvent (methanol). GC and FTIR have similar peaks as in original crude oil samples.

When compare the result with extractions process done by ethanol solvent result given in Table (4.10) below we could observe that extraction processes in 50C with methanol gave batter reduction in acid compounds in crude oil than ethanol even increasing of acid after extraction batter when use methanol (2%) and ethanol (11%).

Table No (4.10) Extraction of acid at 50°C by 10% ethanol

Sample	TAN mg KOH/g	Removal%
Collected crude oil	7.69	0.00
After first extraction	5.62	26.92
After second extraction	4.87	13.35
After third extraction	5.44	-11.70
Total removal after two extraction	Optimum	29%

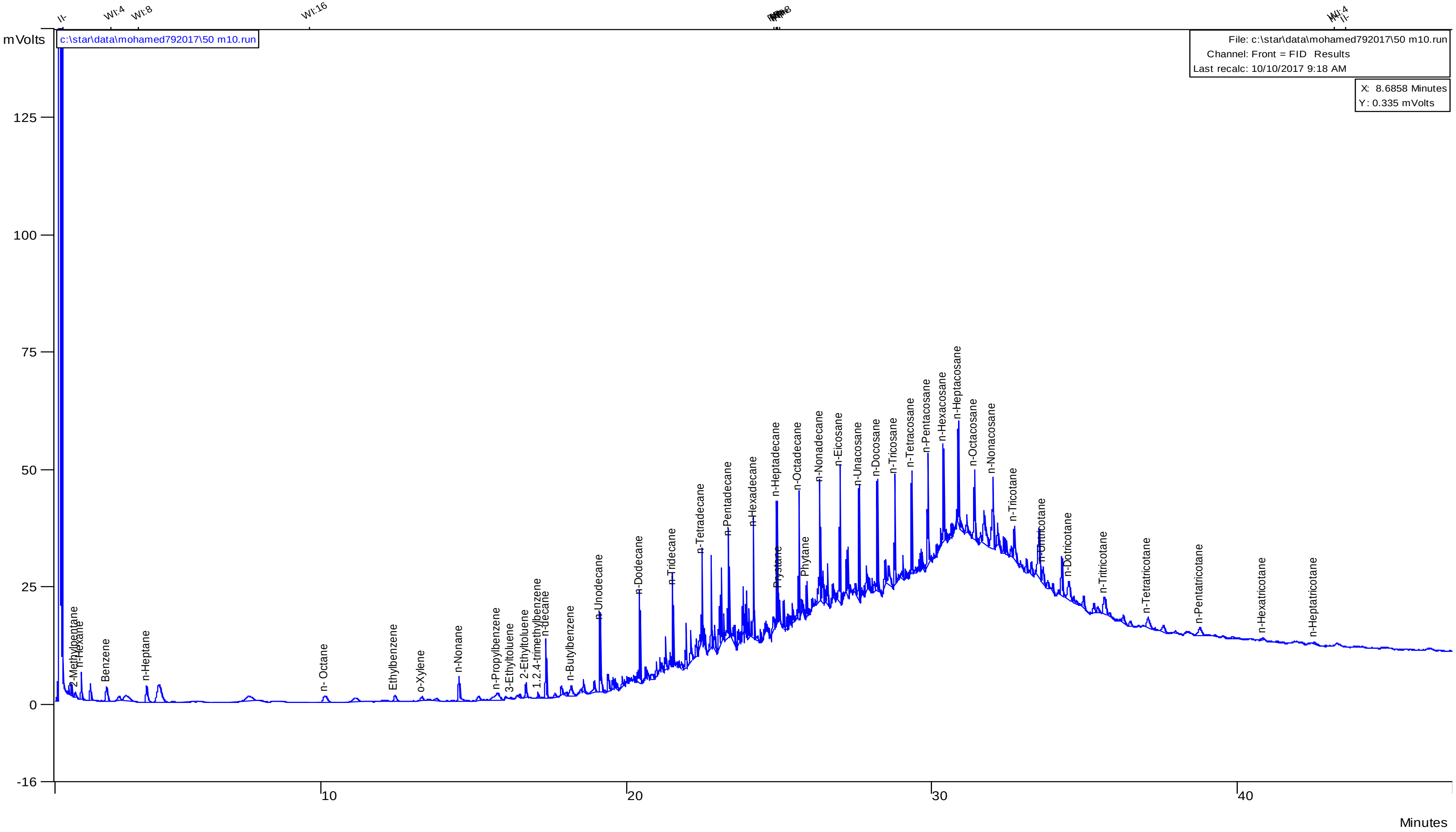


Figure No (4.8) GC of crude oil extracted by 10% of methanol at 50°C

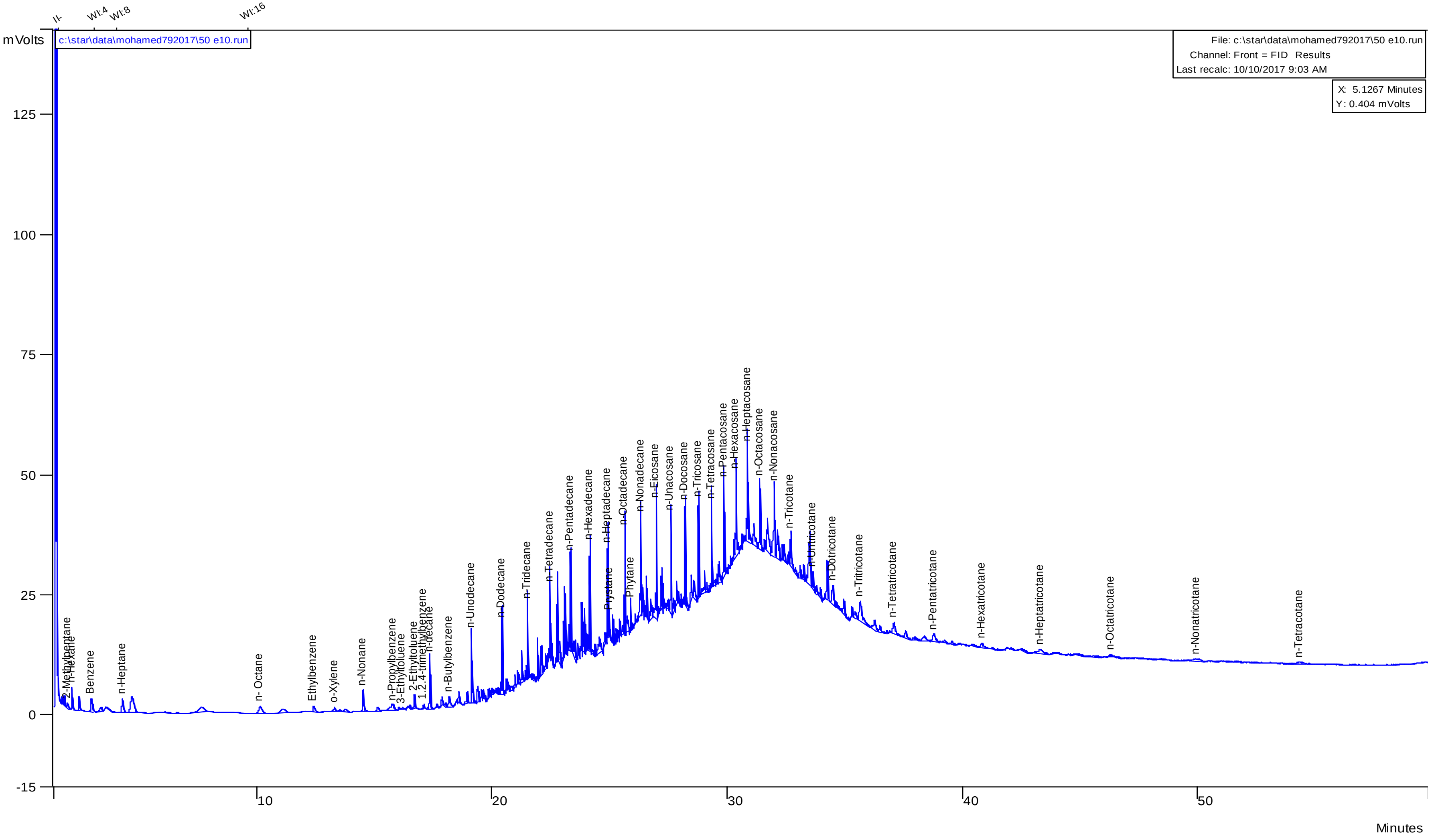


Figure No (4.9) GC of crude oil extracted by 10% of ethanol at 50°C

4.1.6 Extraction of acid in excess of solvent at 50°C:

In these experiments we try to examine increase amount of solvent 100% to determine the effect of it in the extraction processes. The result showed slightly better extraction percentage but the best in overall extraction process by methanol as showed in Table (4.11).

Table No (4.11) Extraction of acid at 50°C by 20% methanol

Sample	TAN mg KOH/g	Removal%
Collected crude oil	7.69	0.00
After first extraction	5.44	29.26
After second extraction	6.31	-15.99
After third extraction	4.88	22.66
Total removal after three extraction	Optimum	36.50%

First extraction gave good percentage of removal for these acids. A although acid increased in second extraction but the increase of removal percentage in third extraction removed all acid were increased in second extraction. From the result of GC and FTIR it was clear that the extraction processes had no effect on the main composition of crude oil.

In extraction process with excess ethanol considerable amount of acid removed in third extraction actually 50% of acids removed from crude oil as showed in Table (4.12).

Table No (4.12) Extraction of acid at 50°C by 20% ethanol

Sample	TAN mg KOH/g	Removal%
Collected crude oil	7.14	0.00
After first extraction	4.42	38.10
After second extraction	5.1	-15.38
After third extraction	3.82	25.10
Total removal after three extraction	Optimum	50%

First extraction removed acid content of crude oil by 38% and it consider highest value of extraction in all processes was done. Backward reaction appeared clearly in second extraction process but third extraction has high magnitude for removing acid (25%). When compare these extractions at 50°C with excess amount of solvent with other extraction was done by ethanol it considers the best but same highest instability for solvent appeared in second extraction (15%). GC and FTIR used to study the effect of extraction process on the main composition of crude oil.

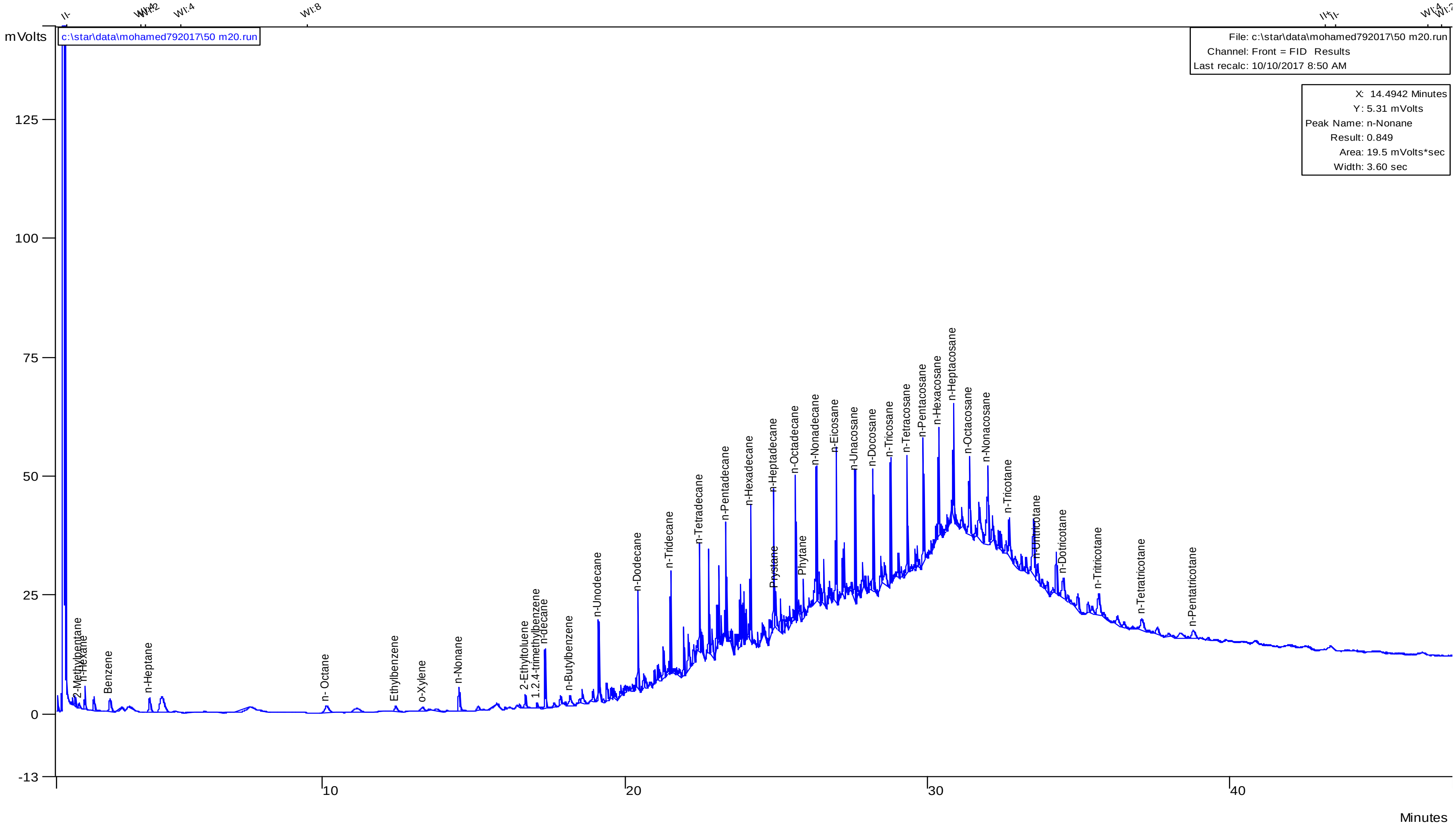


Figure No (4.10) GC of crude oil extracted by 20% of methanol at 50°C

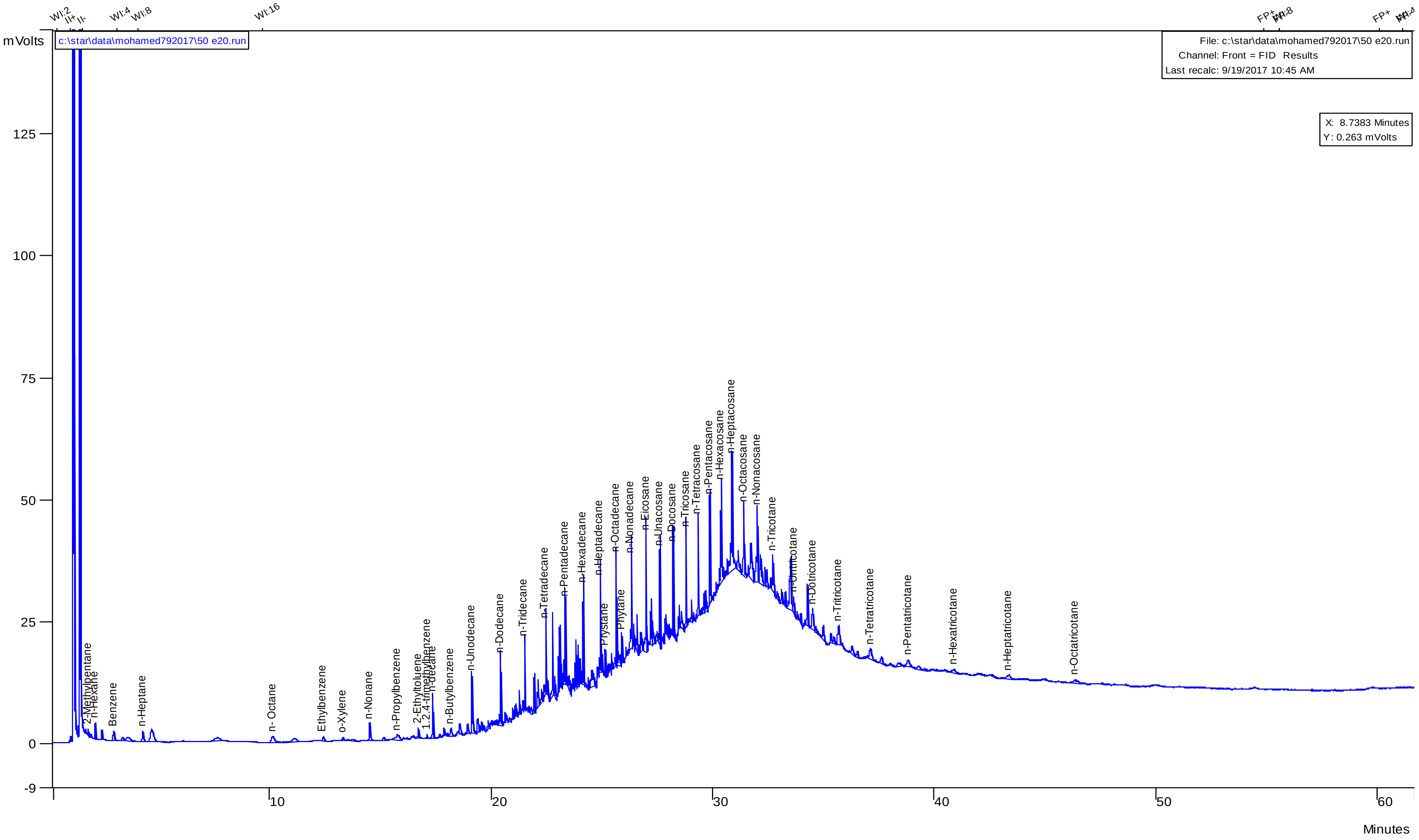


Figure No (4.11) GC of crude oil extracted by 20% of methanol at 50°C

4.1.7 **Optimum extraction percentage for acid:**

when compare the result of extraction acid for all sample with two solvents at different temperature and solvent ratio the following result was found as in Table (4.13).

Table No (4.13) optimum extraction of acids

Exteraction condition	**%**
Rom temp. with 10% Methanol	20.99
Rom temp. with 10% Ethanol	12.61
At 40°C 10% Methanol	24.32
At 40°C 10% Ethanol	31.6
At 40°C 20% Methanol	24.32
At 40°C 20% Ethanol	39
At 50°C 10% Methanol	31
At 50°C 10% Ethanol	29
At 50°C 20% Methanol	36
At 50°C 20% Ethanol	50

From the above results extraction processes with methanol increased gradually with increasing temperature and amount of solvent till reached to 36% at higher temperature (50°C) with excess of methanol.

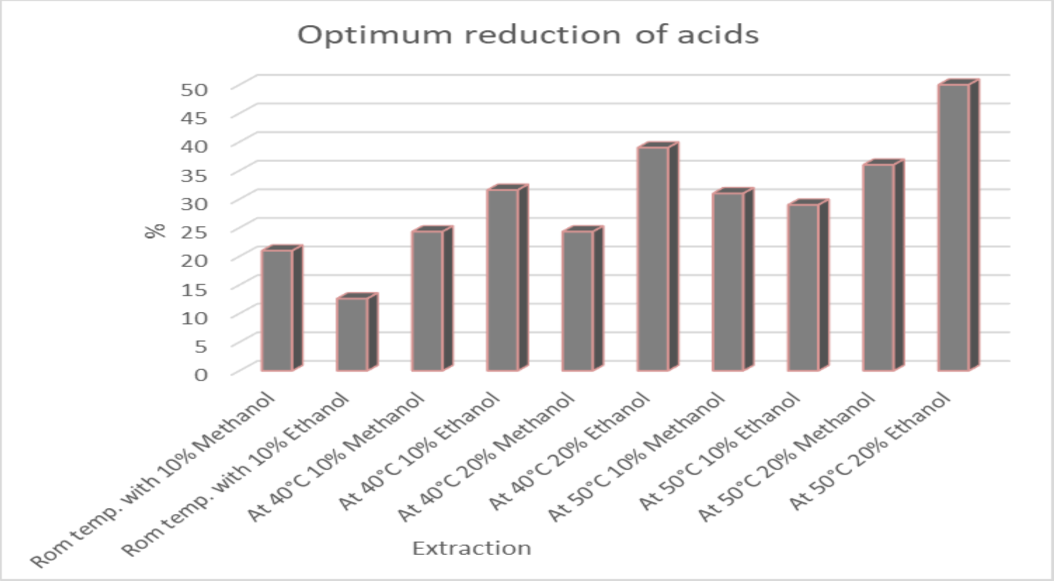


Figure No (4.12) Optimum percentage of extraction

Extraction with ethanol also had same behaviour like extraction with methanol but at 50°C with 10% of ethanol decreased to (29%) and increased again to (50%). ethanol is most effective process for removing acid from heavy, high acid crude oil when compare with Methanol which had the highest percentage of extraction.

4.2 **Physical test for highest reduction processes:**

In addition to the GC and FTIR other test like density pour point was measured for crude oil sample that had highest reduction percentages which gave the following result in Tables (4.14), (4.15) and (4.16).

Table No (4.14) physical and chemical properties of 50% acid removal with excess ethanol at 50°C

Test Name	Test Method	Unit	Result
Density @ 15	ASTM D5002	g/ml	0.94335
API	ASTM D5002		18.38
S.G	ASTM D5002		0.94427
TAN	ASTM D664	mgKOH/g	3.82
Pour point	ASTM D5853	C	12

Table No (4.15) physical and chemical properties of 39% acid reduction with excess ethanol at 40°C

Test Name	Test Method	Unit	Result
Density @ 15	ASTM D5002	g/ml	0.90903
API	ASTM D5002		24
S.G	ASTM D5002		0.9099
TAN	ASTM D664	mgKOH/g	4.68
Pour point	ASTM D5853	C	12

Table No (4.16) physical and chemical properties of 36% acid reduction with excess methanol at 50°C

Test Name	Test Method	Unit	Result
Density @ 15	ASTM D5002	g/ml	0.94133
API	ASTM D5002		18.7
S.G	ASTM D5002		0.94206
TAN	ASTM D664	mgKOH/g	4.88
Pour point	ASTM D5853	C	12

The physical properties in highest removal percentage samples showed variation in density and pour point that confirmed the suggestion of some paraffinic compound was removed from crude oil which reduce the API in some sample to less than 19.00 But these compounds not normal paraffin because the GC results gave the same amount of normal paraffin in collected crude oil before and after extraction processes. So, this leaded as to second suggestion was attributed these decreased in API to removed considerable amount of cycloparaffins.

As showed in Figures (4.13), (4.14) and (4.15) Fourier transform infrared peaks had same shapes, wavenumbers and intensities. Hence all figures showed stretching -CH_2- and CH_3 and also identical to the result appeared by collected crude oil sample before extraction processes, which mean the extraction processes had not effect on the main component of crude oil or functional groups.

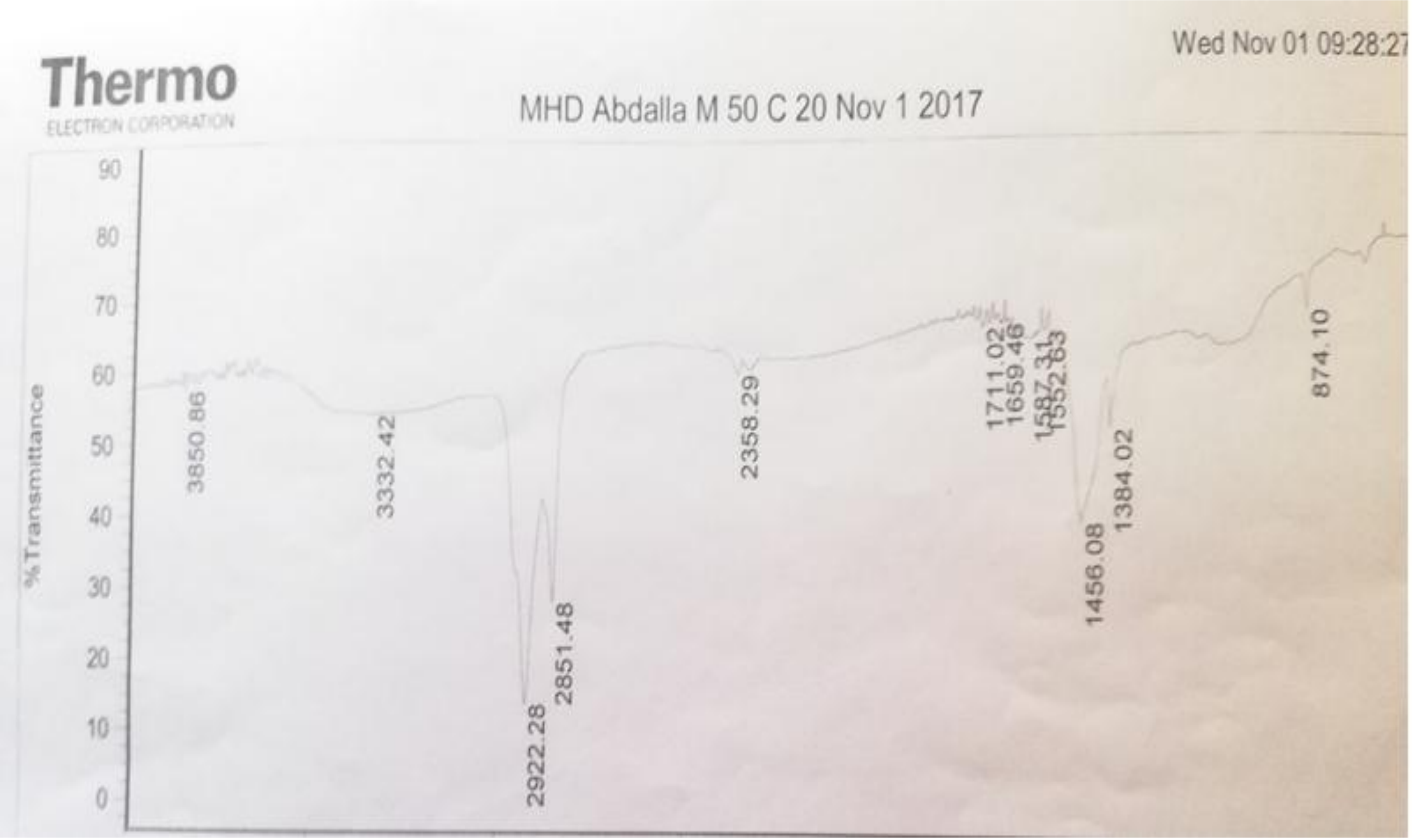


Figure No (4.13) FTIR for extracted crude oil at 50°C with excess ethanol

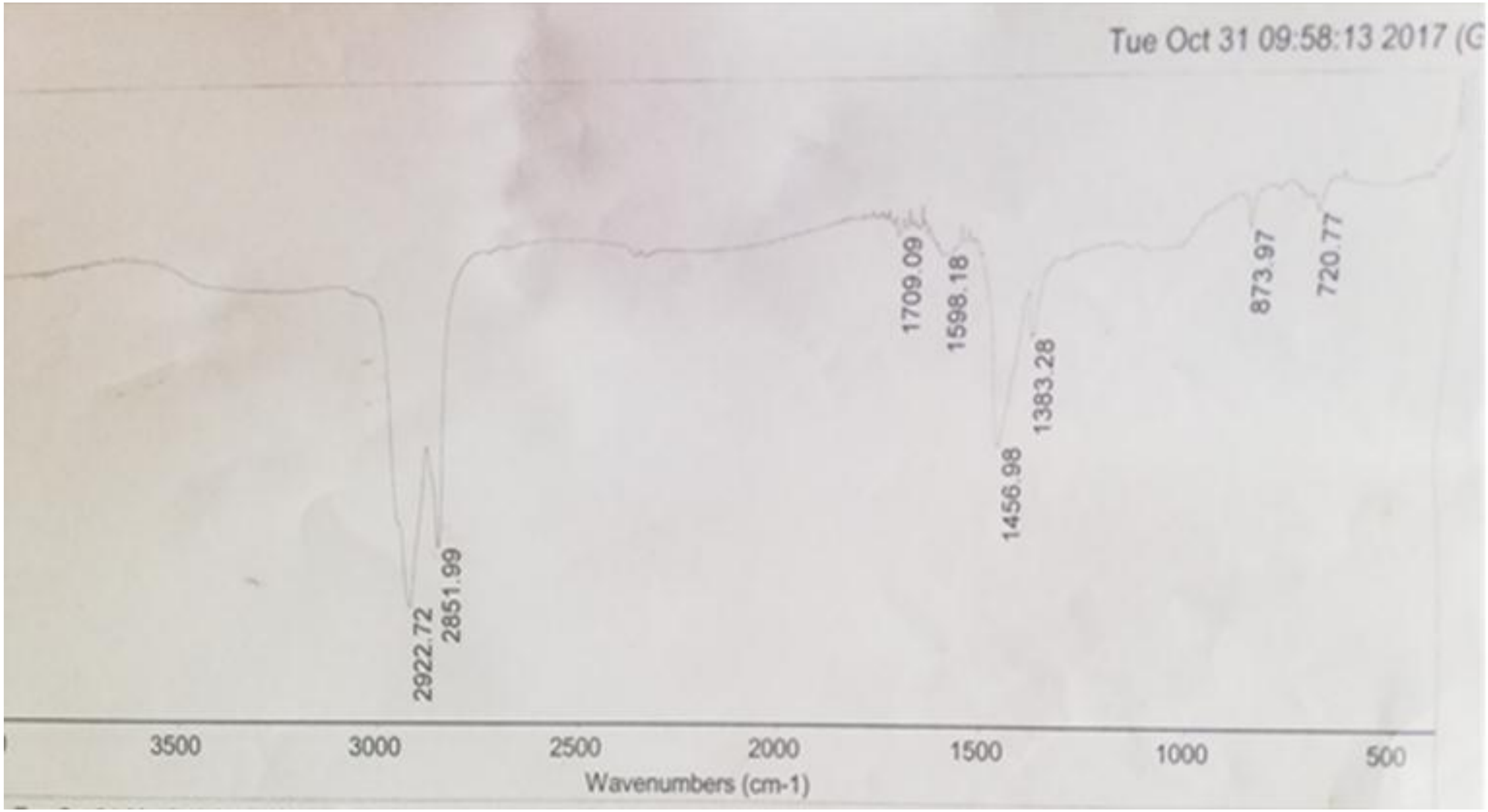


Figure No (4.14) FTIR for extracted crude oil at 50°C with 10% ethanol

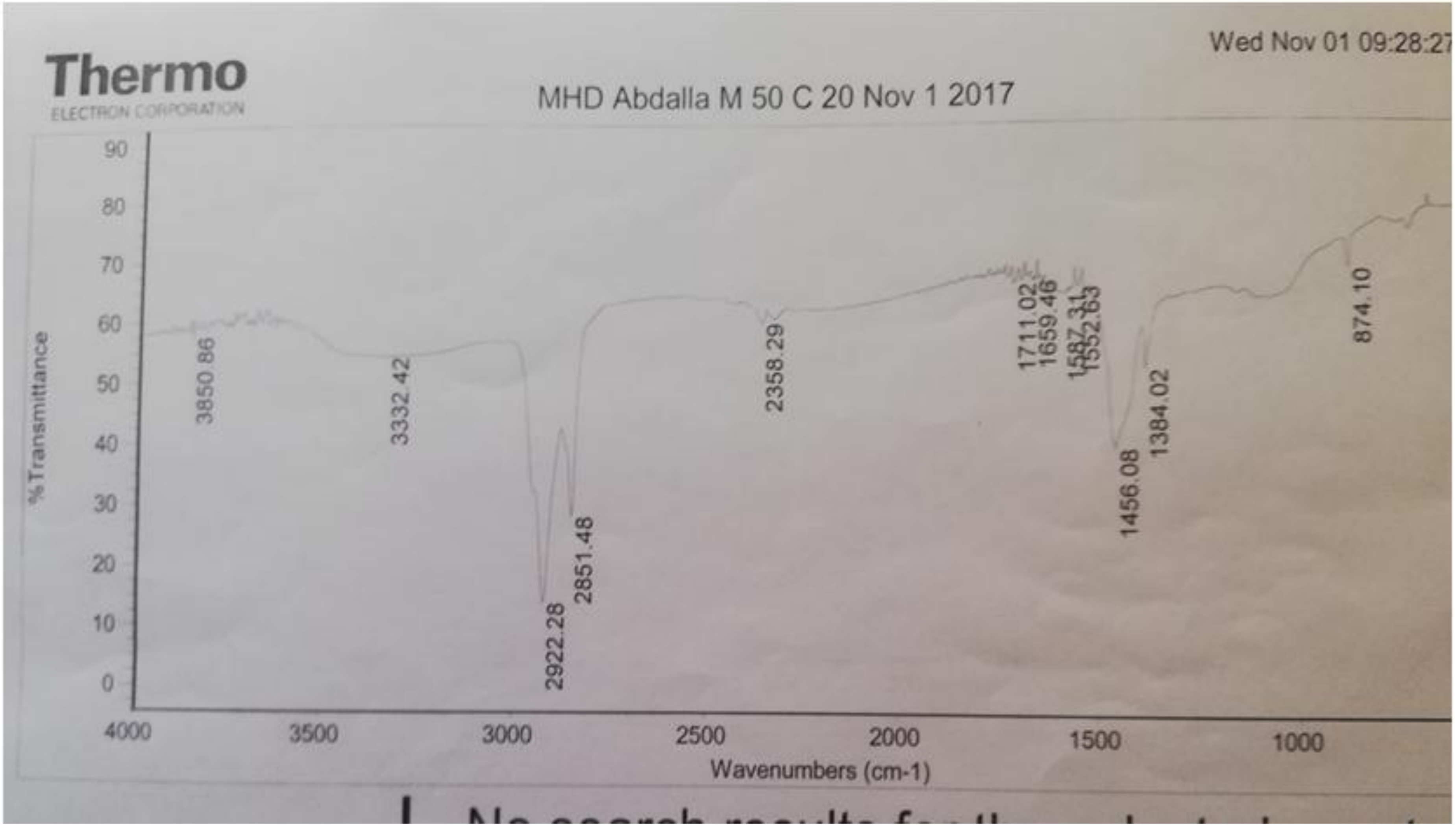


Figure No (4.15) FTIR for extracted crude oil at 50°C with excess methanol

4.3 Conclusion:

- Removal of acid from heavy, high acid Sudanese Crude Oil was done through liquid - liquid extraction using two types of organic solvents (ethanol and methanol).
- Temperature had positive effect in removing process, also amount of solvent.
- Ethanol has higher removal effect when compare with methanol which gave 31% - 39% and 50% room temp 40°C and 50°C respectively, while methanol gave 24%, 31% and 36% under same conditions.
- Density for the highest acid removal samples showed decrease in API density and pour points this may be attributed to the removal compound like cycloparaffins.
- Gas Chromatograph and Fourier transfer infrared results showed similarity in peaks before and after extraction process which mean the extraction processes have no effect on the main skeleton of collected crude oil sample.
- Some samples showed increase in acids after extraction, that illustrated the idea of instability of esterification reaction that might be occurred. So, more control in the extraction process by mean of using catalyst to stop the backward reaction required.

4.4 Recommendations:

- Use of environmentally friend organic solvent like ethanol to reduction acids in Sudanese high acid crude.
- Ethanol also can provide locally from sugar cane.
- It's better to use catalyst to reduce time and stabilize the process.
- Investigate the types of acid in extract using advance instrument like GC-MS or high-performance gas chromatography mass spectroscopy determine exacting the types of compounds which increase the acidity of Sudanese heavy crude oil.

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