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Enhancement of the Physical and Molecular Properties of Sudanese Crude Oil (Rawat) Using Solvent Dewaxing Process

تحسين الخواص الفيزيائية والجزئية لخام النفط السوداني (الراوات) بأستخدام طريقة إزالة الشمع بالمذيب

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By

Mahjoub Ahmed Mahjoub Mohammed

B.Sc., M.Sc. (Chemistry).

Supervisors:

Prof./ El-mugdad Ahmed Ali Khalid (Sudan University of Science and Technology).

Prof./ Magdy Tadrous Zaky (Egyptian Institute for Petroleum Researches).

Prof./ Fathi Samir Soliman Ibrahim (Egyptian Institute for Petroleum Researches).

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قال تعالى:

« وَالَّذِي أَخْرَجَ الْمَرْعَىٰ (4) فَجَعَلَهُ غُثَاءً أَحْوَىٰ (5) »

صدق الله العظيم

"سورة الأعلى : الآية 4 و 5"

Dedication

To:

My parents ...

Sisters, brothers...

And my friends...

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Abstract

This study was conducted to treat the Sudanese crude oil from Rawat area southwest of Kosti which has a high wax content of 26.3% by weight and pour point 54°C, in order to remove the wax and to reduce the pour point and enhance the physical and molecular properties of the treated oil using organic solvent de-waxing technology. The physical and molecular properties of crude oil and the oils produced from the treatments were obtained using American Society for Testing and Materials (ASTM) methods and materials. Methyl Ethyl Ketone (MEK)- Methyl Isobutyl Ketone (MIBK)- Butyl Acetate (BA)- Methyl Tert-butyl Ether (MTBE) were used as de-waxing solvents. The de-waxing temperatures at -5, -10, -15 and -20°C and solvent feed ratio of 10:1, 8:1, 6:1, and 4:1 with constant washing ratio 2:1 and crystallization time 6, 12 and 24 hours. MEK recorded as the best oil production, at 10:1 S/F ratio which is 16.81% with pour point equal 2°C at de-waxing temperature -10°C, while MIBK recorded 29.14% of yield, pour point 5°C at 10:1 S/F and de-waxing temperature -10°C, Due to high cost of this ketone is very expensive, so it has been excluded and also MEK has low yield as a single solvent and requires a companion solvent such as toluene to increase the solubility. Recovery of mixed solvents is not desirable due to the differentiation in their boiling points range, and it is too hard to separate the two solvents upon making distillation and it is recovery for another de-waxing step. When using butyl acetate, the yield was 36% and the pour point was 5°C. Therefore, this represents the best result compared to the previous solvents. Methyl tertiary butyl ether recorded a high yield 68.19% but also a high pour point 28°C because a high percentage of wax was soluble in solvent, the percentage of wax in the oil produced was equal to 18.8%, so the solvent was excluded. Butyl acetate was selected to remove wax from crude oil and solvent ratios

were used 10:1, 8:1, 6:1 and 4:1 and the best ratio was 10:1 and de-waxing temperatures were -5, -10, -15 and -20°C and the best one was -10 degrees, crystallization times are 6 -12 -24 hours and the best time is 24 hours because the size of the crystals is larger and the removal efficiency is higher. Thus, it can be concluded that the process of de-waxing at crystallization time of 24hrs would be suitable and is the one selected for de-waxing of Sudanese crude oil using Butyl Acetate at dilution solvent ratio of 10:1 and at de-waxing temperature of -10°C.

المستخلص

أجريت هذه الدراسة لمعالجة خام البترول السوداني الموجود بمنطقة الراوات جنوب غرب كوستي الذي يحتوي علي نسبة شمع عالية تقدر ب 26.3% بالوزن ودرجة إنسكاب 54 درجة مئوية وذلك بغرض إزالة الشمع لتقلل درجة الإنسكاب وتحسين الخواص الفيزيائية والتركيبية للزيت الناتج من المعالجه باستخدام تقنية إزالة الشمع بالمذيبات العضوية. تم توصيف الزيت الخام والزيت الناتج من المعالجات باستخدام جميع المذيبات وبنسب مختلفة فيزائيا وتركيبيا باستخدام طرق الجمعية الأمريكية للإختبار والمواد. تم إستخدام كل من ميثيل إيثيل كيتون- ميثيل إيزوبوتيل كيتون - خلات البوتيل- ميثيل ثالثي بوتيل الأثير, وإزالة الشمع عند درجات حراره -5, -10, -15, و -20 درجة مئوية ونسبة المذيب لزيت الخام 1:10, 1:8, 1:6, 1:4 ونسبة غسيل الشمع بالمذيب 1:2 وفترة تكوين بلورات الشمع 6- 12- 24 ساعة. سجل ميثيل إيثيل كيتون أفضل إنتاج للزيت المستخلص عند نسبة 1:10 وهي 16.81% وكانت درجة الإنسكاب 2 درجة مئوية وذلك عند درجة حرارة -10 درجة مئوية, بينما سجل ميثيل إيزوبوتيل كيتون إنتاج 29.14% ودرجة إنسكاب 5 درجة مئوية عند نسبة مذيب للخام 1:10 ودرجة الحراره لإزالة الشمع -10 درجة مئوية مع العلم أن سعر هذا الكيتون غالي جدا لذلك تم إستبعاده وأيضا تم إستبعاد ميثيل إيثيل كيتون لقلة إنتاجه كمذيب منفرد ويحتاج إلي مذيب مرافق مثل التولوين وهذا يمثل عائق لإعادة إستخدامه مره اخري لإختلاف درجات غليان كل واحد منهم. عند إستخدام خلات البوتيل وجد أن الناتج نسبته 36% ودرجة الإنسكاب 5 درجة مئوية وعليه هذه النتيجة تمثل أفضل نتيجة مقارنة بالمذيبات السابقة مع ثبوت كل العوامل عليهم. ميثيل ثالثي بوتيل الإثير سجل إنتاج عالي 68.19% لكن درجة إنسكابه أيضا عالية 28 درجة مئوية وذلك لأن نسبة عالية من الشمع كانت ذائبة بالمذيب, وكانت نسبة الشمع بالزيت المنتج تساوي 18.8% ولذلك تم إستبعاد هذا المذيب. وعليه تم إختيار خلات البوتيل لإزالة الشمع من الزيت الخام وأستخدمت نسب المذيب للزيت الخام 1:10, 1:8, 1:6, 1:4 وكانت أفضل نسبة هي 1:10 ودرجات إزالة الشمع -5, -10, -15, و -20 درجة مئوية وكانت أفضل درجة هي -10 درجة مئوية وزمن تكوين بلورات الشمع 6- 12- 24 ساعة وكان أفضل زمن هو 24 ساعة وذلك لأن حجم والبلورات أكبر وعليه كفاءة الإزالة أعلي. وبالتالي، يمكن أن نخلص ذلك بأن عملية إزالة الشمع عند وقت التبلور لمدة 24 ساعة ستكون مناسبة وتم إختيارها لإزالة الشمع من النفط الخام السوداني باستخدام خلات البوتيل عند نسبة مذيب للخام 10:1 وفي درجة حرارة إزالة الشمع -10 درجة مئوية.

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List of Abbreviations

CNPC	China National Petroleum Company
GNPOC	Greater Nile Petroleum Operating Company
ONGC	Oil and Natural Gas Corporation Limited
CPA	Comprehensive Peace Agreement
TBC	Technical Border Committee
ABC	The Abyei Boundary Commission
PCA	the Permanent Court of Arbitration
API	American Petroleum Institute
TBP	True Boiling Point
ASTM	American Society for Testing and Materials
AC	Magnetic fields emanate from manmade electrical systems (power lines, transformers, computers, and anything with an electric motor)
DC	Magnetic field emanates from the earth naturally that is what allows a compass to find magnetic North
pH	Measurement of hydrogen ion concentration
MEK	Methyl Ethyl Ketone
DWO	De-Waxed Oil
IP	International Petroleum test methods
U.V	Ultraviolet
TAPPI	Technical Association of the Pulp and Paper Industry.
MIBK	Methyl Iso-Butyl Ketone
SPD	Short Path Distillation
FDA	Food and Drug Administration
PIM	Powder Injection Molding
HMA	Hot Mix Asphalt
F/S	Solvent to Feed Ratio
GC	Gas Chromatography
BA	Butyl Acetate
MTBE	Methyl Tertiary Butyl Ether
UOP	Universal Oil Products Standards
C_A	Aromatics Carbon
C_P	Paraffinic Carbon
C_N	Naphthenic Carbon
R_A	Aromatic Ring
R_N	Naphthenic Ring
R_T	Total Ring

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Chapter One

Introduction and Literature Review

Chapter One: 1. Introduction and Literature Review

1.1 Brief History:

Oil exploration in Sudan was first initiated in 1959 by Italy's Agip oil company in the Red Sea area. Several oil companies followed Agip in the Red Sea Area but none was successful in their exploration efforts. After the end of the first civil war in 1972 it became possible to extend the oil exploration to southern Sudan. In 1975 the American oil company Chevron was granted a concession in the south and south-west of the country. The first oil discovery in Sudan was made by Chevron in the south of Sudan in 1979, west of the Muglad. Chevron continued its successful exploration and made more significant discoveries in the so called Unity and Heglig fields. In 1983 Chevron, Royal Dutch Shell, the Sudanese government, and the Arab Petroleum Investments Corporation (Apicorp) formed the White Nile Petroleum Company in order to build an oil pipeline from the Sudanese oil fields to Port Sudan on the Red Sea. The projected costs for this project amounted to 1US\$ billion. The plans of Chevron could not be implemented as the second civil war erupted in 1983. Chevron suspended its operations in 1984 and entirely ended its 17 year long involvement in Sudan by selling its interests to the Sudanese company Concorp in 1992. Concorp sold these concessions on to the Canadian oil corporation 'State Petroleum Corporation' a few months. After 1994 Arakis Energy Corporation purchased State Petroleum Corporation and started operating in Sudan. Arakis faced difficulties in securing the needed financing to fulfil its exploration and production agreement with the Sudanese Government. In 1996 it sold 75% of its shares to the China National Petroleum Company (CNPC), Petronas (Malaysia), and Sudapet (Sudan) with which it jointly formed the Greater Nile Petroleum Operating Company (GNPOC). Arakis subsequently sold its 25% share in the

GNPOC to the Canadian company Talisman in 1998 (**Obi, 2007**). The GNPOC made considerable discoveries, increasing the amount of proven reserves in Sudan. It also succeeded in the construction of the pipeline from the Heglig and Unity fields to Port Sudan on the Red Sea. In 1999 the pipeline became operational and carried the first Sudanese oil exports to Port Sudan. In this period and as a result of international public pressure over accusations of being complicit in human rights violations through its operations in Sudan, Talisman sold its shares in the GNPOC to the Indian company Oil and Natural Gas Corporation Limited (ONGC). A consortium made of the French company Total, the American company Marathon, Kuwait Foreign Petroleum Company and the Sudanese company Sudapet was granted a concession in south eastern Sudan (block B) in 1980. The consortium suspended its operations in 1985 as a result of the civil war. Unlike Chevron, Total and its partners did not relinquish their concessions as a result of the civil war and they signed an agreement in December 2004 with the Sudanese government to update the contract. As a result of this there is now a dispute between Total and a UK company, White Nile Ltd, who claims that it signed an agreement with the future government of south Sudan for oil exploration in part of the land believed to be within block B and part of the concession of Total and its partners. In 1997, the Sudanese Government granted another concession in the so called block 5A to the Swedish company Lundin with partners Petronas, OMV (Austrian oil and gas company) and Sudapet. In 2001 the same consortium was granted a concession over block 5B. In 2003 Lundin sold its interest in block 5A to Petronas and OMV sold its interests in Blocks 5A and 5B to the Indian company Oil and Natural Gas Corporation Limited (ONGC) (**Obi, 2007**).

The unified Sudan fought two civil wars. The second civil war ended with the signing of the Comprehensive Peace Agreement that was put into place from

2005 to 2011. South Sudan gained its independence from Sudan in July 2011. However, there are still unresolved issues that have caused tension between the countries after independence. The border between the two countries is undefined, and some areas along the border remain contested. Since its independence in 1956 from joint British and Egyptian rule, Sudan has experienced several armed conflicts that have affected the country's economic development, particularly its natural resources. The longest conflicts in the unified Sudan were the two civil wars (1955-1972). The second civil war ended with the signing of the Comprehensive Peace Agreement (CPA) that was in place from 2005 to 2011. The CPA set standards for sharing oil revenue (50:50 split) and a timetable toward a referendum on the South's independence. A referendum took place in January 2011 in which the people of the South voted to secede from Sudan. In July 2011, Sudan became two countries: Sudan (Khartoum as the capital) and South Sudan (Juba as the capital). The border separating Sudan and South Sudan is still not officially defined, and some areas remain contested. The current de facto border was established when Sudan gained independence in 1956, and it is known as the 1956 border. The CPA called for the border to be demarcated, and a Technical Border Committee (TBC) was established in 2005 to demarcate the 1956 border. The committee agreed on most of the border, but five areas remain disputed, according to a report by the International Crisis Group. One of the most contentious areas, which was excluded in the TBC's mandate, is the Abyei area, located between the states of Bahr al Ghazal, Warrap, and Unity. Oil was discovered in Abyei in 1979, which escalated tensions between both sides. The Abyei Boundary Commission (ABC) was authorized to define the territory, and in 2005 it ruled that the Heglig and Bamboo oil fields fell within Abyei. The North contested the ruling because it placed a significant portion of its oil reserves in the disputed territory. The dispute was later sent to the Permanent

Court of Arbitration (PCA) in The Hague. In 2009, PCA redefined the Abyei area and placed the Heglig and the Bamboo oil fields outside of Abyei. A referendum was scheduled for January 2011 to determine whether Abyei would join Sudan or South Sudan, but the referendum did not occur because of disagreements over voter eligibility. Although uncertainties over border demarcation and the ownership of Abyei remain, the Heglig and Bamboo oil fields are considered today to be in Sudan's South Kordofan state (**Patey, 2014**).

1.2 Important Feed and Product Characterization Properties in Refinery Engineering:

1.2.1 API Gravity:

API gravity of petroleum fractions is a measure of density of the stream. Usually measured at 60 °F, the API gravity is expressed as:

$$^{\circ}\text{API} = 141.5/\text{specific gravity} - 131.5$$

where specific gravity is measured at 60 °F.

According to the above expression, 10 °API gravity indicates a specific gravity of 1 (equivalent to water specific gravity). In other words, higher values of API gravity indicate lower specific gravity and therefore lighter crude oils or refinery products and vice-versa. As far as crude oil is concerned, lighter API gravity value is desired as more amount of gas fraction, naphtha and gas oils can be produced from the lighter crude oil than from the heavier crude oil. Therefore, crude oil with high values of API gravity are expensive to procure due to their quality (**Pachuau, 2018**).

1.2.2 Watson Characterization Factor:

The Watson characterization factor is usually expressed as:

$$K = (T_B)^{1/3}/\textit{specific gravity}$$

Where T_B is the average boiling point in degrees R taken from five temperatures corresponding to 10, 30, 50, 70 and 90 volume % vaporized.

Typically Watson characterization factor varies between 10.5 and 13 for various crude streams. A highly paraffinic crude typically possesses a K factor of 13. On the other hand, a highly naphthenic crude possesses a K factor of 10.5. Therefore, Watson characterization factor can be used to judge upon the quality of the crude oil in terms of the dominance of the paraffinic or naphthenic components **(Pachuau, 2018)**.

1.2.3 Sulfur Content:

Since crude oil is obtained from petroleum reservoirs, sulphur can be present in the crude oil. Usually, crude oil has both organic and inorganic sulphur in which the inorganic sulphur dominates the composition. Typically, crude oils with high sulphur content are termed as sour crude. On the other hand, crude oils with low sulphur content are termed as sweet crude. Typically, crude oil sulphur content consists of 0.5 – 5 wt % of sulphur. Crudes with sulphur content lower than 0.5 wt % are termed as sweet crudes. It is estimated that about 80 % of world crude oil reserves are sour.

The sulphur content in the crude oil is responsible for numerous hydrotreating operations in the refinery process. Strict and tighter legislations enforce the production of various consumer petroleum products with low quantities of sulphur (in the range of ppm). This indicates that large quantities of inorganic sulphur needs to be removed from the fuel. Typically, inorganic sulphur from various intermediate product streams is removed using hydrogen as hydrogen sulphide **(Pachuau, 2018)**.

A typical refinery consists of good number of hydro-treaters to achieve the desired separation. The hydro-treaters in good number are required due to the fact that the processing conditions for various refinery intermediate process streams are significantly different and these streams cannot be blended together as well due to their diverse properties which were achieved using the crude distillation unit (**Pachau, 2018**).

1.2.4 True Boiling Point/ASTM Distillation Curves:

The most important characterization properties of the crude / intermediate / product streams are the TBP/ASTM distillation curves. Both these distillation curves are measured at 1 atm pressure. In both these cases, the boiling points of various volume fractions are being measured. However, the basic difference between TBP curve and ASTM distillation curve is that while TBP curve is measured using batch distillation apparatus consisting of no less than 100 trays and very high reflux ratio, the ASTM distillation is measured in a single stage apparatus without any reflux. Therefore, the ASTM does not indicate a good separation of various components and indicates the operation of the laboratory setup far away from the equilibrium (**Pachau, 2018**).

1.2.5 Viscosity:

Viscosity is a measure of the flow properties of the refinery stream. Typically in the refining industry, viscosity is measured in terms of centistokes (termed as cSt) or saybolt seconds or redwood seconds. Usually, the viscosity measurements are carried out at 100 °F and 210 °F. Viscosity is a very important property for the heavy products obtained from the crude oil. The viscosity acts as an important characterization property in the blending units associated to heavy products such as bunker fuel. Typically, viscosity of these products is specified to be within a specified range and this is achieved by adjusting the viscosities of the streams entering the blending unit (**Pachau, 2018**).

1.2.6 Flash and Fire Point:

Flash and fire point are important properties that are relevant to the safety and transmission of refinery products. Flash point is the temperature above which the product flashes forming a mixture capable of inducing ignition with air. Fire point is the temperature well above the flash point where the product could catch fire. These two important properties are always taken care in the day to day operation of a refinery (**Pachau, 2018**).

1.2.7 Pour Point:

When a petroleum product is cooled, first a cloudy appearance of the product occurs at a certain temperature. This temperature is termed as the cloud point. Upon further cooling, the product will cease to flow at a temperature. This temperature is termed as the pour point. Both pour and cloud points are important properties of the product streams as far as heavier products are concerned. For heavier products, they are specified in a desired range and this is achieved by blending appropriate amounts of lighter intermediate products (**Pachau, 2018**).

1.2.8 Octane Number:

Though irrelevant to the crude oil stream, the octane number is an important property for many intermediate streams that undergo blending later on to produce automotive gasoline, diesel etc. Typically gasoline tends to form in the engines. The knocking tendency of the gasoline is defined in terms of the maximum compression ratio of the engine at which the knock occurs. Therefore, high quality gasoline will tend to knock at higher compression ratios and vice versa. However, for comparative purpose, still one needs to have a pure component whose compression ratio is known for knocking. Iso-octane is eventually considered as the barometer for octane number comparison. While iso-octane was given an octane number of 100, n-heptane is given a scale of 0. Therefore, the octane number of a fuel is equivalent to a mixture of a iso-octane and n-

heptane that provides the same compression ratio in a fuel engine. Thus an octane number of 80 indicates that the fuel is equivalent to the performance characteristics in a fuel engine fed with 80 vol % of isooctane and 20 % of n-heptane. Octane numbers are very relevant in the reforming, isomerisation and alkylation processes of the refining industry. These processes enable the successful reactive transformations to yield long side chain paraffins and aromatics that possess higher octane numbers than the feed constituents which do not consist of higher quantities of constituents possessing straight chain paraffins and non-aromatics (naphthenes) (**Pachua, 2018**).

1.3 Crude Chemistry:

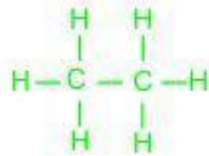
Fundamentally, crude oil consists of 84 – 87 wt % carbon, 11 – 14 % hydrogen, 0 – 3 wt % sulphur, 0 – 2 wt % oxygen, 0 – 0.6 wt % nitrogen and metals ranging from 0 – 100 ppm. Understanding thoroughly the fundamentals of crude chemistry is very important in various refining processes. The existence of compounds with various functional groups and their dominance or reduction in various refinery products is what is essentially targeted in various chemical and physical processes in the refinery. Based on chemical analysis and existence of various functional groups, refinery crude can be broadly categorized **into:**

1.3.1 Paraffins:

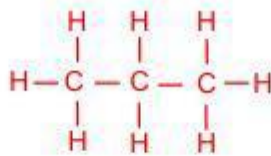
Paraffins refer to alkanes such as methane, ethane, propane, n- and iso- butane, n- and iso- pentane. These compounds are primarily obtained as a gas fraction from the crude distillation unit.



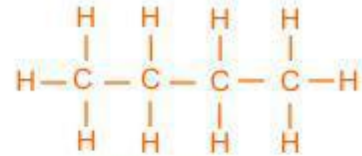
Methane(CH₄)



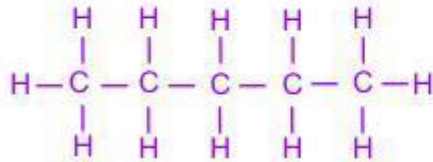
Ethane(C₂H₆)



Propene(C₃H₈)



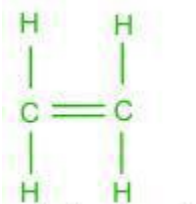
Normal Butane(nC₄H₁₀)



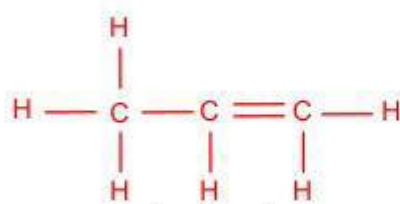
Normal Pentene (C₅H₁₂)

1.3.2 Olefins:

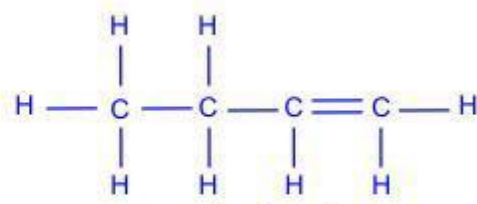
Alkenes such as ethylene, propylene and butylenes are highly chemically reactive. They are not found in mentionable quantities in crude oil but are encountered in some refinery processes such as alkylation.



Ethylene(C₂H₄)



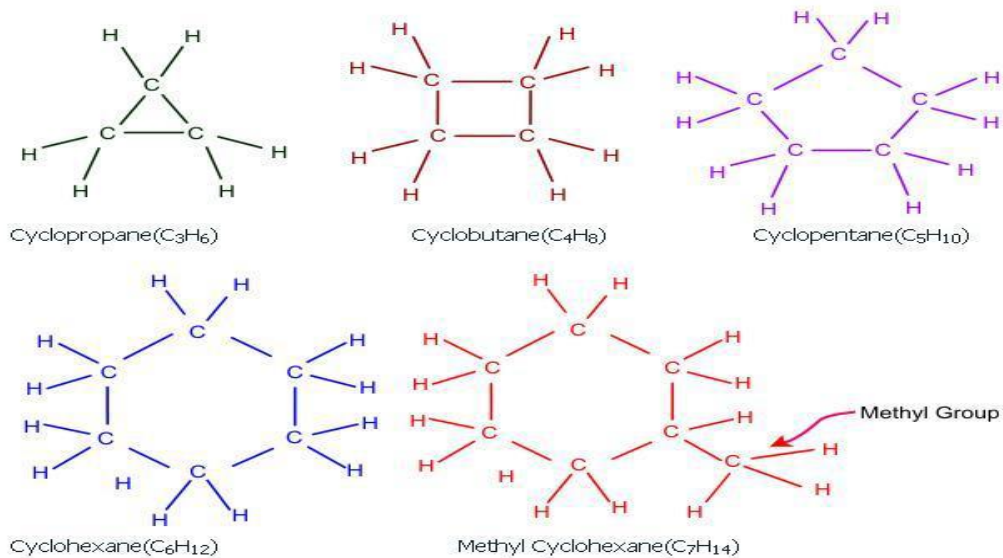
Propylene(C₃H₆)



Butylene(C₄H₈)

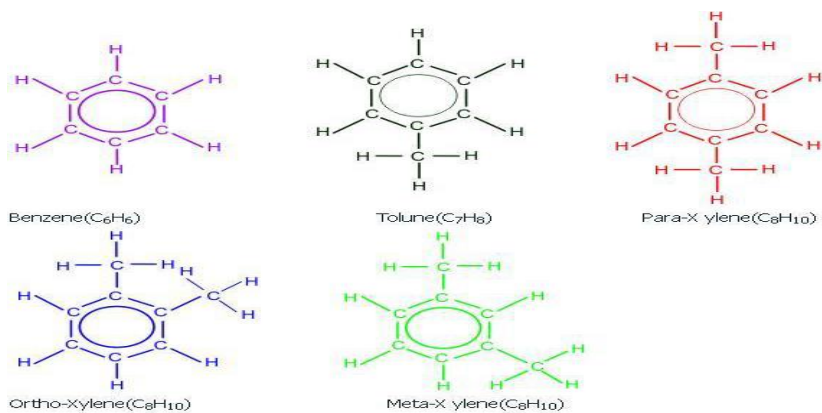
1.3.3 Naphthenes:

Naphthenes or cycloalkanes such as cyclopropane, methyl cyclohexane are also present in the crude oil. These compounds are not aromatic and hence do not contribute much to the octane number. Therefore, in the reforming reaction, these compounds are targeted to generate aromatics which have higher octane numbers than the naphthenes.



1.3.4 Aromatics:

Aromatics such as benzene, toluene o-, m-, and p-xylene are also available in the crude oil. These contribute towards higher octane number products and the target is to maximize their quantity in a refinery process.



1.3.5 Naphthalenes:

Polynuclear aromatics such as naphthalenes consist of two or three or more aromatic rings. Their molecular weight is usually between 150 – 500.



1.3.6 Organic Sulphur Compounds:

Not all compounds in the crude are hydrocarbons consisting of hydrogen and carbon only. Organic sulphur compounds such as thiophene, pyridine also exist in the crude oil. The basic difficulty of these organic sulphur compounds is the additional hydrogen requirements in the hydrotreaters to meet the euro III standards. Therefore, the operating conditions of the hydrotreaters is significantly intense when compared to those that do not target the reduction in the concentration of these organic sulphur compounds. Therefore, ever growing environmental legislations indicate technology and process development/improvement on the processing of organic sulphur compounds.

1.3.7 Oxygen Containing Compounds:

These compounds do not exceed 2 % by weight in the crude oil. Typical examples are acetic and benzoic acids. These compounds cause corrosion and therefore needs to be effectively handled.

1.3.8 Resins:

Resins are polynuclear aromatic structures supported with side chains of paraffins and small ring aromatics. Their molecular weights vary between 500 – 1500. These compounds also contain sulphur, nitrogen, oxygen, vanadium and nickel.

1.3.9 Asphaltenes:

Asphaltenes are polynuclear aromatic structures consisting of 20 or more aromatic rings along with paraffinic and naphthenic chains. A crude with high quantities of resins and asphaltenes (heavy crude) is usually targeted for coke production (**Pachuau, 2018**).

1.4 Refining Operations:

Petroleum refining processes and operations can be separated into five basic areas:

1.4.1 Fractionation (distillation) is the separation of crude oil in atmospheric and vacuum distillation towers into groups of hydrocarbon compounds of differing boiling-point ranges called "fractions" or "cuts."

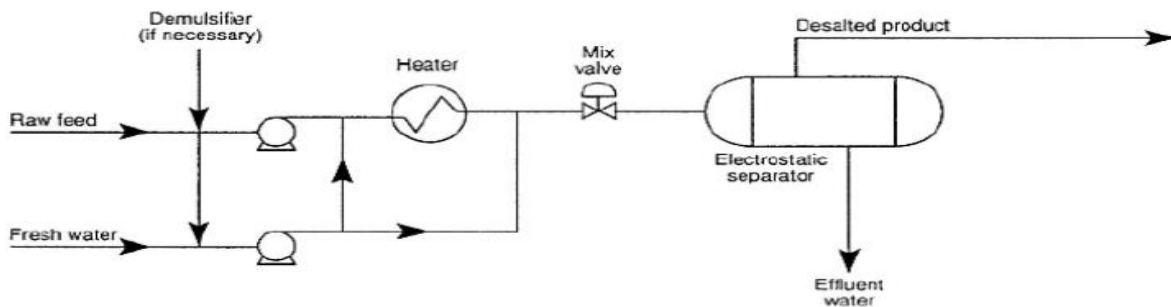
- **Crude Oil Distillation** is more complicated than product distillation, in part because crude oils contain water, salts, and suspended solids.
- **Step 1** in the refining process is to remove these contaminants so as to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning catalysts in processing units.
- **Step 2** most typical methods of crude-oil desalting are chemical and electrostatic separation, and both use hot water as the extraction agent.

In Chemical Desalting, water and chemical surfactant (de-mulsifiers) are added to the crude, which is heated so that salts and other impurities dissolve or attach to the water, then held in a tank to settle out.

Electrical Desalting is the application of high-voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids.

- **Step 3** (and rare) process of filters hot crude using diatomaceous earth.
- The salts are dissolved in the wash water and the oil and water phases are separated in a settling vessel either by adding chemicals to assist in breaking the emulsion or

by developing a high potential electrical field across the settling vessel to coalesce the droplets of salty water more rapidly. Either AC or DC fields may be used or potentials from 12,000 to 35,000 volts are used to promote coalescence. For single-stage desalting units 90 to 95% efficiencies are obtained and two-stage processes achieve 99% or better efficiency. If the pH of the brine exceeds 7, emulsions can be formed because of the sodium naphthenate and sodium sulfide present. For most crude oils it is desirable to keep the pH below 8.0. Better dehydration is obtained in electrical de-salters when they are operated in the pH range of 6 to 8 with the best dehydration obtained at a pH near 6. The pH value is controlled by using another water source or by the addition of acid to the inlet or recycled water. The crude oil feedstock is heated to 65-180°C to reduce viscosity and surface tension for easier mixing and separation of the water. The temperature is limited by the vapor pressure of the crude-oil feedstock. In both methods other chemicals may be added. Ammonia is often used to reduce corrosion. Caustic or acid may be added to adjust the pH of the water wash. Wastewater and contaminants are discharged from the bottom of the settling tank to the wastewater treatment facility (**Gary, Handwerk and Kaiser, 2007**).



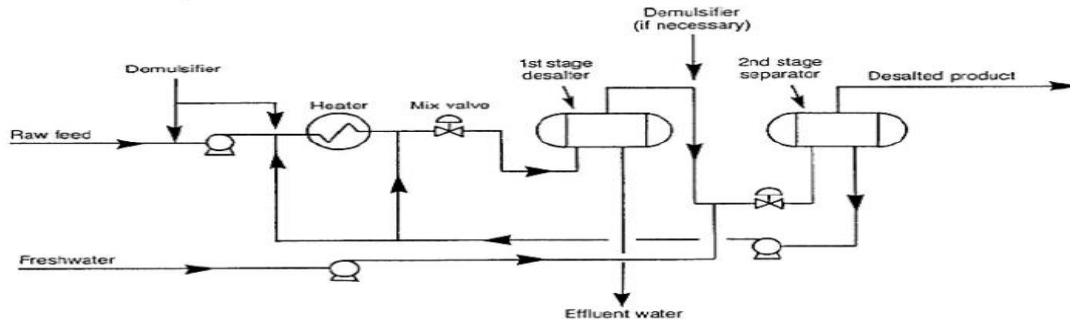


Fig 1.1: Single and Two-stage Electrostatic Desalting Systems

Distillation is based on the fact that the vapour of a boiling mixture will be richer in the components that have lower boiling points. Thus, when this vapour is cooled and condensed, the condensate will contain the more volatile components. At the same time, the original mixture will contain more of the less volatile components. Fractional distillation is useful for separating a mixture of substances with narrow differences in boiling points, and is the most important step in the refining process. Distillation can contribute to more than 50% of plant operating costs. Very few of the components come out of the fractional distillation column ready for market (Gary, Handwerk and Kaiser, 2007).

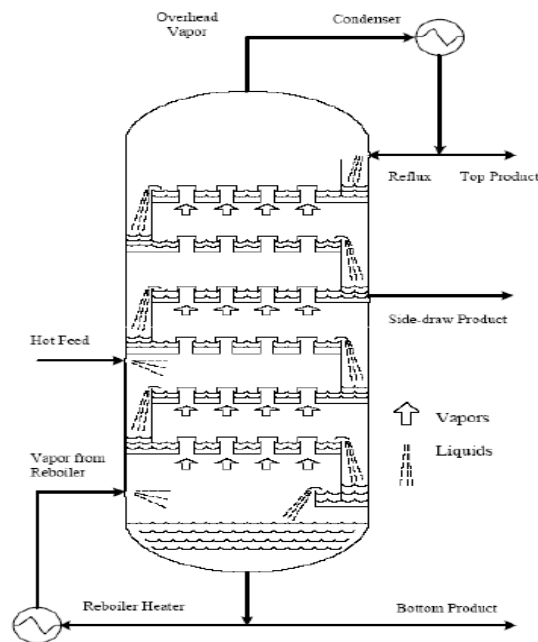


Fig 1.2: Distillation Column with Bubble-cap trays

1.4.1.1 Atmospheric Distillation:

The refining process is the separation of crude oil into various fractions or straight-run cuts by distillation in atmospheric and vacuum towers. The main fractions or "cuts" obtained have specific boiling-point ranges and can be classified in order of decreasing volatility into gases, light distillates, middle distillates, gas oils, and residuum. The desalted crude feedstock is preheated using recovered process heat. The feedstock then flows to a direct-fired crude charge heater then into the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 340-370°C (above these temperatures undesirable thermal cracking may occur). All but the heaviest fractions flash into vapor. As the hot vapor rises in the tower, its temperature is reduced. Heavy fuel oil or asphalt residue is taken from the bottom. At successively higher points on the tower, the various major products including lubricating oil, heating oil, kerosene, gasoline, and uncondensed gases (which condense at lower temperatures) are drawn off. The temperature of crude oil is raised to about 288°C by heat exchange with product and reflux streams. It is then further heated to about 399°C in a furnace and charged to the flash zone of the atmospheric fractionators. The furnace discharge temperature is sufficiently high 343 to 399°C to cause vaporization of all products withdrawn above the flash zone plus about 10 to 20% of the bottoms product. **Reflux is Provided by:**

- a) Condensing the tower overhead vapors and returning a portion of the liquid to the top of the tower
- b) Pump-around and pump back streams lower in the tower. (**Gary, Handwerk and Kaiser, 2007**).

Each of the side stream products removed from the tower decreases the amount of reflux below the point of draw off. Maximum reflux and fractionation is obtained by removing all heat at the top of the tower, but this results in an inverted cone-type

liquid loading which requires a very large diameter at the top of the tower. To reduce the top diameter of the tower and even the liquid loading over the length of the tower, intermediate heat-removal streams are used to generate reflux below the side-stream removal points. To accomplish this, liquid is removed from the tower, cooled by a heat exchanger, and returned to the tower or, alternatively, a portion of the cooled side-stream may be returned to the tower. This cold stream condenses more of the vapors coming up the tower and thereby increases the reflux below that point. Although crude towers do not normally use reboilers, several trays are generally incorporated below the flash zone and steam is introduced below the bottom tray to strip any remaining gas oil from the liquid in the flash zone and to produce a high-flash-point bottoms. The atmospheric fractionator normally contains 30 to 50 fractionation trays. Separation of the complex mixtures in crude oils is relatively easy and generally five to eight trays are needed for each sidestream product plus the same number above and below the feed plate. Thus, a crude oil atmospheric fractionation tower with four liquid side-stream drawoffs will require from 30 to 42 trays. The liquid side-stream withdrawn from the tower will contain low-boiling components which lower the flashpoint. These “light ends” are stripped from each side-stream in a separate small stripping tower containing four to ten trays with steam introduced under the bottom tray. The steam and stripped light ends are vented back into the vapor zone of the atmospheric fractionator above the corresponding side-draw tray. The overhead condenser on the atmospheric tower condenses the pentane and- heavier fraction of the vapors that passes out of the top of the tower. This is the light gasoline portion of the overhead, containing some propane and butanes and essentially all of the higher-boiling components in the tower overhead vapor. Some of this condensate is returned to the top of the tower as reflux, and the remainder is sent to the stabilization section of the refinery gas plant where the

butanes and propane are separated from the C5-180°F (C5-82°C) LSR gasoline (Gary, Handwerk and Kaiser, 2007).

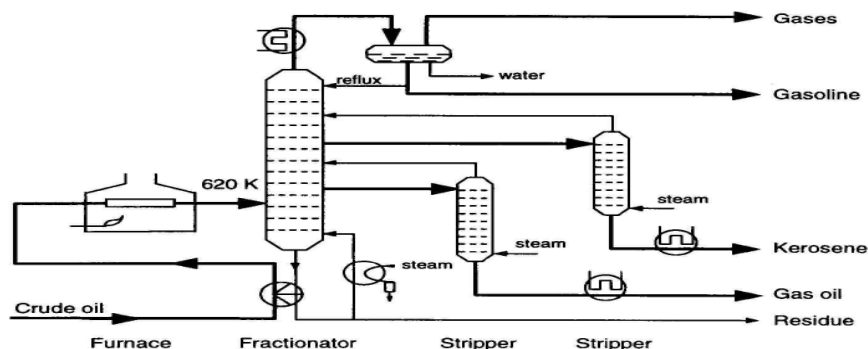


Fig 1.3: Simple Crude Distillation

1.4.1.2 Vacuum Distillation:

The furnace outlet temperatures required for atmospheric pressure distillation of the heavier fractions of crude oil are so high that thermal cracking would occur, with the resultant loss of product and equipment fouling. The process takes place in one or more vacuum distillation towers. The principles of vacuum distillation resemble those of fractional distillation except that larger diameter columns are used to maintain comparable vapor velocities at the reduced pressures. The internal designs of some vacuum towers are different from atmospheric towers in that random packing is used instead of trays. A typical first-phase vacuum tower may produce gas oils, lubricating-oil base stocks, and heavy residual for propane de-asphalting. A second-phase tower operating at lower vacuum may distill surplus residuum from the atmospheric tower, which is not used for lube-stock processing, and surplus residuum from the first vacuum tower not used for de-asphalting. Vacuum towers are typically used to separate catalytic cracking feedstock from surplus residuum. Distillation is carried out with absolute pressures in the tower flash zone area of 25 to 40 mmHg (Gary, Handwerk and Kaiser, 2007).

Addition of steam to the furnace inlet increases the furnace tube velocity and minimizes coke formation in the furnace as well as decreasing the total hydrocarbon

partial pressure in the vacuum tower. Furnace outlet temperatures are also a function of the boiling range of the feed and the fraction vaporized as well as of the feed coking characteristics. furnace outlet temperatures in the range of 388 to 454°C are generally used. The lower operating pressures cause significant increases in the volume of vapor per barrel vaporized and, as a result, the vacuum distillation columns are much larger in diameter than atmospheric towers. It is not unusual to have vacuum towers up to 40 feet in diameter.

1.4.1.3 Light End Fractionation:

Within refineries there are numerous other, smaller distillation towers called columns, designed to separate specific and unique products. Columns all work on the same principles as the towers described previously. For example, a depropanizer is a small column designed to separate propane and lighter gases from butane and heavier components in the light end unit (**Gary, Handwerk and Kaiser, 2007**).

1.4.1.4 Crude Distillation Unit Products:

- **Fuel Gas.** The fuel gas consists mainly of methane and ethane. In some refineries, propane in excess of LPG requirements is also included in the fuel gas stream. This stream is also referred to as “dry gas.”
- **Wet Gas.** The wet gas stream contains propane and butanes as well as methane and ethane. The propane and butanes are separated to be used for LPG and, in the case of butanes, for gasoline blending and alkylation unit feed.
- **LSR Naphtha.** The stabilized LSR naphtha (or LSR gasoline) stream is desulfurized and used in gasoline blending or processed in an isomerization unit to improve octane before blending into gasoline.
- **HSR Naphtha or HSR Gasoline.** The naphtha cuts are generally used as catalytic reformer feed to produce high octane reformat for gasoline blending and aromatics.
- **Gas Oils.** The light, atmospheric, and vacuum gas oils are processed in a hydrocracker or catalytic cracker to produce gasoline, jet, and diesel fuels. The

heavier vacuum gas oils can also be used as feed stocks for lubricating oil processing units.

- **Residuum.** The vacuum still bottoms can be processed in a visbreaker, coker, or de-asphalting unit to produce heavy fuel oil or cracking and/or lube base stocks. For asphalt crudes, the residuum can be processed further to produce road and/or roofing asphalts (**Gary, Handwerk and Kaiser, 2007**).

1.4.2 Conversion Processes:

Can change the size and/or structure of hydrocarbon molecules. These processes include:

Decomposition (dividing) by thermal and catalytic cracking;

Unification (combining) through alkylation and polymerization; and

Alteration (rearranging) with isomerization and catalytic reforming.

1.4.3 Treatment Processes:

To prepare hydrocarbon streams for additional processing and to prepare finished products. Treatment may include removal or separation of aromatics and naphthenes, impurities and undesirable contaminants. Treatment may involve chemical or physical separation e.g. dissolving, absorption, or precipitation using a variety and combination of processes including desalting, drying, hydro-desulfurizing, solvent refining, sweetening, solvent extraction, and solvent de-waxing (**Gary, Handwerk and Kaiser, 2007**).

1.4.3.1 Propane De-asphalting:

Coke-forming tendencies of heavier distillation products are reduced by removal of asphaltenic materials by solvent extraction. Liquid propane is a good solvent (butane and pentane are also commonly used). De-asphalting is based on solubility of hydrocarbons in propane. Vacuum residue is fed to a countercurrent de-asphalting tower. Alkanes dissolve in propane whereas asphaltenic materials (aromatic compounds), ‘coke-precursors’ do not. Asphalt is sent for thermal processing.

1.4.3.2 Solvent Extraction and De-waxing:

Solvent treating is a widely used method of refining lubricating oils as well as a host of other refinery stocks. Since distillation (fractionation) separates petroleum products into groups only by their boiling-point ranges, impurities may remain.

These Include:

- a) Organic compounds containing sulfur, nitrogen, and oxygen
- b) Inorganic salts
- c) Dissolved metals
- d) Soluble salts that were present in the crude feedstock.

In addition, kerosene and distillates may have trace amounts of aromatics and naphthenes, and lubricating oil base-stocks may contain wax. Solvent refining processes including solvent extraction and solvent de-waxing usually remove these undesirables at intermediate refining stages or just before sending the product to storage. The purpose of solvent extraction is to prevent corrosion, protect catalyst in subsequent processes, and improve finished products by removing unsaturated, aromatic hydrocarbons from lubricant and grease stocks. The solvent extraction process separates aromatics, naphthenes, and impurities from the product stream by dissolving or precipitation. The feedstock is first dried and then treated using a continuous countercurrent solvent treatment operation. In one type of process, the feedstock is washed with a liquid in which the substances to be removed are more soluble than in the desired resultant product. In another process, selected solvents are added to cause impurities to precipitate out of the product. In the adsorption process, highly porous solid materials collect liquid molecules on their surfaces.

The solvent is separated from the product stream by heating, evaporation, or fractionation, and residual trace amounts are subsequently removed from the raffinate by steam stripping or vacuum flashing. The most widely used extraction solvents are phenol, furfural, and cresylic acid. Other solvents less frequently used

are liquid sulfur dioxide, nitrobenzene, and 2,2' dichloroethyl ether. The selection of specific processes and chemical agents depends on the nature of the feedstock being treated, the contaminants present, and the finished product requirements (**Gary, Handwerk and Kaiser, 2007**).

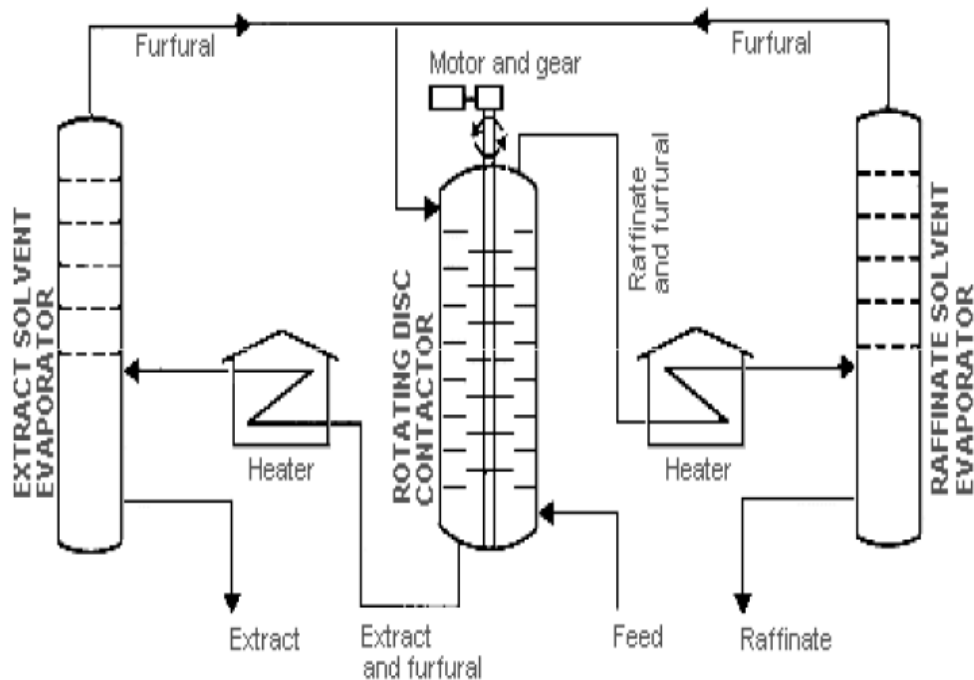


Fig 1.4: Aromatic Solvent Extraction Unit

1.4.3.3 Solvent De-waxing:

Solvent de-waxing is used to remove wax from either distillate or residual base-stock at any stage in the refining process. There are several processes in use for solvent de-waxing, but all have the same general steps, which are:

- Mixing the feedstock with a solvent;
- Precipitating the wax from the mixture by chilling.
- Recovering the solvent from the wax and de-waxed oil for recycling by distillation and steam stripping.

Usually two solvents are used: toluene, which dissolves the oil and maintains fluidity at low temperatures, and methyl ethyl ketone (MEK), which dissolves little wax at low temperatures and acts as a wax precipitating agent. Other solvents sometimes used include benzene, methyl isobutyl ketone, propane, petroleum naphtha, ethylene dichloride, methylene chloride, and sulfur dioxide. In addition, there is a catalytic process used as an alternate to solvent de-waxing.

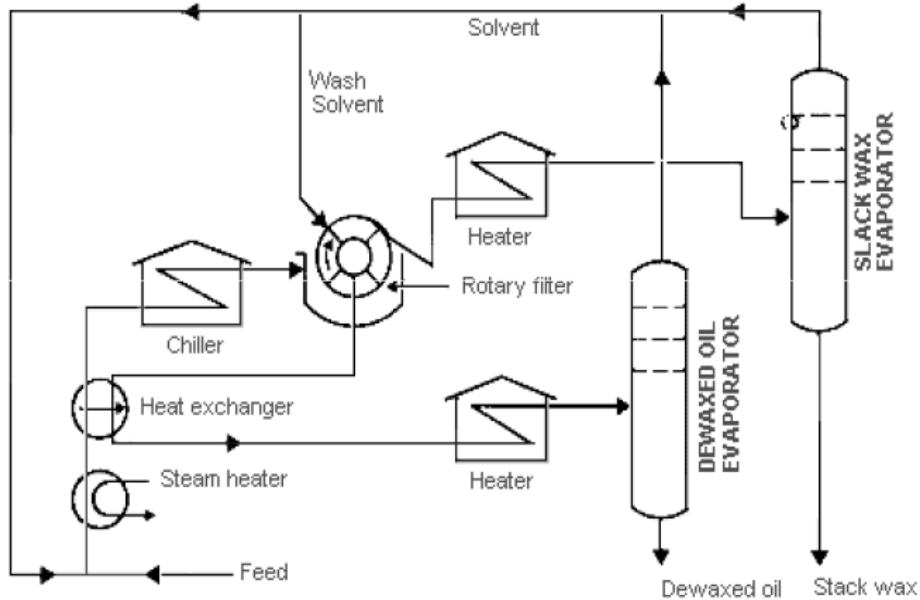


Fig 1.5: Solvent De-waxing Unit

1.4.4 Formulating and Blending:

Is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties.

1.4.4.1 Blending:

Blending is the physical mixture of a number of different liquid hydrocarbons to produce a finished product with certain desired characteristics. Products can be blended in-line through a manifold system, or batch blended in tanks and vessels. In-line blending of gasoline, distillates, jet fuel, and kerosene is accomplished by injecting proportionate amounts of each component into the main stream where

turbulence promotes thorough mixing. Additives including octane enhancers, anti-oxidants, antiknock agents, gum and rust inhibitors, detergents, *etc.* are added during and/or after blending to provide specific properties not inherent in hydrocarbons (Gary, Handwerk and Kaiser, 2007).

1.4.5 Other Refining Operations Include:

- Light-ends recovery.
- Sour-water stripping.
- Solid waste, process-water and wastewater treatment.
- Cooling, storage and handling and product movement.
- Hydrogen production.
- Acid and tail-gas treatment.
- And sulfur recovery.

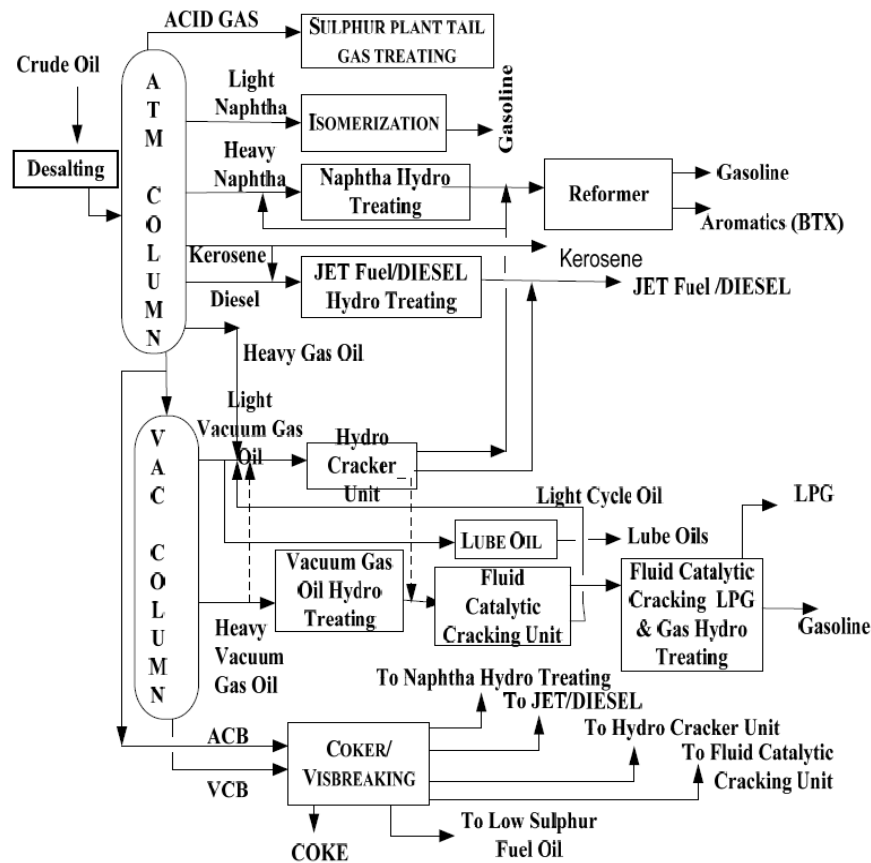


Fig 1.6: Typical Refinery Processes and Products.

1.5 Petroleum Waxes:

Petroleum waxes are broadly defined as the waxes naturally present in various fractions of crude petroleum. Originally, they were considered as by products in the de-waxing of lubricating and gas oils, but, today they are valuable products for many industrial applications (**Mazee, 1973**).

Petroleum waxes are complex mixtures of hydrocarbons, amongst which are n-paraffins, branched chain paraffins and cyclo-paraffins in the range of C₁₈–C₇₀ (**Bennett, 1975**). The quality and quantity of waxes manufactured from crude oils depend on the crude source and the degree of refining to which it has been subjected prior to wax separation (**Letcher, 1984 and Sequeria, 1994**). The composition of wax depends on the temperature at which it is crystallized and it becomes more complex with increasing the molecular weight and / or the boiling range. The residue after removal of the wax is called the “oil” or “de-waxed oil” (DWO) depending on the context (**Thomas, 2008**).

The commercial petroleum waxes may be divided into three principal groups: paraffin waxes, microcrystalline waxes and petrolatums.

Paraffin waxes constitute the major bulk of such waxes, the other two types; produced in comparative quantities; also command a good market because of their certain specific end uses (**Prasad, 2000**). The paraffin waxes are solid hydrocarbons at room temperature and usually produced from low and medium boiling range distillates.

Slack wax is a refinery term for the crude paraffin wax obtained from the solvent de-waxing of paraffin distillates or lube base stocks. Slack wax contains varying amounts of oil (ranging from 20 to 50 wt. %) and must be de-oiled to produce hard or finished waxes (**Mazee, 1973**). If the slack wax separated from residual oil fractions, the oil-bearing slack is frequently called petrolatum (**Concawe, 1999**).

Scale wax is obtained by removing the oil and the low melting wax from the slack wax by sweating or solvent de-oiling. It contains less than 3% of oil.

Microcrystalline waxes are microcrystalline products, solid at room temperature and usually produced from heavy petroleum distillates or residues or tank bottoms.

Petrolatum is a general term applied to a crude microcrystalline wax containing some oil. It is semi-solid, jelly-like materials. Petrolatum is obtained from certain type of heavy petroleum distillates or residues. It is a base material for the manufacturing of medicinal petroleum jelly.

Ozokerite wax is an earth, naturally occurring mineral wax. It is also a microcrystalline wax.

Ceresin is a microcrystalline wax; it is the name formerly given to the hard white wax obtained from fully refined ozokerite. Petroleum ceresin is a similar microcrystalline wax but separated from petroleum. Ceresin and petroleum ceresins appear to have the same composition, structure, physical and chemical properties (Mazee, 1973).

The identification of waxes is a difficult task. Composition, crystal structure, various physical and functional properties have been used as criteria for classifying waxes. Some of the criteria and properties used in classifying of petroleum waxes are represented below.

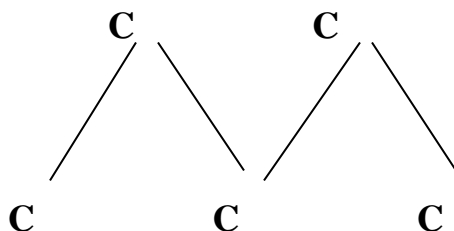
1.5.1. Composition of Petroleum Waxes:

Petroleum waxes are substance, which are solid at normal temperatures. Paraffin and microcrystalline waxes in their pure form consist only solid saturated hydrocarbons. Petrolatum, in contrast to the other two waxes, contains both solid and liquid hydrocarbons. Petrolatum is semi-solid at normal temperatures and is quite soft as compared to the other two waxes.

1.5.1.1. Paraffin Waxes (Macro-Crystalline Waxes):

Paraffin wax is a solid and crystalline mixture of hydrocarbons; it is usually produced in the form of relatively large crystals. It consists mainly of normal paraffin ranging from $C_{16} - C_{30}$ and possibly higher. Varying proportions of slightly branched chain paraffins ranging from $C_{18} - C_{36}$ and naphthenes; especially alkyl-substituted derivatives of cyclo-pentane and cyclohexane; are also present. Generally aromatics are present only in very low percentage, most of them are of the mono-aromatic type with a long paraffinic side chain (Mazee, 1973.; Freund, 1982. ; Letcher, 1984. and Concauwe, 1999).

The average molecular weight of these paraffin waxes is about 360 – 420 (Nakagawa, 1983). There is a general arrangement that carbon atoms in n-paraffins are arranged in a zig – zag fashion:



A paraffin wax melting at $53.5^{\circ}C$ showed a space lattice having C – C bond length of $1.52^{\circ}A$, a C – C – C bond angle of $110^{\circ}A$, a C – H bond length of $1.17^{\circ}A$ and a H – C – H bond angle of $105^{\circ}A$ (Muller, 1930).

1.5.1.2. Microcrystalline Waxes:

Micro-crystalline waxes are not obtained from vacuum distillation cuts, as the macro- and intermediate-paraffin waxes, but from the vacuum residue. The raw material for the production of micro wax is petrolatum or bright stock. This product is divided off from the heavy mineral oil components with the aid of propane de-asphalting, followed by de-aromatization and solvent de-waxing. The petrolatum is then further processed with a de-oiling step, often directly in the de-waxing plant, in which raw micro wax is obtained. Following that, the raw micro wax must be

subjected to finishing process. A white, odorless product is achieved by a hydro-finishing process, which is suitable for use in food contact applications (**Meyer, 2009**).

Microcrystalline waxes are petroleum waxes containing substantial proportion of hydrocarbons other than normal paraffins. They consist of highly branched chain paraffins; in contrast to the macro-crystalline; cyclo-paraffins and small amounts of n-paraffins and alkylated aromatics (**Letcher, 1984 and Mazee, 1973**). The share in long-chain linear n-alkanes is usually considerably under 40%. The mean chain length of the n-alkanes is approximately C₃₄ to C₅₀. Long-chain, branched iso-alkanes predominantly contain chain lengths up to C₇₀ (**Meyer, 2009**).

The branched-chain structures of the composition C_nH_{2n+2} are found. Iso-paraffin of mono-methyl alkane, 2-methyl alkanes being found. As the position of the methyl group moves farther from the end of the chain, the amount of the corresponding alkane becomes smaller. The branched chains in the microcrystalline waxes are probably located at random along the carbon chain while in paraffin wax, they are near the end of the chain (**Sachane, 1945; Leavy et al. 1961 and Mazee, 1973**).

The cyclo-alkanes however consist mainly of mono-cyclic systems. Monocyclopentyl, monocyclohexyl, dicyclohexyl paraffins and polycycloparaffins are also found. Some microcrystalline waxes are mainly composed of multiple-branched iso-paraffins and mono-cycloparaffins (**Mazee, 1973**). Beside that non hydrogenated micro waxes also contain mainly mono-cyclic aromatic and heterocyclic compounds (**Meyer, 2009**).

Microcrystalline waxes have higher molecular weights (600 - 800), densities and refractive indices than paraffin waxes (**Letcher, 1984; Mazee, 1973 and Sequeria, 1994**).

1.5.2. Properties of Petroleum Waxes:

The characteristic properties of petroleum waxes can be grouped in three classes; physical, mechanical and food–grade properties.

1.5.2.1. Physical Properties:

It is a very complex task to establish relationships between the chemical composition of petroleum waxes and their applicability in various fields. It is therefore, of great importance to know their physical properties for manufacturing control and to determine with greater certainty whether the wax in question is suitable for a given application.

Almost all the physical properties of petroleum waxes – among others like congealing and melting points, viscosity, density and refractive index – are influenced by the average length of hydrocarbon chain; distribution of their individual components and the degree of branching. All three parameters increase with higher temperature of oil distillation cut from which the wax originates **(Kuszlik et al., 2010 and Freund, 1982)**.

The important properties of waxes are: carbon number, melting point, hardness, oil content and viscosity.

a) Carbon Number:

Paraffin waxes are composed of 40-90 wt% normal paraffins of about 22 to 30 carbon atoms and possibly higher, accordingly, differ very little in physical and chemical properties. Straight chain alkanes in the range from 20 up to 36 carbon atoms show transition points in the solid phase. Thus two modifications are known, stable at different temperatures and with different crystal habitus **(Mazee, 1973)**.

Microcrystalline waxes contain substantial proportions of highly branched or cyclic hydrocarbons in the range from 30 to 75 carbon atoms **(Ferris, 1963; Letcher, 1984 and Sequeria, 1994)**.

b) Color:

Color is an index of degree of refining. Paraffin waxes are generally white in color, whereas microcrystalline waxes and petrolatums range from white to almost black. A fully refined wax should be virtually colorless when examined in the molten state. For pharmaceutical purposes the color of petrolatum is taken as an index of its purity; two grades are recognized in the British Pharmacopoeia; yellow and white (**Gottshall & McCue, 1973**).

Several methods are available for determining color, all based upon measurements in the molten state. All require the comparison of the color of the molten wax with colored glasses of varying color intensity. All visual methods have disadvantage of subjectivity. A direct-reading colorimeter is to be preferred (**Mazee, 1973**).

c) Melting Point:

The melting point is one of the most widely tests used to determine the quality and type of waxes. Petroleum waxes do not melt at sharply defined temperatures because they are mixtures of hydrocarbons with different melting points.

Paraffin waxes, relatively simple mixtures, usually have a narrow melting range and are generally lower in melting point than microcrystalline waxes. They usually melt between 46 and 68°C. The melting point of paraffin waxes increases with molecular weight. The branching of the carbon chain, at identical molecular weights, results in a decrease in the melting point. Paraffin waxes can be classified on the basis of the melting point to soft (lower m.p.) and hard (higher m.p.) paraffin waxes.

Microcrystalline waxes and petrolatums are more complex and therefore melt over a much wider temperature range. They usually melt between 60 and 93°C and 38 to 60°C, respectively (**Freund, 1982 and Sequeria, 1994**).

The three most common methods of measuring melting points are drop melting point (**ASTM D-127**), cooling curve or setting point (**ASTM D-87**) and congealing point (**ASTM D-938**).

The drop melting point method is suitable for amorphous waxes, e.g., petrolatums. The setting point (Cooling Curve or Plateau) method is not suitable for microcrystalline wax, petrolatums or waxes containing large amounts of non-normal hydrocarbons (The plateau rarely occurs in cooling curves of such waxes).

The congealing point method was originally intended for petrolatum, but is now used for both microcrystalline and paraffin waxes.

d) Oil Content:

Oil content is an indication of the quality of the wax. The method of determination depends upon the differential solubility of oil and wax in a given solvent.

Paraffin wax, microcrystalline wax and petrolatum have different degree of affinity for oil content. Paraffin wax has little affinity for oil content. It may be taken as a degree of refinement. Fully-refined wax usually has an oil content of less than 0.5 percent. . Waxes containing more than this amount of oil are referred to as “Scale wax”, although an intermediate grade known as “Semi-refined wax” is sometimes recognized for waxes have an oil content of about 1 percent. A high oil content tends to plasticize the wax and has an adverse effect on color stability.

Microcrystalline waxes have a greater affinity for oil than paraffin waxes because of their smaller crystal structure. The oil content of microcrystalline wax is 1-4 wt%, depending on the grade of wax. Waxes containing more than 20 percent oil would usually be classed as petrolatums (**Gottshall and McCue, 1973**).

e) Viscosity:

Viscosity of molten wax is of importance in applications, quality control and standardization.

In petroleum industry, the waxes are classified on the basis of whether the waxes are produced from lower or higher viscosity oil fractions. Paraffin waxes are generally obtained from low viscosity lubricating oil fractions. Microcrystalline waxes are obtained either from high viscosity distillate fractions or from heavy residues.

No definite relationship between the viscosities of normal and branched paraffins. Alkanes with one side chain often have lower viscosities than that of the normal alkane. The viscosity of alkanes with two or three side chains is higher than that of the corresponding n-alkanes (**Freund, 1982**).

Paraffin waxes do not differ much in viscosity; viscosity being in the range of 4.2 to 7.4 cSt at 210°F (99°C). Microcrystalline waxes considerably more viscous and vary over a wide range from 10 to 20 cSt or higher (**Gottshall and McCue, 1973**).

Slack wax obtained from heavy distillate is probably intermediate in character and should, therefore, be more appropriately classified as semi-crystalline wax or intermediate. A series of high viscosity, high melting very hard waxes derived from residual stocks and tank bottoms have been produced. It is clear that classification according to viscosity is also not perfect.

1.5.2.2. Mechanical Properties:

The mechanical properties of petroleum waxes are of considerable importance for most applications and numerous tests have been developed for characterizing the hardness, the brittleness and resistance to rupture.

Hardness: The hardness and crystallization behavior of macro – crystalline paraffin waxes is interfered distinctly by their distribution width, average chain length and n-alkane content (**Meyer, 2006**).

Hardness is the resistance against the penetration of a body (needle, or cone, or plunger rod) under a defined load, this body being made of a harder material than the substance being tested. To measure the hardness of paraffin waxes, penetration tests are widely accepted. It is a common feature of strength and hardness tests that the test specimens are subjected to short-time stresses (**Freund, 1982**).

Penetration measurement is the most wide-spread method for determining the hardness and the thermal sensitivity of petroleum waxes. Macro-crystalline waxes change to a greater extent with temperature than that of microcrystalline waxes. An

increase in oil content results in an increase in penetration values of both macro- and microcrystalline waxes (**Mazee, 1973**).

Penetration can be determined by measurement of the depth of penetration of needle or cone into a wax specimen. Two techniques for measuring hardness (cone penetration for softer waxes and needle penetration for harder waxes) have been standardized by **ASTM** and **IP**, (*ASTM D-937: IP-179 & ASTM D-1321*).

1.5.2.3. Food Grade Properties:

These properties concern waxes and petrolatums for food grade. Their potential toxicity could be attributed to aromatic residues. The latter are characterized directly by using U.V spectra in the spectral zone corresponding to aromatics.

Each country has adopted its own code governing waxes, which come into contact with food and non-food grade (**US Pharmacopoeia, 2011**).

1.5.3. Congealing Point – Refractive Index Relationship:

The classification of waxes has become difficult task for the wide variety of waxes made available through the expansion of refining technology. Classification according to composition in terms of hydrocarbons of different molecular structure, requires sophisticated compositional analysis.

Although the division of waxes into macro- and micro-crystalline waxes on the basis of crystal size is valid to a great extent, there is no sharp line separating the two groups. Consequently, attempts have been made to define waxes by means of physical and mechanical properties. But it has been found that much property identified some of the waxes differently. Since it is not possible to define waxes completely by any one criterion, a melting point–refractive index classification was considered as it has been found that different types of hydrocarbons exhibits different relationships between melting point and refractive index. In a group of hydrocarbons of the same melting point, the normal alkane exhibits the lowest

refractive index, progressive branching raises the refractive index and cyclic structures raise it even more, as shown in Figure 1 (Ferris, 1963).

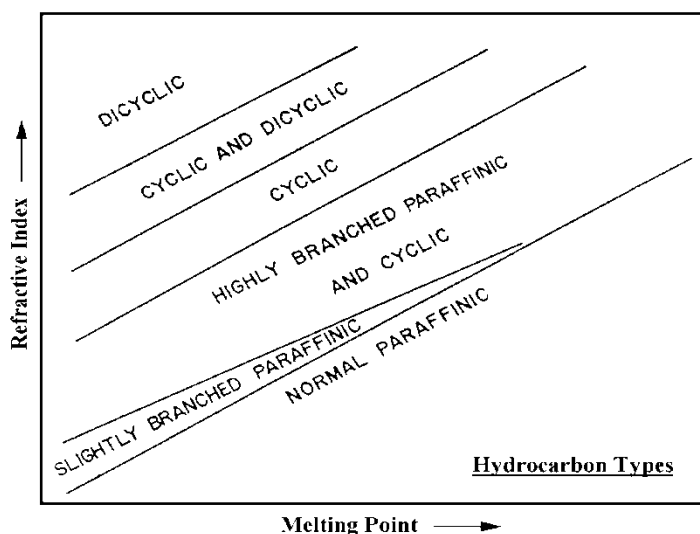


Fig. 1.7: Relationship between Melting Point and Refractive Index for Different Types of Hydrocarbons.

A chart of this type therefore offers an excellent means of determining the overall composition of a wax, and of differentiating paraffin waxes from microcrystalline waxes. It became apparent that it would be almost impossible to force all waxes into one or the other of two categories. It was adopted a third class of waxes which is semi-microcrystalline waxes.

The final effort was based on the correlation of congealing point and refractive index at 98.9 °C. Congealing point was selected because it is applicable to all petroleum waxes. This proposal was adopted in 1963; by *TAPPI-ASTM* technical committee on petroleum waxes; to classify the waxes as macro-crystalline (paraffin), semi-microcrystalline and microcrystalline waxes. The distinction between these groups is made on the basis of viscosity. The proposal is as follows:

$$n_D^{210^\circ\text{F}} = 0.0001943t + 1.3994$$

Where “t” is the congealing point temperature in °F.

A paraffin wax is a petroleum wax consisting mainly of normal alkanes, characterized by a refractive index less than that obtained by the above equation.

A semi-microcrystalline wax is a petroleum wax containing substantial proportions of hydrocarbons other than normal alkanes, characterized by a refractive index higher than that given by the above equation and by a viscosity at 98.9 °C of less than 10 centistokes.

A microcrystalline wax is a petroleum wax containing substantial proportions of hydrocarbons other than normal alkanes, characterized by a refractive index higher than that given by the above equation and by a viscosity at 210°F of 10 centistokes or higher (**Ferris, 1963 and Gottshall and McCue, 1973**).

1.6 De-waxing Processes:

De-waxing process is the important operation in the production of lubricating oils. Dewaxing is the removal of wax from lube feed stocks fraction to produce lubricants with low pour points suitable for use at low temperature.

De-waxing processes have been developed at an early stage for the reduction of the wax content of oils by crystallization; cooling the waxy oil without addition of a solvent; in order to improve the low temperature properties (**Brenken and Richter 1979; Klamann et al.1984 and Sequeria, 1994**).

1.6.1 Solvent De-waxing Process:

The trend in new de-waxing processing is towards solvent away from filter pressing (**Ryan and Burke, 1907**) and naphtha centrifuge (**Prince, 1997**). The solvent de-waxing process is based on the separation of paraffins in the temperature range of the desired pour point. This method is affected by low temperature solvent treatment, and its operation is independent of the structure and distribution of various paraffinic components. It is applicable theoretically and practically over the whole range of distillate fractions and residual stocks (**Hoppe, 1964**).

The solvent de-waxing is influenced by many parameters such as type of solvents, cooling rate, and temperature and solvent to oil ratio. Several pure solvents or mixtures of solvents have been in use for solvent de-waxing.

The rate of cooling has a strong influence on crystal formation and particle characteristic. A high cooling rate is found to promote the formation of small crystals but they are of the needle type that clogs the filter.

Solvent de-waxing processes are classified according to the nature of the solvent employed or the type of equipment used to separate the wax (**Ghedamu, Watkinson and Epstein, 1997**).

Crystal structure of the paraffin wax is of great importance in commercial solvent de-waxing processes due to the importance of rapid filtration rate, particularly when rotary filters are used for separating the liquid and solid phases. The crystal size and the consequent filtration rate depend on the boiling range width and paraffin concentration of the distillate fraction, previous treatment of the feedstock, the method of dilution and the cooling rate (**Wilson, Keith and Haylett, 1936 and Nimer, Mohamed and Rabah, 2010**).

1.6.1.1 Propane De-waxing Process:

Propane de-waxing process was developed and firstly used in 1932. It is applicable for bright stock manufacture, the propane de-waxing is usually combined with de-asphalting process. Therefore, the oil containing propane from de-asphalting can be directly de-waxed. Thus removal of propane by distillation after de-asphalting is eliminated.

Propane is the most popular de-waxing solvent due to the cheap of the solvent, non-corrosive and readily available in most refineries (**Sequeira, 1989**).

The main disadvantage of propane de-waxing process is due to the relatively high solvent power for paraffin waxes, therefore, it is much more difficult to obtain easily filterable paraffin wax crystals. De-waxing additives have then to be used for

distillates and often for residual stocks (**Marple and Landry, 1965**). Also the high solubility of wax in the solvent leads to a large de-waxing temperature differential. The use of ketone solvent as a wax anti-solvent in combination with propane has been proposed for improving the economics of the propane de-waxing process (**Eagen, et al. 1975**). Research and development studies indicated that a mixture of propylene with acetone was superior to propane in both the ultimate pour point capability and filter rate. In addition, the required amount of filter aid was also less. Exxon Research and Engineering Co., therefore, developed a commercial process for this solvent (**Clontz, 1971; Eagen, et al. 1975 and Freund, 1982**).

1.6.1.2 Ketone De-waxing Process:

The first commercial ketone de-waxing process was put into operation in 1927. The solvent originally used was a mixture of acetone – benzene (**Kalichevsky and Kobe, 1956 and Sequeria, 1994**).

Methyl ethyl ketone (MEK) has replaced acetone in practically all of the benzene–acetone units because of its higher boiling point which minimize solvent losses. Today, the MEK process is the most widely applied de-waxing process (**Sherwood, 1957 and Sequeira, 1982**).

The MEK process is suitable for de-waxing the entire range of lube oils, either prior or subsequent to the solvent extraction (**Eagen, et al. 1975 and Singh, Chaudhary and Kishore, 1982**).

Ketone solvents containing no aromatic component, e.g. methyl iso-butyl ketone (MIBK), can be used alone for de-waxing. MIBK shows better performance than MEK-toluene blends as far as filtration, de-waxing temperature and yield of de-waxed oil are concerned (**Mueller, 1940**).

The most widely used ketone processes are the Texaco solvent de-waxing process and the Exxon Dilchill process.

A- Texaco Solvent De-waxing Process:

This process is commonly called MEK process, normally uses a mixture of MEK and toluene as the de-waxing solvents and sometimes uses a mixture of other ketones and aromatic solvents.

In this process the waxy feedstock is heated to 10–15 °F above the cloud point of the oil and diluted with solvent while chilling at a controlled rate in double pipe scraped–surface exchangers and chillers. Two to four volumes of solvent using an incremental dilution procedure for low to medium viscosity stocks and a double dilution controlled shock–chilling procedure for high viscosity stocks (**Rudnick & Shubkin, 1999 & Sequeria, 1999**).

B- Exxon Dilchill De-waxing Process:

This process is a modification of Texaco solvent de-waxing process. In this process a special crystallizer is used in place of the scraped–surface exchangers. Direct chilling of the feedstock in the crystallizer is accomplished using a cold solvent, multiple dilution and shock–chilling technique in a highly sheared environment. This high degree of mixing is used as a means of overcoming the poor filtration obtained with the conventional shock chilling techniques. **Eagen et al.** have reported an increase in filtration rate of 40 to 50 % and a decrease in the solvent oil ratios of 10 to 30% have been reported for Dilchill de-waxing as compared to conventional MEK de-waxing (**Eagen, et al. 1975**).

De-waxing with selective solvents for lube oil production from paraffin–base crudes requires high investments and operating expenses. For this reason (**Clontz, 1971**), proposed a number of methods of increasing the efficiency have been proposed: proportioned feed of a mixture of selective solvents while cooling the feedstock solution; slow mixing of the cooled solution; feed of inert gas before filtration to enlarge the wax crystals; selection of an effective ketone; use of special modifier additives capable of forming wax crystals of the necessary shape during cooling of the feedstock.

1.6.1.3 Di / Me De-waxing Process:

The Di / Me de-waxing process uses a mixture of dichloroethane and methylene dichloride as the de-waxing solvent. A few refineries in Europe use this process. This process was developed by Edeleanu Gellschaft. The main advantage of the process is that very low oil–content slack waxes (2–6 wt. %) can be obtained in a single filter stage. The process is only slightly sensitive to changes in solvent ratio and maintaining low de-waxing temperature differential value. In general chlorinated solvents have disadvantage of being hydrolyzed thus becoming corrosive, particularly in the solvent recovery equipment (**Scholten, 1983**).

1.6.2 Urea De-waxing Process:

Urea de-waxing relies upon the fact that various straight chain organic compounds and also slightly branched compounds are capable of forming complexes with urea, called adducts, which are crystalline at room temperature. These adduct crystals can be separated.

Urea has been used for de-waxing lower boiling mineral oil fractions, it was used for both the manufacture of low pour point oil and / or pure n-paraffins from paraffinic feedstock (**Bailey et al., 1951**).

In recent years, the urea de-waxing process has new and greater flexibility to make special products from a wider range by crude oil types (**Brenken and Richter 1979**). The success of urea de-waxing depends on the structure of paraffins to be isolated and on their influence on the pour point. The paraffinic components, which affect the pour point, are not only linear but also branched chain paraffins. The weight ratios of these components depend on the origin and boiling range of the particular fraction. However, urea is not very selective for the removal of long chain branched hydrocarbons; urea will remove hydrocarbons containing branched and rings providing the molecule contains a long unbranched chain (**Scholten, 1983**).

1.6.3 Refining of Petroleum Waxes:

Petroleum waxes were considered as by-products in the de-waxing of lubricating and gas oil. They were used as components of furnace residual fuel oil. Today they are available petroleum products.

The specifications for finished waxes depend on their end use which determines the degree of refining, required. Refined wax is achieved by de-oiling and hydrogenation or acid treatment and adsorption processes.

1.6.3.1 De-oiling Processes (Wax Fractionation Processes):

Slack waxes and petrolatums separated from lubricating oil and residual feed-stocks respectively in de-waxing operation, usually contain from 2 to 45 wt. % oil. Low oil content wax (0.1 to 1.0 wt. %); with a specific melting point and penetration; is produced by selective removal of the oil and low melting waxes. The solidification temperature and the hardness of the wax; which is indicated by the needle penetration value; are important characteristics. This process is called de-oiling or wax fractionation.

The commercial wax de-oiling or fractionation processes are the sweating process, the re-crystallization process, the warm-up de-oiling process, and the spray de-oiling process (**Eagen, et al. 1975 & Sequeria, 1994**).

a) The Sweating Process:

Sweating serves the purpose of de-oiling and fractionating the wax. It is the oldest wax de-oiling process, which has been replaced with the more modern processes. In this process, the molten wax is solidified by chilling in large pans contained in large ovens. The wax is slowly heated in these ovens wherein the oil and lower melting point wax are separated from the higher melting point wax. Sweating is an extremely slow process, one cycle take more than 50 hours.

This process can be used for the de-oiling slack waxes yielding well developed macro-crystalline, preferably needle-shaped paraffin wax crystals. Petrolatums and slack waxes, which contain too large quantities of iso-paraffins, cannot be sweated because their structure is very finely crystalline. This type must be handled by solvent de-oiling process since it is suitable for any type of feedstock (**Kalichevsky and Kobe, 1956 and Sequeria, 1994**).

b) The Wax Recrystallization Process:

The Wax re-crystallization process is the most predominant de-oiling process. It was developed as a replacement for the wax sweating process. It is sometimes called wax fractionation process and can be used to fractionate or de-oil all type of waxes (**Sequeria, 1994 and Richter, 2000**). The wax cake from the primary or the secondary de-waxing filters is heated until the wax is totally dissolved in the solvent. Additional warm solvent is blended with the wax cake solution. The mixture is cooled to a predetermined temperature to crystallize the desired wax fractions. The mixture is filtered through a rotary vacuum filter and the wax cake receives a final wash. The filtration temperature of the wax in the third stage is conducted at a higher

temperature than that used in the first or second de-waxing filtration and the temperature used is selected to adjust wax melting point and penetration.

In contrast to conventional de-oiling processes, petrolatums and microcrystalline waxes varying in properties can be produced by wax fractionation (**Freund, 1982 and Sequeria, 1994**).

Many studies have been carried on wax de-oiling solvents. The effecting of acetone–toluene solvent mixture was studied for de-oiling a slack wax. The author concluded that the de-oiling efficiency depends on the iso-alkane content of paraffin. He also recorded that the maximum acetone content depends on the extent of dilution and base material, thus for low–molecular weight slack wax, a 60- 65 % acetone content was feasible (**Beasley, 2017**).

Different solvents have been evaluated for fractional crystallization of slack waxes and have been compared with methyl isobutyl ketone (MIBK) and the solvent mixture methyl ethyl ketone (MEK) containing benzene (B) and toluene (T) (60:20:20 by weight, respectively). The study indicated that, the most suitable solvents for separating paraffin waxes; with standard specifications; from slack waxes are MIBK, ethyl and butyl acetate and mixture of MEK, benzene and toluene (60:20:20) (**Mohamed et al., 2008**).

Multistage fractional crystallization technique was used to de-oil microcrystalline waxes with n-hexane and ethyl alcohol solvent mixtures (**Mohamed and Zaky, 2004**).

The effect of selective solvent mixtures on the crystal structures of paraffin wax during de-oiling process was studied. The authors found that MEK-MIBK solvent mixture promoted the formation of large rounded wax crystals, which gave porous cake giving fast filtration rate (**Chebanov, Sokolova and Pereverzev, 1987**).

c) The Warm-Up De-oiling Process:

This Process is always operated in conjunction with solvent de-waxing process. The slack wax from solvent de-waxing is diluted and mixed with warm solvent and filtered at a temperature, which provides a hard wax of desired melting point. The warm-up de-oiling procedure is more cost-effective than the recrystallization procedure for manufacture of low oil content waxes because capital and energy requirements are lower; the hard wax is not melted and recrystallized before filtration. In addition, scraped-surface exchangers and chillers are not required (**Eagen, et al. 1975; Gudelis , Eagen and Bushnell, 1973; Sequeira, 1982 and Sequeria, 1994**).

Esso Research and Engineering Co. has developed a Dilchill de-waxing and de-oiling within one plant. They are used the warm-up de-oiling technique to refine the slack wax (**Sparks and Perry, 1956**).

There are three unusual characteristics of the crystals from the Dilchill process and these make them suitable for carrying out the warm-up de-oiling operation without an intermediate re-crystallization operation.

First, the crystals are initially so large that they still filter well after the soft wax is re-dissolved.

Secondly, the compact, coherent structure does not allow the crystals to fall into pieces when mixed with warm solvent.

Thirdly, the "layered" structure allows the undesirable soft wax to be re-dissolved without affecting the core of the crystal. The refined wax from the Dilchill process

is essentially equal to that obtained from conventional solvent re-crystallization plant.

d) The Spray De-oiling Process:

It can be used to de-oil macro-crystalline wax containing up to 15 wt.% oil. This process like the sweating process is not suitable for the de-oiling of mal-crystalline wax.

Molten wax is atomized under pressure into the top of the tower. The finely dispersed droplets of wax fall through a rising stream of air which is cooled to slightly below ambient conditions. The solidified wax settles to the bottom of the tower as a dry powder.

The oil which adheres to the wax is removed by a counter current flow of cooled dichloromethane solvent at a temperature between -40 and 60 °F through a system of two or more mixer settlers and separated into two layers in a settling tank.

The wax leaving the last settler is centrifuged and washed with fresh solvent. The solvent is recovered from the hard and soft wax by flash vaporization and the dry solvent is recycled in the process (**Sequeria, 1994**).

In Hindustan Leves Ltd. a slack wax containing 24.8 wt.% oil was de-oiled by pouring the molten wax into cold acetone with vigorous stirring. The washed twice with cold acetone to give paraffin wax containing 1 wt. % oil (**Chen and Partridge, 1992**).

1.6.3.2 Solvent Percolation Technique:

Many authors carried out a study deals with the application of solvent percolation technique to separate oil from commercial microcrystalline wax flakes produced from tank bottom sludges. Wax de-oiling has been accomplished by percolating industrial hexane through a packed bed of the wax flakes at ambient temperature and removing the solvent from the wax oil and oil phases to get hard wax and foot oil respectively.

In this technology, mechanical mixing and filtration operation have been substituted with percolation of solvent through wax flakes, thereby eliminating mixed phase in the process and the need of expensive scraped surface crystallizers, rotary-drum filters and refrigeration equipment as required in conventional solvent de-oiling (**Agrawal and Kumar, 1994**).

Fractional crystallization and solvent percolation techniques were tested for separation of paraffin waxes from light, middle and heavy slack waxes. The study indicated that fractional crystallization technique is more suitable for de-oiling the heavy slack wax. However, percolation technique is a preferable technique for separation of paraffin waxes from light and middle slack waxes (**Zaky, Mohamed and Farag, 2007**).

1.6.3.3 Supercritical Fluid Fractionation:

Supercritical fluid de-oiling and fractionation of paraffin wax is compared with short path distillation (SPD) and static crystallization. Detailed cost analyses of the different processes are made and compared. From these cost analysis it appears that SPD is the fractionation process for light paraffin wax. However, supercritical fluid fractionation appears to be the more attractive for the fractionation of medium to heavy paraffin waxes (**Crause and Nieuwoudt, 2003**).

1.6.4 Crystal Modifiers for De-waxing and De-oiling Improvement:

Commercial processes for de-waxing and de-oiling residual feed-stocks are complex and laborious. The greatest difficulties are related to the stage of filtering slurries of solid hydrocarbons that tend to form an inter-crystalline structure.

Improving processes for obtaining solid hydrocarbons, use is made of various additives that have a modifying effect on the crystal structure of solid hydrocarbons. The modifiers offer a means for a considerable improvement in the basic indices of the process and in the quality of the end-product without any additional costs, using existing equipment. The effect of a modifier on the crystallization of solid

hydrocarbons is usually rated on the basis of the melting point of the microcrystalline wax, the oil content in the microcrystalline wax, and the slurry filtration rate **(Kazakova et al., 1986)**.

Observation of the cooling rate behavior of complex-wax-containing crude oils treated with crystal modifiers versus untreated samples showed the successfully treated (crystal-modified) samples cooled at a more rapid rate than untreated samples **(Becker, 1997)**.

The formation of large, multilayer, aggregated crystals requires not only the proper selection of process conditions but also the choice of modifiers that will rearrange the structural formations of paraffinic hydrocarbons in the required direction. Many organic additives had been tested in the laboratory as modifiers for structural conversions of the solid phase. The group of additives tested for this purpose includes pour-point depressants with surface and bulk action, certain organometallic compounds, and all possible macromolecular substances with a polymeric structure. Many of these additives, while they have a strong modifying effect, will lose this property when the medium is moist **(Zolotarev & Nigmatullin, 1994)**.

For improving the crystallization of solid hydrocarbons; during the de-oiling of petrolatum to produce microcrystalline wax; a non-polar modifier was added to the wax de-oiling solvent mixtures. The resulting microcrystalline wax contained 0.5 wt.% oil **(Kazakova et al., 1989)**.

The influence of polar modifiers in the process of de-oiling residual feed-stocks (petrolatums) offers considerable promise for the intensification of this complex process.. Additives with various functional actions that are used as polar modifiers of the structure of hydrocarbon crystals are surfactants. Not all of the modifiers that are effective in de-waxing of the hydro-treated raffinate can be used for modification of solid hydrocarbon crystal structure in the production of high-melting microcrystalline waxes. Whether or not the phase separation rate in filtering the solid

hydrocarbon slurry will be increased, and whether the oil content in the microcrystalline wax will be lowered, will depend on the length of the radical and the polarity of the modifier molecule (**Kazakova et al., 1990**).

(**Zolotarev and Nigmatullin, 1994**) were studied the purification and de-oiling of slack wax with aluminum chloride complex. It can be used as a means for obtaining paraffin waxes with quality at the export-grade level, and for increasing the paraffin yield by 2 – 4 %. The slack wax after purification, as it has reduced oil content, can be de-oiled in two filtration stages. The third-stage vacuum filters that are thus liberated can be used to increase the feed capacity of the unit.

(**Nigmatullin et al., 1995**) were investigated the use of ionic modifiers; aqueous sodium chloride and aqueous iron sulfate; for de-oiling petrolatum and slack wax, respectively. They concluded that the aqueous sodium chloride solution increases the selectivity of the highest-melting hydrocarbons from the petrolatum. But modifier did not affect the filtration rate and the modification function of iron sulfate was related to co-crystallization because crystal lattices of iron and solid paraffin waxes were similar (**Nigmatullin, 1997**).

A pulsed-mixing industrial crystallizer has been part of the de-waxing system in production of lube oils and waxes. During a pilot run, the crystallizer was tested in processing residual raffinate and raffinate of the 420-490oC cut of mixed West Siberian crude oils. The results demonstrated the existence of reserves in optimizing of de-waxing technology using a pulsed crystallizer. Implementation of this technology and a series of measures to improve the feedstock quality allowed manufacturing wax with 0.9-1.6 wt. % oil content (**Yakovlev et al., 2002**).

A process was developed for de-oiling of slack waxes with a pulsed crystallizer which proposes totally eliminating scraper crystallizer-regenerative and evaporative from the process scheme. Replacing all the regenerative and evaporative scraper crystallizers with one pulsed crystallizer reduces the metal requirement of the

crystallization equipment by more than ten times and consequently eliminates operating costs for servicing and repairing the scraper crystallizers. In addition, due to the higher hermetic sealing of the pulsed crystallizer in comparison to scraper crystallizers, losses of selective solvents are reduced, i.e., the environmental safety increases (**Yakovlev and Boldinov, 2008**).

The operating indices of units for de-waxing with selective solvents using membrane filters and a modifier additive were compared with respect to production of lube oils from Baku crudes. It showed that selection of the modifiers (DN-MA, obtained by copolymerization of methacrylic and acrylic acid esters) for de-waxing lube oils with selective solvents was thus a high-priority direction in improving the technology of the process to increase its efficiency (**Kuliev, Veliev and Kulieva, 2003**).

Also, the use of modifier (DN-MA additive, an alkyl methacrylate copolymer) in the optimum amount (15 wt. %), was the most effective. It was possible to obtain de-waxed lube oil with a high yield and improved physicochemical properties, reduced the oil content in slack wax by 2.5 times, and increased the filtration rate of the cooled solution by 2 - 4.8 times (**Veliev, 2007**).

Trends for improving the production of oils and solid hydrocarbons were examined by optimization of crystallization of solid hydrocarbons by using ultrasound. In treating a suspension with ultrasound, the bonds between solid hydrocarbon crystals are destroyed and conditions are created for their growth, so that the rate and efficiency of separation of the solid phase from the liquid phase increase (**Sochevko and Tugusheva, 2010**).

1.6.5 Finishing Process:

Finishing was used as additional clean up step added to the end of conventional refining processes. Although acid and clay are still used to some extent for the finishing of lubricating oil base stocks and wax, these processes have for the most part been replaced with hydrogen finishing processes. Finishing processes improve

color, color stability, oxidation stability and inhibitor response, also to reduce nitrogen, sulfur and aromatic contents (**Sequeria, 1994 and Kramer, Lok and Krug, 2001**).

1.6.5.1 Adsorption Process:

Adsorption process used to remove polar compounds from petroleum waxes thus improving color, chemical, thermal and color stability. The process variables include the type of adsorbent, adsorbent dosage and treating temperature. This process has been replaced with hydrogen finishing in the manufacture of petroleum waxes. Various types of fuller's earth, activated carbon, silica gel, bauxite, bentonite, natural or synthetic aluminum silicates are suitable adsorbents (**Freund, 1982**).

The high adsorbing power of clays makes them suitable for removing the undesirable hetero-atom compounds from the oleum treated wax containing the aromatics. Finishing with clay includes two different techniques:-

Clay contacting: involves the mixing of wax with activated clay at definite temperature for a short period of time followed by separation of the wax and clay. This process may be used alone or in combination with the acid treating process for the finishing and neutralization of petroleum waxes (**Sequeria, 1994**).

Clay Percolation: is an adsorption technique which may be a continuous process, but must commonly a static bed of clay is used to purify, decolorize and finish lube feed-stocks and waxes. Clay percolation has in large part been replaced by hydrogen finishing but is still in limited use for the manufacture of waxes. The process variables include temperature, flow rate, throughput and type of clay.

Some refineries used bauxite (hydrated aluminum oxide) as adsorbent for refining petroleum waxes especially microcrystalline waxes due to its higher adsorption behavior towards mono-aromatics with long alkyl chain and condensed ring structures (**Kumar and Gupta, 1996**).

Many authors studied the use of composite adsorbents composed of waste fluidized catalyst and activated white clays for refining petroleum waxes. The fluidized catalyst can be used directly or after chemical treatment. The method is practicable, convenient and enhanced the wax yield by 4%.

Bentonite clay blended with 40 wt% of spent catalyst had been used to refine paraffin wax. The paraffin product had similar properties, such as photo-stability, color, as compared with those of traditional clay refining process. The method had the advantages of lower consumption, lower cost and environmental protection. The deoiled sludge could be used as building sealant (**Chen et al., 2008**).

Many authors prepared and examined nano materials (ex. Layered double hydroxides and γ -alumina) and stated that these materials removed sulfur and di-aromatic compounds in high efficiency from petroleum waxes. Furthermore, the two nano-materials improved the physical properties of crude waxes. Also, the results clearly indicated that these materials were considered to be selective adsorbents for di-aromatic compounds (**Saber, Hefny and Al Jaafari, 2011 and Zaki et al., 2013**).

1.6.5.2 Hydro-finishing Process:

Hydrofinishing is a mild hydrogenation process used in place of the older and more costly acid and clay finishing processes. Owing to the wide-spread applications of petroleum waxes in food, pharmaceutical and cosmetic fields, hydro-finishing is applied to complete their purification to produce products meeting the established specifications, including the FDA (U.S Food and Drug Administration) (**Saber, Hefny and Al Jaafari, 2011**).

Hydro-finishing processes are used to improve color and color stability, which is also related to improvement of oxidation stability, appears to be related to the removal of sulfur and other impurities. Unlike the hydrogen refining processes, the hydro-finishing processes do not saturate aromatics nor break carbon-carbon bonds.

The hydro-finishing temperature and pressure are highly dependent on the quality of the feedstock, product specifications and the type of catalyst used. Suitable hydro-finishing catalysts consist of nickel-molybdenum on alumina and Nickel-tungsten on alumina or silica-alumina (**Saber, Hefny and Al Jaafari, 2011**).

1.6.6 Applications of Petroleum Waxes:

Petroleum waxes in their various fields of application require many different specifications. These can only partly be satisfied by a suitable choice of feedstock and the manufacturing processes, or even by some modifications of these processes. As the consumption of wax products in the world wax market increases; especially for food, pharmaceutical and cosmetic grades and specialty wax; the increase of profitability of wax production will lie on the improvement of blending and modification techniques for macro and micro-crystalline waxes as base materials as well as the development and applications of new wax products (**Shaokang, 2001**).

Petroleum waxes are based in a wide variety of applications. Some of the most important applications used in industrial and other fields are discussed below.

1.6.6.1 The Paper Industry:

The paper industry is by far the largest user of petroleum wax. One of the most characteristic properties of petroleum wax is their chemical inertness or resistance to attack by acids, alkalis, air or oxygen etc. Petroleum wax is insoluble in water and in the form of thin continuous film it is practically impervious to air and moisture.

Petroleum waxes are used in the paper industry especially for impregnation, coating and lamination. In addition, they are used as additives to paper sizes (**Freund, 1982**).

1.6.6.2 Household Chemicals:

Various grades of paraffin and microcrystalline waxes are used in household chemicals. The main consumers for petroleum waxes are polishes and candles. Petroleum waxes are used as additives in many polishes, and a substantial part of candle material is petroleum wax.

The demands of the candle industry require over 50% of the worldwide production **(Saleh, Ahmed and Zaky, 2008)**. Paraffin waxes having melting point between 48 and 54 °C are suitable for candle manufacture **(Freund, 1982)**.

Polishes industry is one of the most important applications in which the petroleum waxes are used as additives in many polishes. The high gloss characteristics of some petroleum waxes makes them suitable ingredients for polishes, particularly for the “paste” type which commonly used on floors furniture, cars and footwear **(Bennett, 1975 and Gottshall and McCue, 1973)**.

1.6.6.3 Cosmetics Industry:

Waxes and wax-like materials are used in many cosmetics products. The following petroleum products such as vaseline oil, petrolatum, paraffin and microcrystalline waxes are in use for cosmetic purposes.

Paraffin and microcrystalline waxes make a significant difference to the resistance to mechanical impact, hardness and softening point properties of cosmetic preparations. Microcrystalline waxes are tougher than paraffin waxes, they exhibit plastic flow under the effect of compression, while paraffin waxes have compressive strength.

Lipsticks constitute the major application of waxes in cosmetics. The outstandingly important property of waxes used for lipsticks is their melting point. The most important starting materials for their manufacture are various natural and synthetic waxes, fats, fatty alcohols, petrolatums, petroleum waxes and dyes (**Giuliani and Merusi, 2009**).

Paraffin waxes, petrolatum and vaseline oil are used in the manufacture of cosmetic creams (cleansing, cold, massage and sport) beauty masks and face make-up (**Freund, 1982**).

Hair wax product with liquid or creamy consistency was prepared for treating or setting up a human hairstyle containing at least 40 wt. % of an aqueous or aqueous-alcoholic carrier medium, at least 5 wt. % of an emulsifier and at least 2 wt. % of wax (**Maillefer et al., 2011**).

1.6.6.4 Dental Industry:

Dentists and dental laboratories use quantities of various wax compounds as base-plate wax, inlay-casting wax, impression compound, set-up wax, bite wax, sticky wax and carving wax (**Bennett, 1975**).

(**Schiemann et al., 2007**) were found that by blending 98 wt.% of petrolatum with 2 wt.% of flavoring, an ointment with stable and pleasant taste, can be used for protecting the oral cavity and specifically the teeth, gums and tongue.

1.6.6.5 The Match Industry:

The match industry is one of the oldest consumers of paraffin waxes. Paraffin impregnation of the matches, usually made of wood, has the objective of ensuring rapid ignition of the matchwood after striking the match-head. In addition, waxing improves adhesion of the match-head to the matchwood and resistance to moisture. The latter is of particular importance for matches stored and used in high moisture climates.

Previously, lower-melting paraffin waxes (42 to 46 °C) were preferred for match impregnation. At present higher-melting waxes (46 to 54 °C) are more widespread in use. Still higher-melting waxes could be used, but are too expensive. The oil content of paraffin waxes for impregnation must not exceed 5 wt. %; the usual value is around 3 wt. % (**Freund, 1982**).

1.6.6.6 The Rubber Industry:

The rubber industry is also one of the most important paraffin wax consumers, using it for a variety of purposes. Paraffin wax, when used as an additive to rubber increases the stiffness of the product. This is of major importance in press-molded rubber products.

Almost all types of petroleum waxes are in use in the rubber industry. In the manufacture of air tubes, paraffin waxes containing 2 to 5 wt. % oil are used to ease molding and to achieve uniform surface resistance to abrasion in the type. Blends of paraffin and microcrystalline waxes are used in the manufacture of sealing rings for preserve jars and other types of sealing rings. For industrial purpose rubber goods, e.g. batteries, shoes, bands and toys, where requirements of color and odor are not so critical, less refined petrolatums of darker color are used (**Freund, 1982 & Prasad,, 2000**).

1.6.6.7 Building Construction:

Aqueous emulsions of petroleum waxes have found a wide range of applications in recent years. The more recent application of petroleum wax emulsions is in the field of building construction to protect the surface of green concrete structures. It is well known that green concrete must continually be kept moist during the curing process (**Freund, 1982**). The corrosion and wear resistance of concrete road pavements increase by treating or coating the concrete surface with petrolatum. The stabilization action of petrolatum is attributed to its interactions with the calcium oxide containing phases of concrete (**Schweitzer, 2003**).

A microcrystalline wax; characterized with high congealing point and viscosity and low penetration; was used for manufacturing of a special type of waxy asphalt of penetration grade 60/70 which used as a binder in hot mix asphalt (HMA) production using local high absorptive aggregates. The prepared mixes showed their suitability for use as a wearing or base course for the medium and low traffic roads (**Saleh, Ahmed & Zaky, 2008**).

1.6.6.8 The Electrical Industry:

The electrical industry used large amounts of different types of petroleum waxes for insulation at ambient temperature. Petroleum waxes are good insulating agents of electricity in addition to providing water or water–vapor resistance. The important requirements for petroleum waxes to be used in the electrical industry are flexibility, ductility and low thermal expansion coefficients. Therefore, petroleum waxes are used in electric industry as impregnating agents and potting compounds in many applications.

Petroleum waxes and petroleum waxes with additives are much used for building up blocking layers, e.g. for capacitors, for cable terminals and couplings, for impregnating cable–insulation paper, for filling the space between cables and around the coupling (**Freund, 1982**).

1.6.6.9 The Inks Industry:

The ink industry includes two types of inks: printing inks and carbon paper inks.

a) Printing Inks:

Waxes have long been used in printing inks for controlling their working and drying properties and to improve scratch resistance.

(Pasetto & Baldo, 2010) found that, a special wax useful for printing inks was manufactured by oxidation at 125 °C in the presence of catalysts using paraffin wax and microcrystalline wax as a raw material. Also, he compared the performance of this special wax with that of beeswax for printing inks.

b) Carbon Paper Inks:

There are two classes of waxes employed in carbon-paper inks. The amorphous waxes, such as ozokerite, ceresin, and petroleum waxes, body the ink or absorb and hold the oil vehicle. The hard crystalline waxes are the essential ingredients in carbon-paper inks. They hold the ink in a solid form and permit the handling of the coated papers with a reasonable amount of cleanliness.

(Cooper & Jacob, 1984) were studied the composition for preparing carbonless copying paper. They manufactured these papers by mixing 95-97 wt. % of ceresin and 3-5 wt.% of polyethylene or polyethylene wax in the melt at 130-140°C. Also, they found that this mixture give better smoothness than the usual 70:30 paraffin-ceresin composition.

1.6.6.10 Manufacture of Metals and Ceramics:

Powder injection molding (PIM) is an advanced technology for processing metal and ceramic powders for forming desired shapes at relatively low processing cost (Hsu, Lin & Lo, 1996) The PIM consists of the formulation of a binder, the preparation of feedstock by mixing of binder and metal or ceramic powders, injection molding of the feedstock into a mold, removal of the binder from the feedstock (solvent and thermal de-binding) and sintering of the metal or ceramic powders (Zaky, 2004).

Successful production of parts by the PIM process is closely related to the formulation of mainly organic binder system to be used with the powders. Petroleum waxes are often used as primary binder components. They have low melting point, good wetting behavior, short molecular chain, low viscosity and decompose with small volume change. The secondary binder component, which remains in green molded part, retains the shape of the part, preventing slumping and distortion. The additives aid in improving the interaction between the various constituents, improve wetting, and help in avoiding separation **(German, 1997 & Liu et al., 2002)**

The effect of solvent de-binding variables on the shape maintenance of green molded bodies consisting of poly (ethylene-ran-vinyl acetate) – paraffin wax – stearic acid based binder and 17-4PH stainless steel powder was investigated. Data indicated that selection of organic solvent of higher solubility such as n-hexane is more important to enhance the de-binding rate, and the extraction temperature of 50 °C, solvent to feed ratio of 7:1 by weight and extraction time of 2.25 h are the most suitable conditions for extracting all the major binder and stearic acid constituents completely from the binder mixture without affecting the shape maintenance of green molded parts **(Zaky, 2004)**.

The formulation of wax-based binders from paraffin waxes, feedstock preparation and solvent de-binding of the soluble binder constituents (paraffin wax and stearic acid) from the green molded parts were evaluated. Data revealed that the formulated binder system consisted of 35 wt.% EVA containing vinyl acetate content of 9 wt.%, 62 wt.% of heavy paraffin wax and 3 wt.% of SA provided an excellent wax-based binder system and the solvent immersion was a preferable solvent debinding technique for saving the amount of solvent used as compared with the evaporation–condensation technique **(Zaky, Soliman & Farag, 2009)**.

1.7 Research Objectives:

1.7.1 Main Objective:

The main objective of this study is to enhance the physical and molecular properties of Sudanese crude oil (Rawat).

1.7.2 Specific Objectives:

- To decrease the pour point and wax content of Sudanese feed.
- To select the suitable solvent for de-waxing process.
- To determine the suitable de-waxing temperature, feed/solvent F/S ratio and crystallization time for Butyl Acetate de-waxing process for Sudanese crude oil.

Chapter Two

Materials and Methods

Chapter Two: 2. Materials and Methods

2.1 Materials:

2.1.1 Chemicals:

- 1- Methyl Ethyl Ketone, 99%, (Riedel-deHaen).
- 2- Methyl Isobutyl Ketone, ACS for analysis, Reagent Ph. Eur-Reag. USP (Carlo Erba).
- 3- Butyl Acetate, 99% (Morgan Chemical IND. Co., Egypt).
- 4- Methyl Tertiary Butyl Ether, 99% (Riedel-deHaen).
- 5- Petroleum Ether 40-60°C, for analysis (Carlo Erba).
- 6- n-Heptane, 99% (Carlo Erba).
- 7- Benzene, Pure reagent for analysis (ADWIC)
- 8- Methanol, 99.5% (Piochem. Co.)
- 9- Silica Gel 60-200 mesh size (Loba Chemie, India).
- 10- Aluminum oxide, for chromatographic analysis (Riedel-deHaen).

2.1.2 Instruments:

- 1- Digital Refractometer; model RFM870, Bellingham and Stanley Ltd. (UK).
- 2- X-ray fluorescence sulfur meter analyzer; model Spectro Phoenix II (USA).
- 3- GC apparatus used was model (Perkin Elmer instrument, Clarus 500, England), equipped with a hydrogen flame ionization detector and fused silica capillary column (30 cm x 0.25 mm i.d.), packed with poly (dimethyl siloxane) HP-1 (non-polar packing) of 0.5 μm film thickness.
- 4- Density meter, Anton Paar Model: SVM 3001
- 5- SETA Cloud and Pour Point Refrigerator, SETA Model: STANE HOPE
SETA

2.2 Methods:

2.2.1 Sample:

Sudanese crude oil sample was obtained from Rawat field located at a distance of 132 kilometers southwest of Kosti in Sudan is by using standard sampling method.

(Color: black. **Quantity:** 50 liters. **Net weight:** 44 kg. **Gross weight:** 48.5 kg.

Sampling time and date: 18/11/2018, 1:00 pm. **Sample well:** central 10).



2.2.2 Solvent Dewaxing Technique

In this study solvent de-waxing technique was used using different de-waxing solvents at different dilution solvent ratios of 4:1, 6:1, 8:1 and 10:1 by weight and under constant washing solvent ratio of 2:1 by weight. In the stage of solvent de-waxing, the high melting components of wax precipitated while the low melting components (low melting point wax and soluble oil) remained in the solution. The process of solvent de-waxing was repeated using butyl acetate solvent at different de-waxing temperatures ranging from -5 to -20°C at intervals of 5°C and at different times of crystallization ranging from 6 to 24 hours.

A known weight of Sudanese crude oil was dissolved in the corresponding amount of solvent in a beaker and heated till the mixture became homogeneous. Then the mixture was cooled gradually at room temperature for half an hour and transferred to a refrigeration unit at 5°C for 24 hours. The beaker and the Buchner funnel were transferred to a controlled temperature unit and gradually cooled to the desired de-waxing temperature for 3 hours. The beaker contents were transferred to the Buchner funnel and filtered through a Whatman filter paper No.43 using controlled suction (8.6 Psi). The precipitated wax cake and oil were washed with an additional solvent at the same de-waxing temperature and added at small increments. Solvents were removed from the precipitated wax cake by distillation.

2.2.2.1 Solvent De-waxing Variables

a) Solvent Type

Solvent de-waxing using various single solvents at fixed de-waxing temperature of -10°C and fixed washing solvent ratio of 2:1 by weight and at different dilution solvent ratios of 4:1, 6:1, 8:1 and 10:1 by weight.

The de-waxing solvents are methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), butyl acetate (BA) and methyl tertiary butyl ether (MTBE).

b) Dilution solvent ratios

Solvent de-waxing using various single solvents (MEK, MIBK, BA and MTBE) at different dilution solvent ratios of 4:1, 6:1, 8:1 and 10:1 by weight and at fixed de-waxing temperature of -10°C and fixed washing solvent ratio of 2:1 by weight.

c) Dewaxing Temperature

Solvent de-waxing technique at various de-waxing temperatures ranging from -5 to -20°C at intervals of 5°C by using butyl acetate solvent at fixed dilution and washing solvent ratios of 10:1 and 2:1 by weight, respectively.

d) Time of Crystallization

Solvent de-waxing technique at different times of crystallization (6, 12 and 24 hours) and at constant de-waxing temperature of -10°C by using butyl acetate solvent at fixed dilution and washing solvent ratios of 10:1 and 2:1 by weight.

2.2.3. Physical Characteristics

The physical characteristics of the Sudanese crude oil and isolated oil products were carried out according to American Society for Testing and Materials (*ASTM*), International Petroleum test methods (*IP*) and Universal Oil Products standards (*UOP*). The standard methods for analysis are as follows:

Congealing point	ASTM D-938
Pour point	ASTM D-97
Density	ASTM D-4052
Specific gravity	ASTM D-4052
API gravity	ASTM D-4052
Refractive index	ASTM D-1747
Kinematic viscosity	ASTM D-445
Mean molecular weight	ASTM D-2502
Wax content	UOP-64
Water content	ASTM E-203
Asphaltene content	IP-143
Carbon residue, wt. %	ASTM D-189
Total acid number (Potentiometric titration method)	ASTM D-664
Sulfur content, X-ray fluorescence sulfur meter	ASTM D-4294

2.2.4. Molecular Type Composition

2.2.4.1. Aromatic Content

The total aromatic content of the Sudanese crude oil and the oil products was determined using liquid-solid column chromatography technique (**Snyder, 1975**).

A 1.3 cm diameter column packed with activated alumina for chromatographic purposes (65g) and activated (60-200 mesh) silica gel (65g) to a total height of 130 cm was used. The column was then moistened with 100 ml of n-heptane (in case of crude oil) or petroleum ether 40-60°C (in case of oil products) to dissipate the heat of adsorption. A 10 grams sample of the crude oil or the oil product dissolved in few milliliters of n-heptane or petroleum ether 40-60°C was transferred to the column. The column was then eluted with 300 ml n-heptane or petroleum ether 40-60°C followed by 200 ml benzene and finally 100 ml of a 1:1 mixture of absolute methanol and benzene. Fractions of 25 ml were collected from the column, the solvent distilled off and the refractive index at 20°C of each fraction was determined. According to the refractive indices data, the fractions were combined into saturates, mono-, di- and poly-aromatics. The saturate hydrocarbons have refractive indices not more than 1.48. The mono-cyclic, bi-cyclic and poly-cyclic aromatics have refractive indices from 1.48 to 1.53, 1.53 to 1.59 and higher than 1.59, respectively (**Mair & Rossini, 1958**).

2.2.4.2. n-Paraffin Content

n-Paraffin content was determined for the saturates of Sudanese crude oil and the oil products using gas chromatography technique (GC).

In the chromatograph, the injector was heated to 350 °C. The column temperature was programmed from 80 to 300 °C at a fixed rate of 3 °C/min., and nitrogen (oxygen-free) was used as a carrier gas with flow rate of 2 ml/min. The detector was heated to 350 °C, and the flame operated with air and hydrogen flow rates adjusted to optimize the detector sensitivity. The sample was melted and 0.1µl of it was introduced into the injector. A mixture of pure n-paraffins was used as standards. The peak area of each resolved component (consisting of n- and iso-paraffins) is determined individually. However, the unresolved complex mixture (hump) is presumably composed of non n-paraffins iso- and cyclo-paraffins.

2.2.4.3. Structural Group Analysis

Carbon distribution analysis; the percentage of aromatics carbon ($\%C_A$), paraffinic carbon ($\%C_P$) and naphthenic carbon ($\%C_N$) and ring content analysis; aromatic ring (R_A), naphthenic ring (R_N) and the total ring (R_T); per average molecule were determined by n-d-m method (This method covers the calculation of the carbon distribution and ring content of olefin-free petroleum oils from measurements of refractive index, density and molecular weight). (**Van Nes & Van Westen, 1951**) for the oil products.

Chapter Three

Results and Discussion

Chapter Three: 3. Results and Discussion

3.1. Characterization of Sudanese Crude Oil:

Table 3.1: The Physical Characteristics and Molecular type Composition of Sudanese Crude Oil (Rawat):

Physical Characteristics	Value
Melting Point (congealing point) °C	54
Density at 15.56 °C	0.8794
Specific Gravity at 15.56 °C	0.8802
API Gravity at 15.56 °C	29.25
Refractive Index at 70 °C	1.4745
Kinematic Viscosity at 100 °C, mm ² /s	9.23
Mean Molecular Weight	628
Wax Content, wt.%	26.3
Asphaltene Content, wt.%	0.28
Carbon Residue, wt.%	4.29
Sulfur Content, wt.%	1.80
Total Acid Number, wt.%	1.282
Water Content, wt.%	0.1
Molecular type composition	Value
Saturates content, wt.%	57.50
n-paraffins content, wt.%	47.14
Iso and cyclo- paraffins content, wt.%	10.36
Aromatics content, wt.%	42.50
Mono-aromatics, wt.%	1.50
Di-aromatics, wt.%	13.30
Poly-aromatics, wt.%	27.70

Table 3.2: Preliminary Distillation of Sudanese Crude Oil (Rawat), (ASTM D-1160):

Initial Boiling Point (IBP: 130 °C):

Temperature, °C	Recovered ml
155	1.5
180	2
205	4
230	5
255	10
280	14
305	15
Recovery	16
Residue	82
Loss	2

The physical characteristics and the molecular type composition for the Sudanese crude oil were carried out according to American Society for Testing and Materials (ASTM), are presented in Table 3.1. Data indicates that the Sudanese crude oil has high pour point (54°C) and mean molecular weight (628) and low refractive index (1.4745) due to its high saturates content; especially its n- paraffins content (47.14%) and consequently its high wax content (26.3%); and at the same time high aromatics content (42.50%). Thus, in order to produce lubricating oils (having good fluidity characteristics at low temperatures) from the Sudanese crude oil, the pour point must be reduced by subjecting to solvent de-waxing process (a crystallization–filtration process) (Avilino, 1994 & Speight, 2007).

3.2 Effect of Solvent Type:

Table 3.3: The physical characteristics, molecular type composition and structural group analysis of de-waxed oils obtained using different solvents at de-waxing temperature of -10 °C and S/F for dilution and washing 4:1 and 2:1 respectively.

Physical Characteristics	De-waxed Oils Obtained Using			
	MEK	MIBK	BA	MTBE
Yield on Sudanese Crude Oil, wt.%	14.29	12.09	16.40	33.99
Pour Point, °C	- 7	7	7	10
Density at 20°C	0.8883	0.9300	0.9155	0.8782
Density at 15.56°C	0.8892	0.9308	0.9163	0.8790
Specific Gravity at 15.56°C	0.8901	0.9317	0.9172	0.8798
API Gravity at 15.56°C	27.47	20.37	22.77	29.33
Refractive Index at 70 °C	1.4779	1.4934	1.4919	1.4703
Kinematic Viscosity at 40 °C,	25.00	100	123.00	25.62
Kinematic Viscosity at 100 °C,	5.50	12.00	13.30	4.90
Viscosity Index	166	110	103	115
Mean Molecular Weight	478	576	584	406
Sulfur Content, wt.%	0.4666	0.5506	0.5563	0.3926
Wax Content, wt.%	0.05	0.4	0.3	15.90
Total Acid Number, wt.%	1.775	0.931	1.6317	0.295
Molecular Type Composition				
Saturates Content, wt.%	57.52	50.11	58.01	59.37
n-paraffins Content, wt.%	28.09	28.22	33.50	45.55
Iso and Cyclo- paraffins Content,	29.43	21.89	24.51	13.82
Aromatics Content, wt.%	42.48	49.89	41.99	40.63
Mono-aromatics, wt.%	11.90	14.20	11.50	3.93
Di-aromatics, wt.%	18.07	23.99	14.89	20.47
Poly-aromatics, wt.%	12.51	11.70	15.60	16.23
Structural Group Analysis				
Carbon Distribution Analysis				
% C _A	16.33	13.83	18.36	13.83
% C _N	12.93	31.71	16.40	18.00
% C _R	29.26	45.54	34.76	31.83
% C _P	70.74	54.46	65.24	68.17
Ring Content Analysis				
R _A	0.97	0.99	1.34	0.69
R _T	2.00	4.16	3.10	1.82
R _N	1.03	3.17	1.76	1.13

Table 3.4: Effect of solvent type on the physical characteristics, molecular type composition and structural group analysis of de-waxed oils obtained using different solvents at de-waxing temperature of -10 °C and S/F for dilution and washing 6:1 and 2:1 respectively.

Physical Characteristics	De-waxed Oils Obtained Using			
	MEK	MIBK	BA	MTBE
Yield on Sudanese Crude Oil, wt.%	19.14	27.30	23.71	42.67
Pour Point, °C	- 5.5	7	8	17
Density at 20°C	0.8959	0.9134	0.9031	0.8805
Density at 15.56°C	0.8967	0.9142	0.9039	0.8813
Specific Gravity at 15.56°C	0.8976	0.9150	0.9048	0.8821
API Gravity at 15.56°C	26.15	23.14	24.90	28.91
Refractive Index at 70 °C	1.4784	1.4853	1.4853	1.4690
Kinematic Viscosity at 40 °C, mm ² /s	26.00	61.54	65.18	26.39
Kinematic Viscosity at 100 °C,	5.75	8.70	9.00	5.30
Viscosity Index	173	115	113	138
Mean Molecular Weight	495	507	521	436
Sulfur Content, wt.%	0.4621	0.5068	0.4432	0.3846
Wax Content, wt.%	0.10	0.35	0.29	16.20
Total Acid Number, wt.%	1.692	1.20	0.561	0.3232
Molecular Type Composition				
Saturates Content, wt.%	57.03	50.83	58.12	59.88
n-paraffins Content, wt.%	25.90	30.10	34.12	44.20
Iso and Cyclo- paraffins Content,	31.13	20.73	24.00	15.68
Aromatics Content, wt.%	42.97	49.17	41.88	40.12
Mono-aromatics, wt.%	11.31	13.94	9.92	4.50
Di-aromatics, wt.%	18.50	22.69	15.44	22.40
Poly-aromatics, wt.%	13.16	12.54	16.52	13.22
Structural Group Analysis				
Carbon Distribution Analysis				
% C _A	13.34	13.09	17.32	10.82
% C _N	21.00	28.70	15.57	22.41
% C _R	34.34	41.79	32.89	33.23
% C _P	65.66	58.21	67.11	66.77
Ring Content Analysis				
R _A	0.82	0.82	1.12	0.58
R _T	2.53	3.27	2.55	2.10
R _N	1.71	2.45	1.43	1.52

Table 3.5: Effect of solvent type on the physical characteristics, molecular type composition and structural group analysis of de-waxed oils obtained using different solvents at de-waxing temperature of -10 °C and S/F for dilution and washing 8:1 and 2:1 respectively.

Physical Characteristics	De-waxed Oils Obtained Using			
	MEK	MIBK	BA	MTBE
Yield on Sudanese Crude Oil, wt.%	19.75	29.17	33.00	60.55
Pour Point, °C	- 4.5	6	5.5	25
Density at 20°C	0.9055	0.8956	0.8933	0.8879
Density at 15.56°C	0.9063	0.8964	0.8941	0.8887
Specific Gravity at 15.56°C	0.9072	0.8973	0.8950	0.8896
API Gravity at 15.56°C	24.47	26.20	26.61	26.93
Refractive Index at 70 °C	1.4796	1.4801	1.4796	1.4700
Kinematic Viscosity at 40 °C, mm ² /s	27.00	39.67	40.06	55.00
Kinematic Viscosity at 100 °C,	5.90	6.60	7.10	7.00
Viscosity Index	172	120	140	90
Mean Molecular Weight	498	468	490	441
Sulfur Content, wt.%	0.4635	0.4635	0.4707	0.3425
Wax Content, wt.%	0.15	0.27	0.27	17.20
Total Acid Number, wt.%	1.572	2.27	0.558	2.425
Molecular Type Composition				
Saturates Content, wt.%	56.70	51.82	58.20	60.33
n-paraffins Content, wt.%	21.96	37.90	34.47	41.80
Iso and Cyclo- paraffins Content,	34.74	13.92	23.73	18.53
Aromatics Content, wt.%	43.30	48.18	41.80	39.67
Mono-aromatics, wt.%	10.61	11.06	6.00	5.90
Di-aromatics, wt.%	19.35	21.92	18.30	24.27
Poly-aromatics, wt.%	13.34	15.20	17.50	9.50
Structural Group Analysis				
Carbon Distribution Analysis				
% C _A	10.47	15.73	15.83	8.62
% C _N	30.52	17.97	15.46	29.63
% C _R	40.99	33.70	31.29	38.25
% C _P	59.01	66.30	68.71	61.75
Ring Content Analysis				
R _A	0.64	0.91	0.96	0.46
R _T	3.14	2.31	2.23	2.52
R _N	2.50	1.40	1.27	2.06

Table 3.6: Effect of solvent type on the physical characteristics, molecular type composition and structural group analysis of de-waxed oils obtained using different solvents at de-waxing temperature of -10 °C and S/F for dilution and washing of 10:1 and 2:1, respectively.

Physical Characteristics	De-waxed Oils Obtained Using			
	MEK	MIBK	BA	MTBE
Yield on Sudanese Crude Oil, wt.%	16.81	29.14	36.00	68.19
Pour Point, °C	2	5	5	28
Density at 20°C	0.9100	0.8918	0.8927	0.8935
Density at 15.56°C	0.9108	0.8926	0.8935	0.8943
Specific Gravity at 15.56°C	0.9117	0.8935	0.8943	0.8952
API Gravity at 15.56°C	23.7	26.87	26.72	26.57
Refractive Index at 70 °C	1.4868	1.4739	1.4778	1.4720
Kinematic Viscosity at 40 °C, mm ² /s	57	26.79	36.98	56.50
Kinematic Viscosity at 100 °C,	8.25	5.15	6.50	7.57
Viscosity Index	115	124	129	95
Mean Molecular Weight	503	430	480	457
Sulfur Content, wt.%	0.5128	0.4256	0.4546	0.3243
Wax Content, wt.%	0.18	0.15	0.23	18.80
Total Acid Number, wt.%	1.498	3.36	0.644	1.825
Molecular Type Composition				
Saturates Content, wt.%	56.33	56.90	55.90	60.98
n-paraffins Content, wt.%	24.83	35.20	34.17	40.50
Iso and Cyclo- paraffins Content,	31.50	21.70	21.73	20.48
Aromatics Content, wt.%	43.67	43.10	44.10	39.02
Mono-aromatics, wt.%	11.50	9.53	10.60	7.60
Di-aromatics, wt.%	18.55	14.82	33.50	31.42
Poly-aromatics, wt.%	13.62	18.75	-----	-----
Structural Group Analysis				
Carbon Distribution Analysis				
% C _A	16.23	11.37	14.43	8.08
% C _N	21.55	26.86	18.83	32.21
% C _R	37.78	38.23	33.26	40.29
% C _P	62.22	61.77	66.74	59.71
Ring Content Analysis				
R _A	1.02	0.60	0.84	0.44
R _T	2.88	2.44	2.30	2.80
R _N	1.86	1.84	1.46	2.36

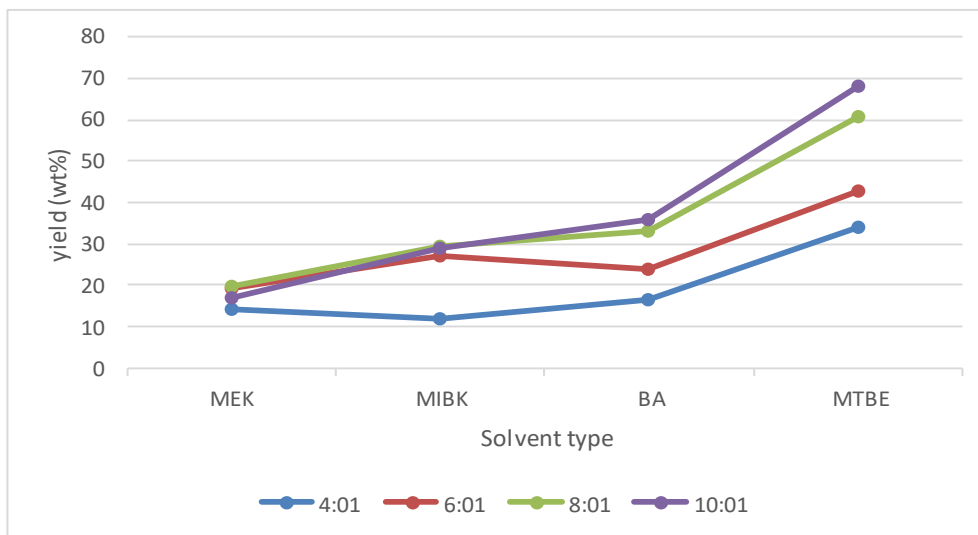


Fig 3.1: Relationship between solvent type and yield (A).

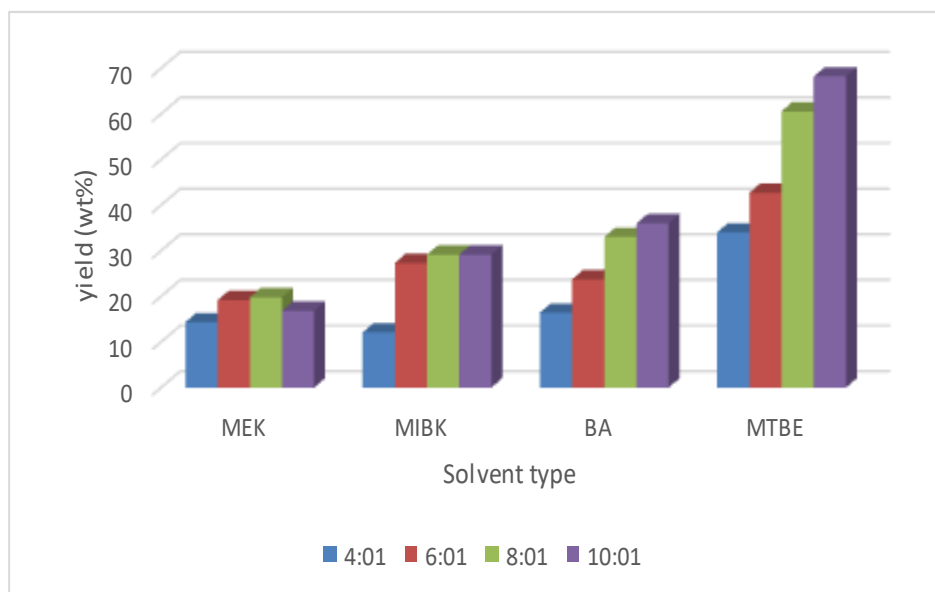


Fig 3.2: Relationship between solvent type and yield (B).

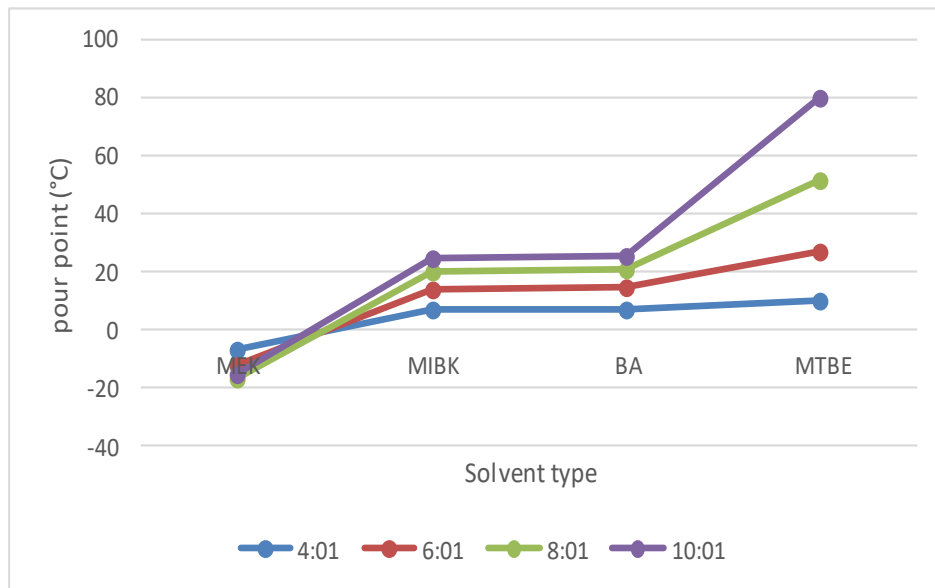


Fig 3.3: Relationship between solvent type and pour point (A).

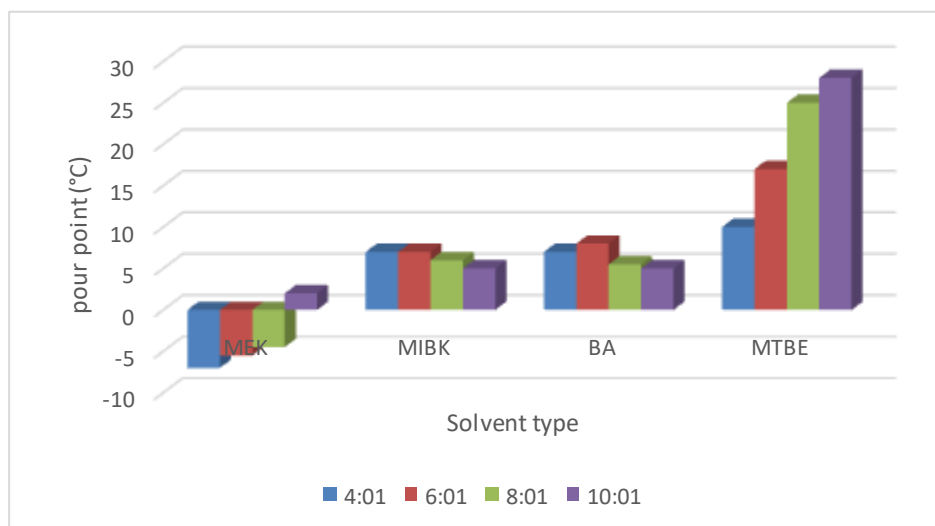


Fig 3.4: Relationship between solvent type and pour point (B).

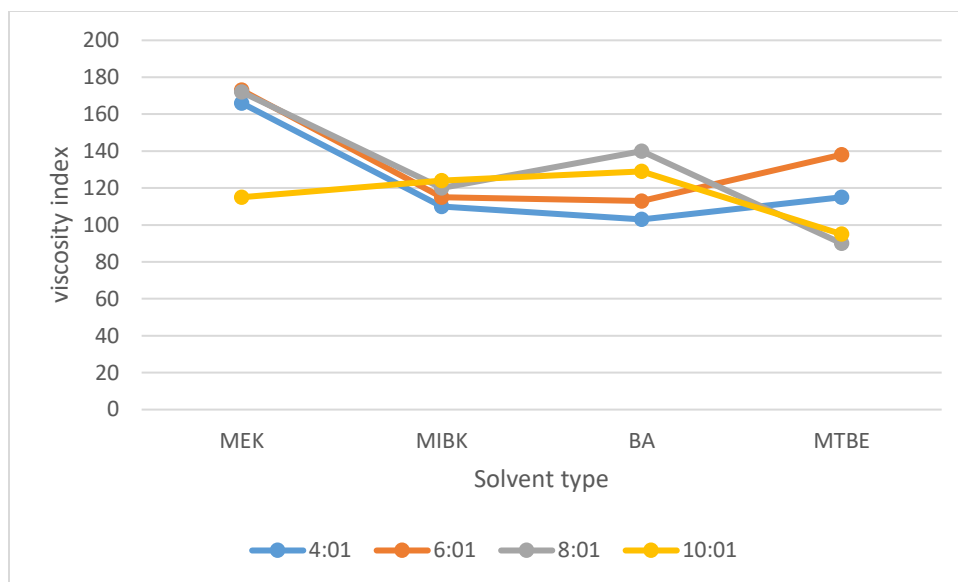


Fig 3.5: Relationship between solvent type and viscosity index (A).

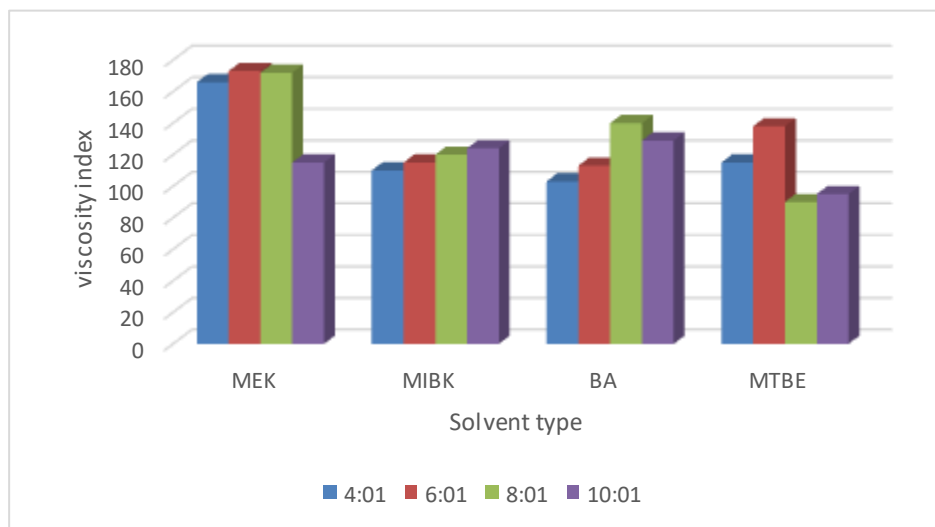


Fig 3.6: Relationship between solvent type and viscosity index (B).

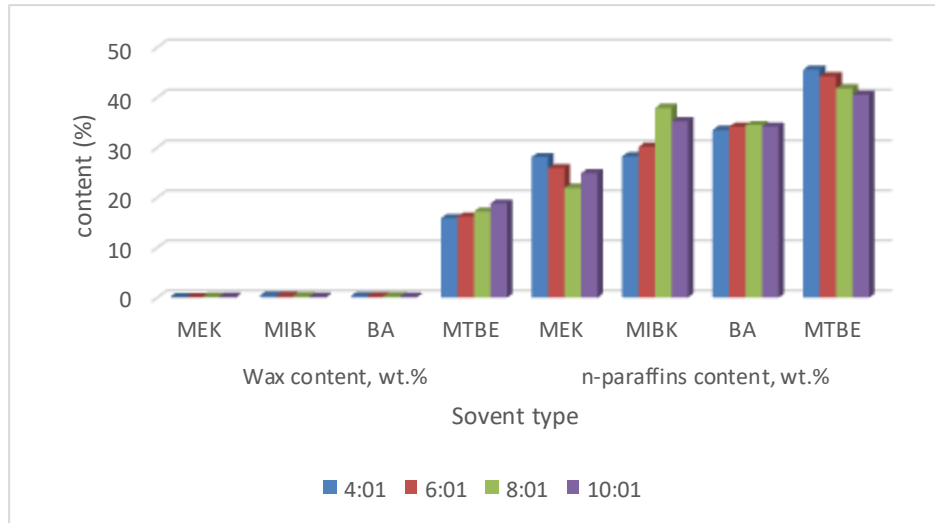


Fig 3.7: Relationship between solvent type and wax content and n-paraffin content (A).

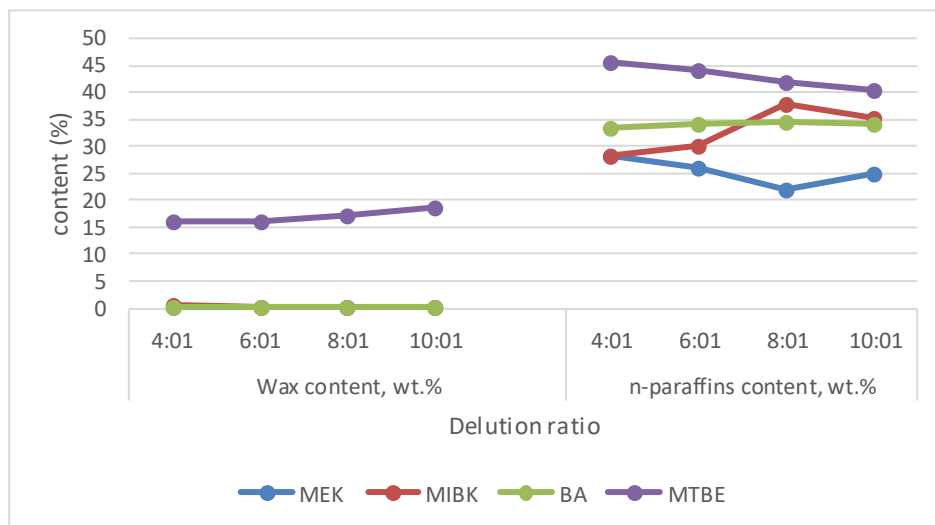


Fig 3.8: Relationship between solvent type and wax content and n-paraffin content (B).

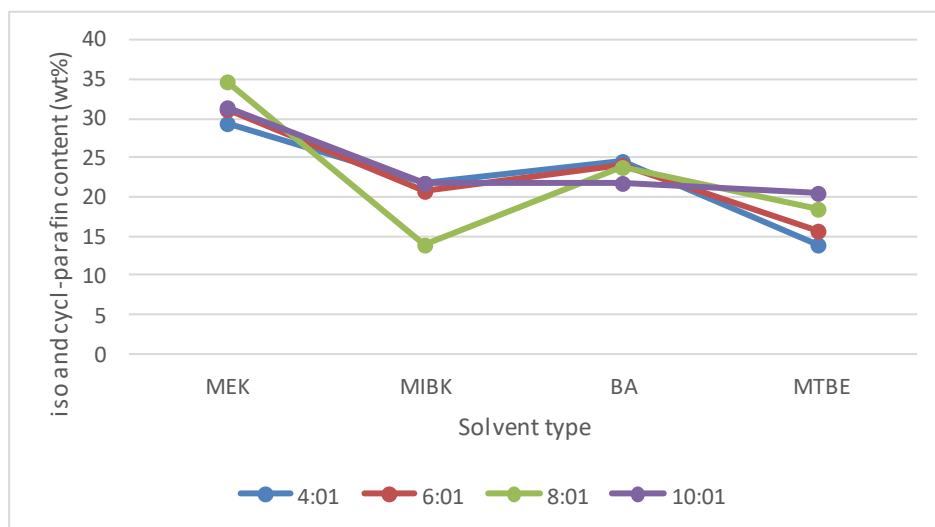


Fig 3.9: Relationship between solvent type and iso and cyclo-paraffin content (A).

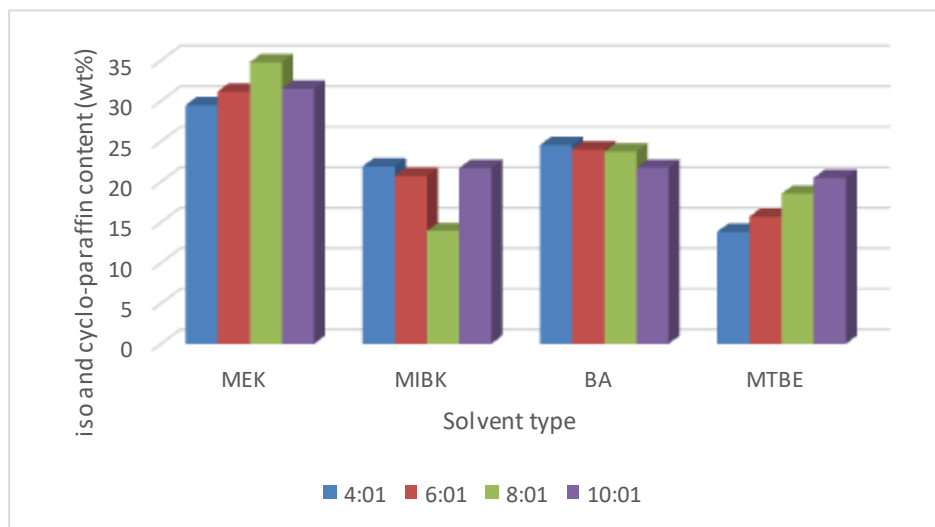


Fig 3.10: Relationship between solvent type and iso and cyclo-paraffin content (B).

The effect of solvent type is studied using different solvents as MEK, MIBK, BA and MTBE at de-waxing temperature of $-10\text{ }^{\circ}\text{C}$ and at different dilution solvent ratios ranging from 4:1 to 10:1 by weight (Tables 3.3 to 3.6).

— Data indicates that the yield of the de-waxed oils (Fig. 3.1 or 3.2) separated at all solvent to feed ratios increases in the following order:

MEK < MIBK < BA < MTBE

► MEK tends to precipitate the wax and at the same time has high solubility to low molecular weight oil, so it needs another solvent added to it (co-solvent such toluene) to increase its efficiency of solubility of the oil inherent to the wax crystals. But addition of toluene to MEK causes blocking of the crude sample through de-waxing process (i.e., it is difficult to separate the oil from the wax). This is due to the nature of the composition of crude oil obtained from Sudanese Rawat Company. Also, recovery of mixed solvents is not desirable due to the differentiation in their boiling points range and it's too hard to separate the two solvents upon making distillation and to be recovered for another de-waxing step.

► MIBK solvent is very expensive and tends to precipitate the wax and has mean solubility to oil, (i.e., it does the two operations at the same time), thus it gives mean yield of oil. Also, recovery of solvent is desirable because it is a single solvent.

► BA is a cheap solvent and also tends to precipitate the wax and has moderate solubility to oil, (i.e., it does the two operations at the same time), thus it gives

moderate yield of oil. Also, recovery of solvent is desirable because it is a single solvent.

▶ MTBE has moderate price but it is not selective solvent because it has high random solubility to each wax and low molecular weight oil, so it gives high yield.

Also, data indicate that the pour point of the de-waxed oils (Fig. 3.3 or 3.4) separated at all solvent to feed ratios decreases in the following order:

MTBE > MIBK \geq BA > MEK

▶ MEK solvent gives the separated de-waxed oil of the lowest pour point and consequently, the lowest wax and n-paraffin contents and the highest iso and cyclo-paraffins content (Fig. 3.7 & 3.9 or 3.10).

▶ MIBK and BA solvents give the separated de-waxed oil of mean pour points and consequently, the mean wax and n-paraffin contents and the mean iso and cyclo-paraffins content (Fig. 7 & 9 or 10).

3.3 Effect of Dilution Solvent Ratio:

Table 3.7: Effect of solvent dilution ratio on the physical characteristics, molecular type composition and structural group analysis of the de-waxed oils obtained by using MEK at de-waxing temperature of -10 °C and S/F for washing 2:1.

Physical Characteristics	S/F for Dilution Solvents			
	4:1	6:1	8:1	10:1
Yield on Sudanese Crude Oil, wt.%	14.29	19.14	19.75	16.81
Pour Point, °C	- 7	- 5.5	- 4.5	2
Density at 20°C	0.8883	0.8959	0.9055	0.9100
Density at 15.56°C	0.8892	0.8967	0.9063	0.9108
Specific Gravity at 15.56°C	0.8901	0.8976	0.9072	0.9117
API Gravity at 15.56°C	27.47	26.15	24.47	23.70
Refractive Index at 70 °C	1.4779	1.4784	1.4796	1.4868
Kinematic Viscosity at 40 °C, mm ² /s	25.00	26.00	27.00	57.00
Kinematic Viscosity at 100 °C, mm ² /s	5.50	5.75	5.90	8.25
Viscosity Index	166	173	172	115
Mean Molecular Weight	478	495	498	503
Sulfur Content, wt.%	0.4666	0.4621	0.4635	0.5128
Wax Content, wt.%	0.05	0.10	0.15	0.18
Total Acid Number, wt.%	1.775	1.692	1.572	1.498
Molecular Type Composition				
Saturates Content, wt.%	57.52	57.03	56.70	56.33
n-paraffins Content, wt.%	28.09	25.90	21.96	24.83
Iso and cyclo- paraffins Content, wt.%	29.43	31.13	34.74	31.50
Aromatics Content, wt.%	42.48	42.97	43.30	43.67
Mono-aromatics, wt.%	11.90	11.31	10.61	11.50
Di-aromatics, wt.%	18.07	18.50	19.35	18.55
Poly-aromatics, wt.%	12.51	13.16	13.34	13.62
Structural Group Analysis				
Carbon Distribution Analysis				
% C _A	16.33	13.34	10.47	16.23
% C _N	12.93	21.00	30.52	21.55
% C _R	29.26	34.34	40.99	37.78
% C _P	70.74	65.66	59.01	62.22
Ring Content Analysis				
R _A	0.97	0.82	0.64	1.02
R _T	2.00	2.53	3.14	2.88
R _N	1.03	1.71	2.50	1.86

Table 3.8: Effect of solvent dilution ratio on the physical characteristics, molecular type composition and structural group analysis of de-waxed oils obtained using MIBK at de-waxing temperature of -10 °C and S/F for washing 2:1.

Physical Characteristics	S/F for Dilution Solvents			
	4:1	6:1	8:1	10:1
Yield on Sudanese Crude Oil, wt.%	12.09	27.30	29.17	29.14
Pour Point, °C	7	7	6	5
Density at 20°C	0.9300	0.9134	0.8956	0.8918
Density at 15.56°C	0.9308	0.9142	0.8964	0.8926
Specific Gravity at 15.56°C	0.9317	0.9150	0.8973	0.8935
API Gravity at 15.56°C	20.37	23.14	26.20	26.87
Refractive Index at 70 °C	1.4934	1.4853	1.4801	1.4739
Kinematic Viscosity at 40 °C, mm ² /s	100	61.54	39.67	26.79
Kinematic Viscosity at 100 °C, mm ² /s	12.00	8.70	6.60	5.15
Viscosity Index	110	115	120	124
Mean Molecular Weight	576	507	468	430
Sulfur Content, wt.%	0.5506	0.5068	0.4635	0.4256
Wax Content, wt.%	0.4	0.35	0.27	0.15
Total Acid Number, wt.%	0.931	1.20	2.27	3.36
Molecular Type Composition				
Saturates Content, wt.%	50.11	50.83	51.82	56.90
n-paraffins Content, wt.%	28.22	30.10	37.90	35.20
Iso and cyclo- paraffins Content, wt.%	21.89	20.73	13.92	21.70
Aromatics Content, wt.%	49.89	49.17	48.18	43.10
Mono-aromatics, wt.%	14.20	13.94	11.06	9.53
Di-aromatics, wt.%	23.99	22.69	21.92	14.82
Poly-aromatics, wt.%	11.70	12.54	15.20	18.75
Structural Group Analysis				
Carbon Distribution Analysis				
% C _A	13.83	13.09	15.73	11.37
% C _N	31.71	28.70	17.97	26.86
% C _R	45.54	41.79	33.70	38.23
% C _P	54.46	58.21	66.30	61.77
Ring Content Analysis				
R _A	0.99	0.82	0.91	0.60
R _T	4.16	3.27	2.31	2.44
R _N	3.17	2.45	1.40	1.84

Table 3.9: Effect of solvent dilution ratio on the physical characteristics, molecular type composition and structural group analysis of de-waxed oils obtained using butyl acetate at de-waxing temperature of -10 °C and S/F for washing 2:1.

Physical Characteristics	S/F for Dilution Solvents			
	4:1	6:1	8:1	10:1
Yield on Sudanese Crude Oil, wt.%	16.40	23.71	33.00	36.0
Pour Point, °C	7	8	5.5	5
Density at 20°C	0.9155	0.9031	0.8933	0.8927
Density at 15.56°C	0.9163	0.9039	0.8941	0.8935
Specific Gravity at 15.56°C	0.9172	0.9048	0.8950	0.8943
API Gravity at 15.56°C	22.77	24.90	26.61	26.72
Refractive Index at 70 °C	1.4919	1.4853	1.4796	1.4778
Kinematic Viscosity at 40 °C, mm ² /s	123.00	65.18	40.06	36.98
Kinematic Viscosity at 100 °C, mm ² /s	13.30	9.00	7.10	6.50
Viscosity Index	103	113	140	129
Mean Molecular Weight	584	521	490	480
Sulfur Content, wt.%	0.5563	0.4432	0.4707	0.4546
Wax Content, wt.%	0.3	0.29	0.27	0.23
Total Acid Number, wt.%	1.6317	0.561	0.558	0.644
Molecular Type Composition				
Saturates Content, wt.%	58.01	58.12	58.20	55.90
n-paraffins Content, wt.%	33.50	34.12	34.47	34.17
Iso and cyclo- paraffins Content, wt.%	24.51	24.00	23.73	21.73
Aromatics Content, wt.%	41.99	41.88	41.80	44.10
Mono-aromatics, wt.%	11.50	9.92	6.00	10.60
Di-aromatics, wt.%	14.89	15.44	18.30	33.50
Poly-aromatics, wt.%	15.60	16.52	17.50	-----
Structural Group Analysis				
Carbon Distribution Analysis				
% C _A	18.36	17.32	15.83	14.43
% C _N	16.40	15.57	15.46	18.83
% C _R	34.76	32.89	31.29	33.26
% C _P	65.24	67.11	68.71	66.74
Ring Content Analysis				
R _A	1.34	1.12	0.96	0.84
R _T	3.10	2.55	2.23	2.30
R _N	1.76	1.43	1.27	1.46

Table 3.10: Effect of solvent dilution ratio on the physical characteristics, molecular type composition and structural group analysis of de-waxed oils obtained using MTBE at de-waxing temperature of -10°C and S/F for washing 2:1.

Physical Characteristics	S/F for Dilution Solvents			
	4:1	6:1	8:1	10:1
Yield on Sudanese Crude Oil, wt.%	33.99	42.67	60.55	68.19
Pour Point, °C	10	17	25	28
Density at 20°C	0.8782	0.8805	0.8879	0.8935
Density at 15.56°C	0.8790	0.8813	0.8887	0.8943
Specific Gravity at 15.56°C	0.8798	0.8821	0.8896	0.8952
API Gravity at 15.56°C	29.33	28.91	26.93	26.57
Refractive Index at 70 °C	1.4703	1.4690	1.4700	1.4720
Kinematic Viscosity at 40 °C, mm ² /s	25.62	26.39	55.00	56.50
Kinematic Viscosity at 100 °C, mm ² /s	4.90	5.30	7.00	7.57
Viscosity Index	115	138	90	95
Mean Molecular Weight	406	436	441	457
Sulfur Content, wt.%	0.3926	0.3846	0.3425	0.3243
Wax Content, wt.%	15.90	16.20	17.20	18.80
Total Acid Number, wt.%	0.2950	0.3232	2.425	1.825
Molecular Type Composition				
Saturates Content, wt.%	59.37	59.88	60.33	60.98
n-paraffins Content, wt.%	45.55	44.20	41.80	40.50
Iso and cyclo- paraffins Content, wt.%	13.82	15.68	18.53	20.48
Aromatics Content, wt.%	40.63	40.12	39.67	39.02
Mono-aromatics, wt.%	3.93	4.50	5.90	7.60
Di-aromatics, wt.%	20.47	22.40	24.27	31.42
Poly-aromatics, wt.%	16.23	13.22	9.50	-----
Structural Group Analysis				
Carbon Distribution Analysis				
% C _A	13.83	10.82	8.62	8.08
% C _N	18.00	22.41	29.63	32.21
% C _R	31.83	33.23	38.25	40.29
% C _P	68.17	66.77	61.75	59.71
Ring Content Analysis				
R _A	0.69	0.58	0.46	0.44
R _T	1.82	2.10	2.52	2.80
R _N	1.13	1.52	2.06	2.36

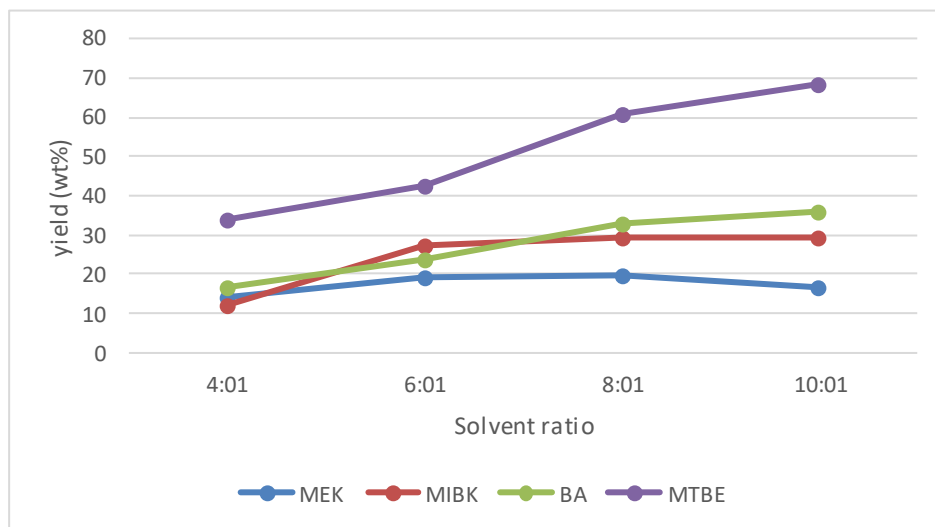


Fig 3.11: Relationship between solvent ratio and yield (A).

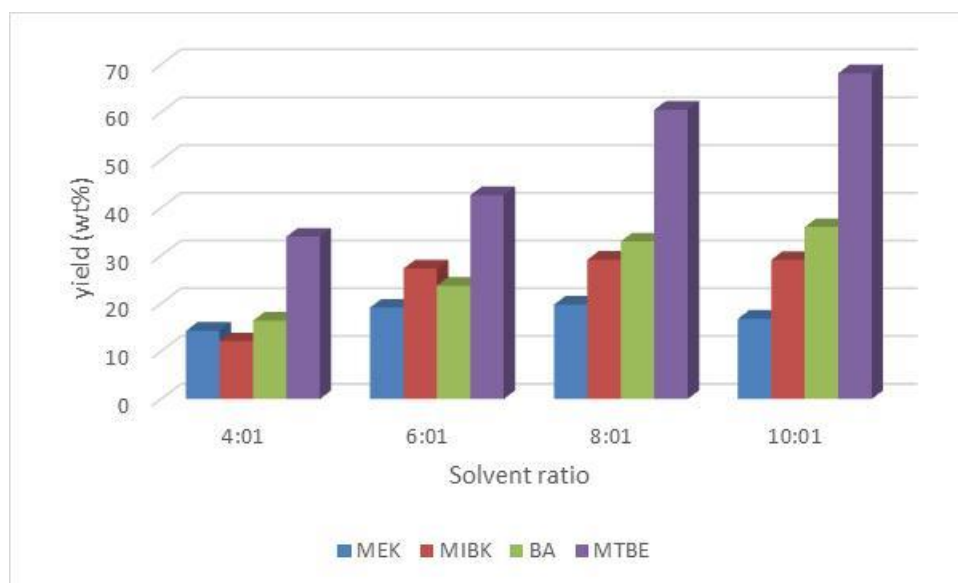


Fig 3.12: Relationship between solvent ratio and yield (B).

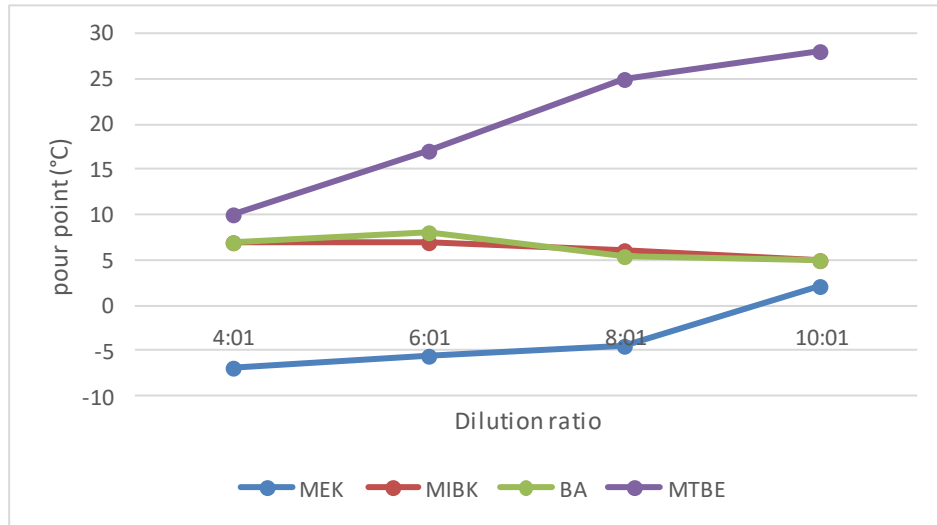


Fig 3.13: Relationship between dilution ratio and pour point (A).

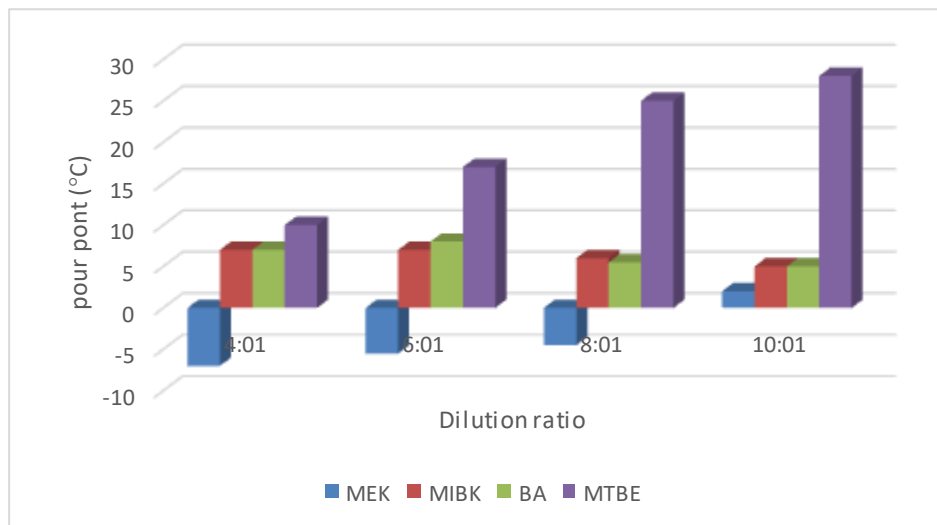


Fig 3.14: Relationship between dilution ratio and pour point (B).

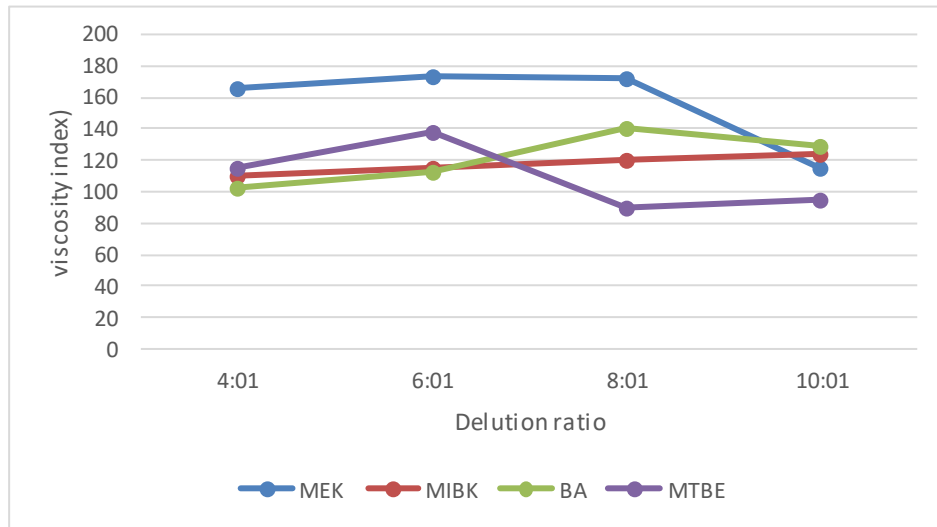


Fig 3.15: Relationship between dilution ratio and viscosity index (A).

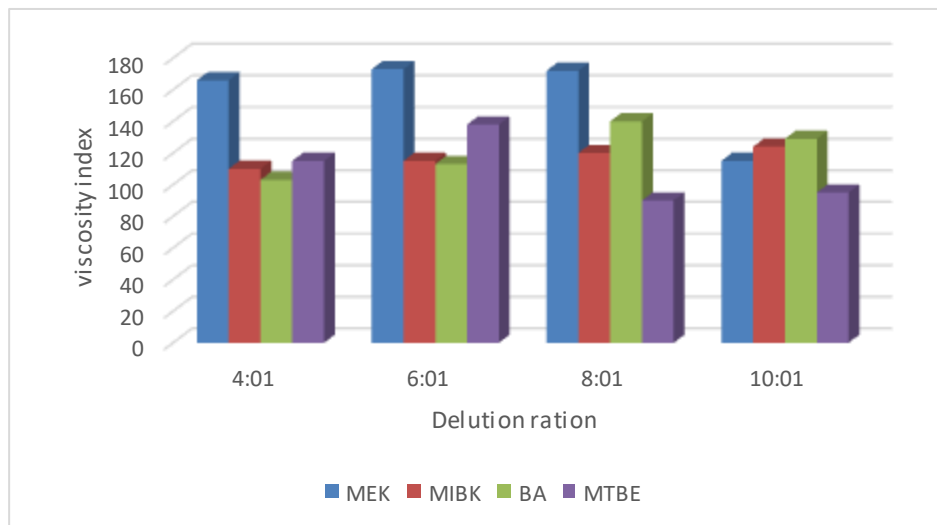


Fig 3.16: Relationship between dilution ratio and viscosity index (B).

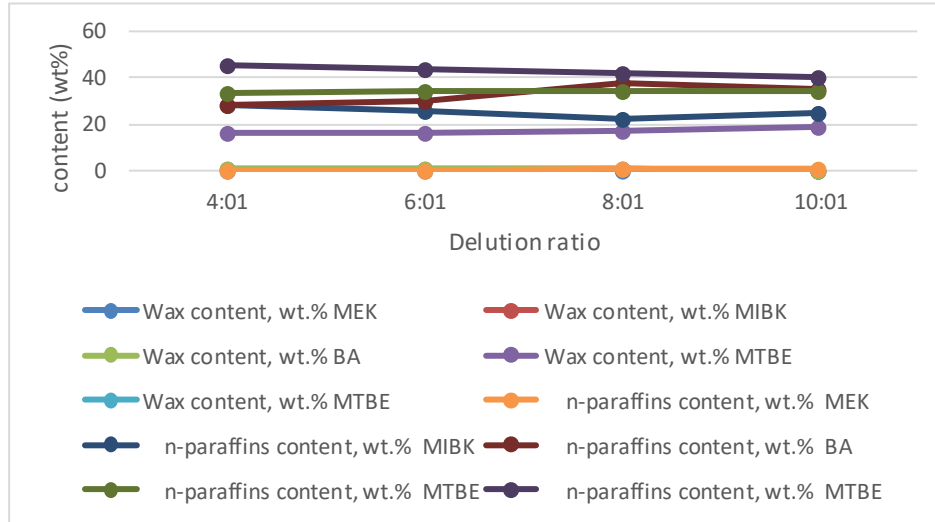


Fig 3.17: Relationship between dilution ratio and wax content and n-paraffin content (A).

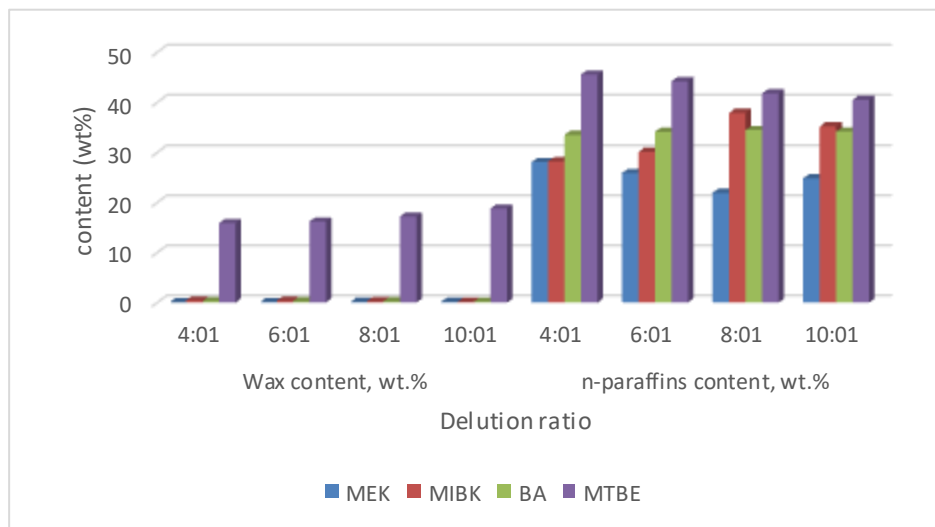


Fig 3.18: Relationship between dilution ratio and wax content and n-paraffin content (B).

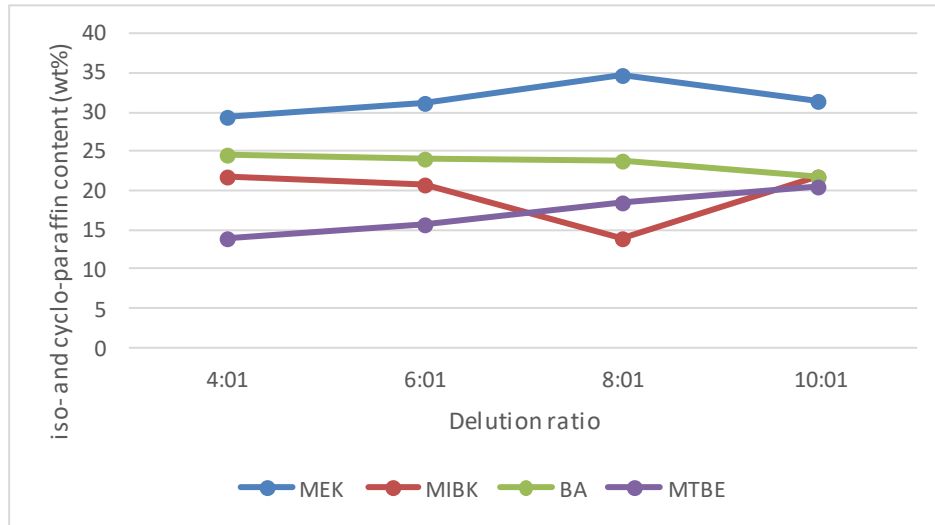


Fig 3.19: Relationship between dilution ratio and iso and cyclo-paraffin content (A).

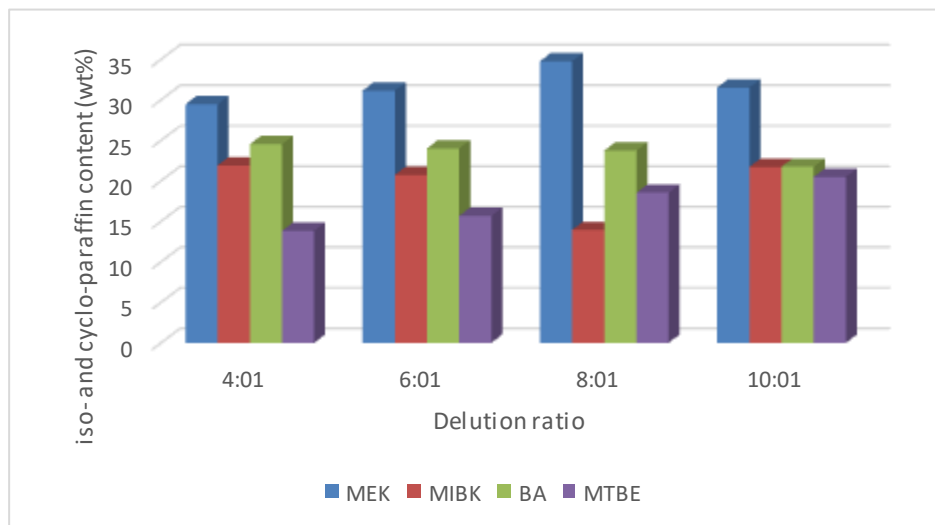


Fig 3.20: Relationship between dilution ratio and iso and cyclo paraffin content (B).

The rate of filtration of the de-waxed oil increases with dilution. The amount of solvent used in de-waxing technique have an obvious effect upon the yield, quality molecular type composition and structural group analysis of the de-waxed oils isolated from Sudanese crude oil by using **MEK** and **MTBE** solvents at de-waxing temperature of -10°C (Table 3.7 & 3.10). Data indicate that, the yield of the separated de-waxed oil increases with increasing of dilution solvent ratio from 4/1 to 8/1 (Fig. 3.11 or 3.12). But, further increase in dilution solvent ratio to 10/1, the yield of the separated de-waxed oil decreases by using MEK solvent and still increases by using MTBE solvent. This may be attributed to that MEK firstly dissolves the oil and precipitates the wax at the same time and with further increase in dilution solvent ratio it starts to precipitate the wax only. While, MTBE has the highest solvent power so it randomly dissolves the oil and the wax with the highest yields at the same time. Although, the increase of dilution solvent ratio by using the two solvents is accompanied with the improvement of lubricating oil characteristics in terms of increasing the mean molecular weight, density, refractive index, viscosity and viscosity index (Fig. 3.15 or 3.16) for the de-waxed oils as a result of their decreased saturated content specially n-paraffin content (Fig. 3.17 or 3.18) and consequently their increased iso- and cyclo-paraffin content (Fig. 3.19 or 3.20) by using MEK and their lower increase in saturated content specially iso- and cyclo-paraffin content and decrease in n-paraffin content by using MTBE solvent. This may be attributed to the increase of solvent power towards the high molecular weight iso and cyclo-paraffins present in Sudanese crude oil by using the two solvents. Data of structural group analysis are parallel to the previous results whereas, % C_P decrease and % C_N and R_N increase as the dilution solvent ratio increases from 4/1 to 8/1 by using MEK and from 4/1 to 10/1 by using MTBE.

Also, it is obvious that by using MEK and MTBE solvents, the increase of dilution solvent ratio from 4/1 to 10/1 increases the de-waxing temperature differential (i.e., increases the pour point from -7 to 2°C by using MEK solvent and from 10 to 28°C by using MTBE solvent): the spread between de-waxing temperature and the pour point of the de-waxed oil: by 3 to 12°C using MEK and by 20 to 38°C by using MTBE, respectively higher than the de-waxing temperature (-10°C). Data of wax content are parallel to the previous results whereas, wax content increases from 0.05 to 0.18% by using MEK and from 15.90 to 18.80% by using MTBE solvent with increasing of solvent ratio from 4/1 to 10/1. This means that MTBE gives the highest de-waxing temperature differential and wax content, i.e., it is not suitable for de-waxing of Sudanese crude oil.

Otherwise, by using **MIBK** and **BA** solvents, the yield of the separated de-waxed oil increases with increasing of dilution solvent ratio from 4/1 to 10/1. The results can be justified by the fact that the high solvent ratio result in a greater reduction of the mixture's viscosity and the solvent itself enhances the formation and growth of wax crystals, which in turn, resulted in an improved filtration performance. More so, the greater ratio of solvent to oil molecules which have a greater solubility preference for the oil than the wax serves to improve the de-waxing performance, i.e., decreases the pour point of the de-waxed oil with increasing the solvent ratio from 4/1 to 10/1. Data of wax content are parallel to the previous results whereas, the wax content decreases as the solvent ratio increases. Although, the increase of dilution solvent ratio by using the two solvents is accompanied with the improvement of lubricating oil quality in terms of decreasing the mean molecular weight, density, refractive index, viscosity, and increasing viscosity index for the de-waxed oils as a result of their increased saturated content specially n-paraffin content and consequently their decreased iso- and cyclo-paraffin content by using MIBK and BA. This may be

attributed to the increase of solvent power towards the low molecular weight n-paraffins present in Sudanese crude oil by using the two solvents. Data of structural group analysis are parallel to the previous results whereas, % C_P increases and % C_N and R_N decrease as the dilution solvent ratio increases from 4/1 to 10/1.

More specifically, it appears that when a high solvent to oil ratio (S/F = 10/1 by weight) is used and a higher yield of oil is achieved due to the increase of the solubility of the solvent. Thus, it can be concluded that, BA solvent is selected as the suitable solvent for de-waxing Sudanese crude oil at dilution solvent ratio of 10/1 by weight and at de-waxing temperature of -10°C.

3.4 Effect of de-waxing temperature:

Table 3.11: Effect of de-waxing temperature on the physical characteristics, molecular type composition and structural group analysis of de-waxed oils obtained using butyl acetate at S/F for dilution and washing of 10/1 and 2:1, respectively.

Physical Characteristics	De-waxing Temperatures, °C			
	-5	-10	-15	-20
Yield on Sudanese Crude Oil, wt.%	28.17	36.0	26.08	22.61
Pour Point, °C	6.5	5	3	-6.5
Density at 20°C	0.8902	0.8927	0.8964	0.8975
Density at 15.56°C	0.8910	0.8935	0.8972	0.8983
Specific Gravity at 15.56°C	0.8919	0.8943	0.8981	0.8992
API Gravity at 15.56°C	27.16	26.72	26.05	25.87
Refractive Index at 70 °C	1.4757	1.4778	1.4813	1.4774
Kinematic Viscosity at 40 °C, mm ² /s	32.83	36.98	45.67	31.59
Kinematic Viscosity at 100 °C, mm ² /s	6.20	6.50	7.20	5.50
Viscosity Index	140	129	118	111
Mean Molecular Weight	478	480	500	432
Sulfur Content, wt.%	0.4363	0.4546	0.4787	0.4538
Wax Content, wt.%	0.17	0.23	0.38	0.51
Total Acid Number, wt.%	0.51	0.644	0.602	1.573

Molecular Type Composition				
Saturates Content, wt.%	56.01	55.90	54.55	55.99
n-paraffins Content, wt.%	34.50	34.17	33.18	33.07
Iso and Cyclo- paraffins Content,	21.51	21.73	21.27	22.92
Aromatics Content, wt.%	43.99	44.10	45.45	44.01
Mono-aromatics, wt.%	10.44	10.60	10.77	10.98
Di-aromatics, wt.%	33.55	33.50	28.50	21.41
Poly-aromatics, wt.%	-----	-----	6.18	11.62
Structural Group Analysis				
Carbon Distribution Analysis				
% C _A	13.14	14.43	16.18	12.65
% C _N	19.77	18.83	15.67	26.88
% C _R	32.91	33.26	31.85	39.53
% C _P	67.09	66.74	68.15	60.47
Ring Content Analysis				
R _A	0.78	0.84	1.01	0.67
R _T	2.31	2.30	2.34	2.55
R _N	1.53	1.46	1.33	1.88

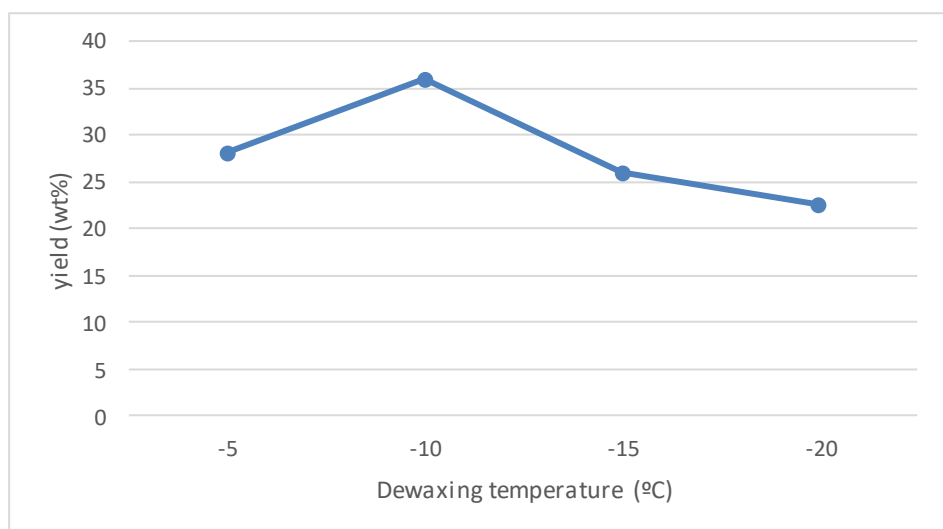


Fig 3.21: Relationship between de-waxing temperature and yield (A).

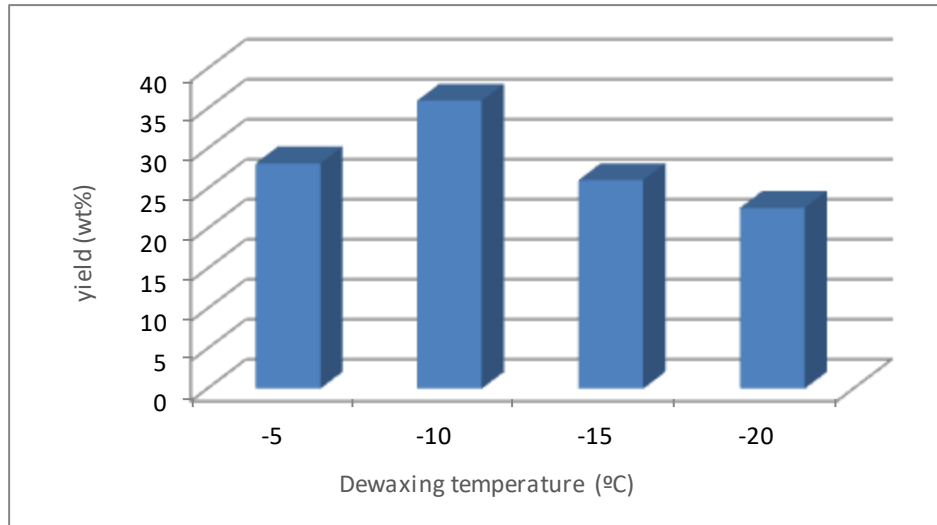


Fig 3.22: Relationship between de-waxing temperature and yield (B).

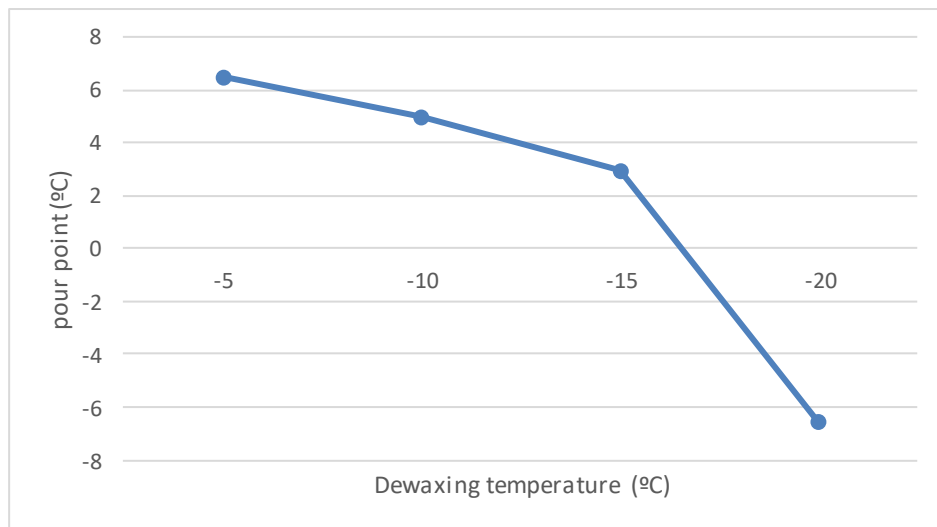


Fig 3.23: Relationship between de-waxing temperature and pour point (A).

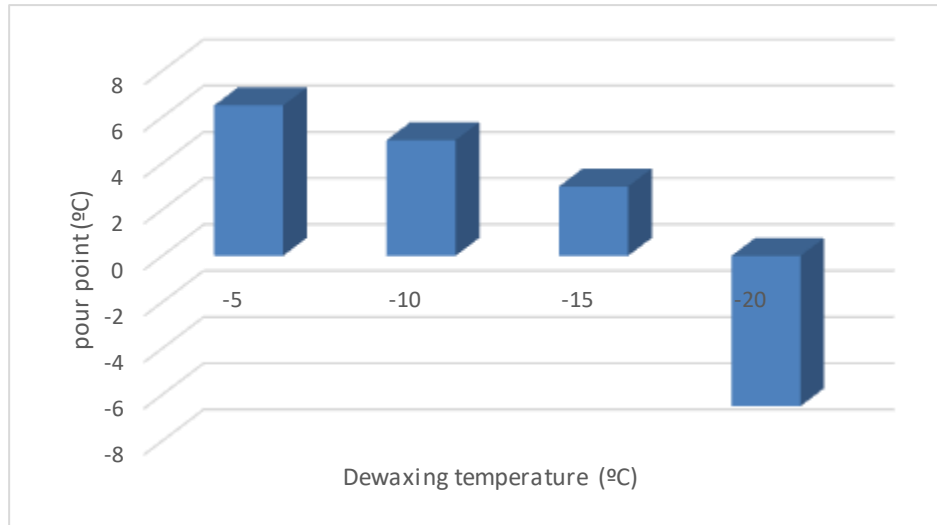


Fig 3.24: Relationship between de-waxing temperature and pour point (B).

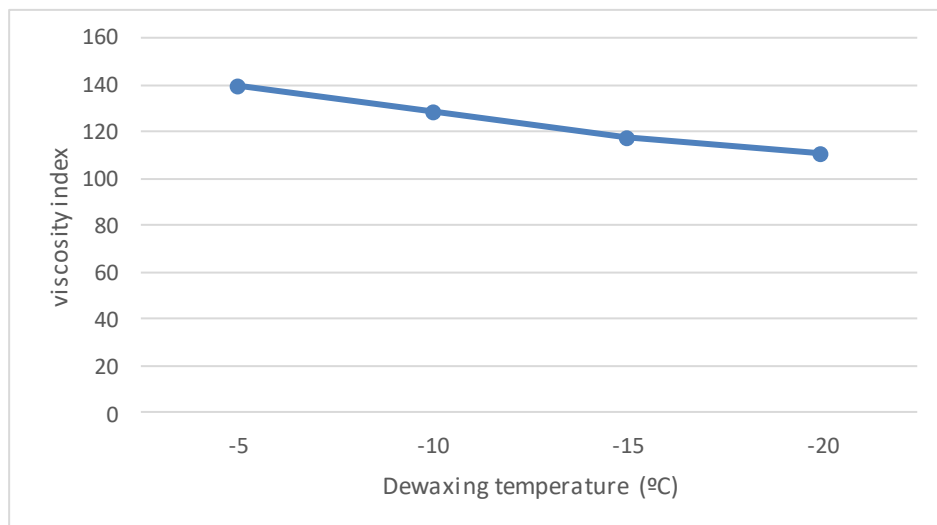


Fig 3.25: Relationship between de-waxing temperature and viscosity index (A).

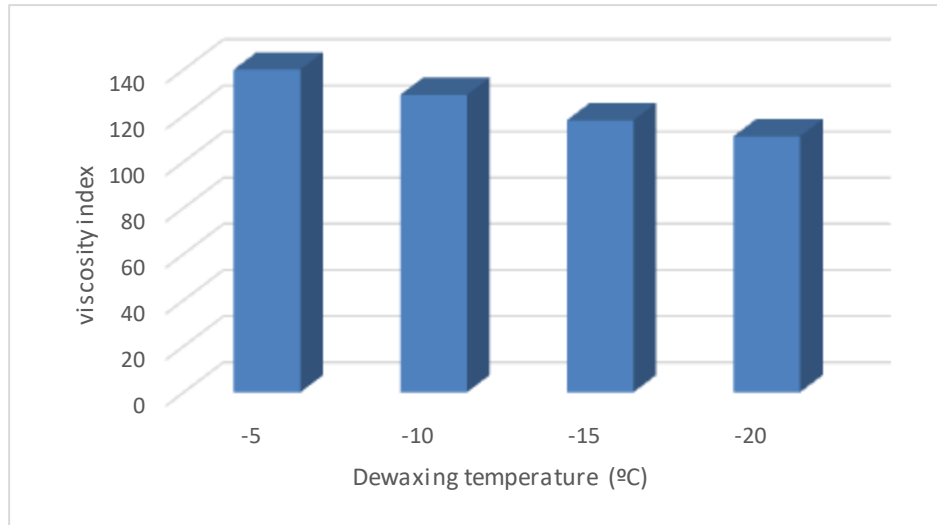


Fig 3.26: Relationship between de-waxing temperature and viscosity index (B).

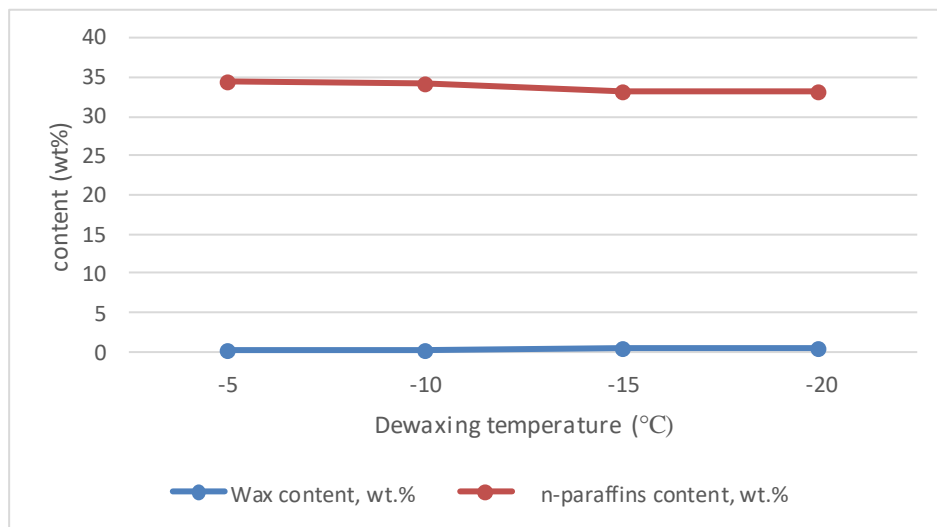


Fig 3.27: Relationship between de-waxing temperature and wax content and n-paraffin content (A).

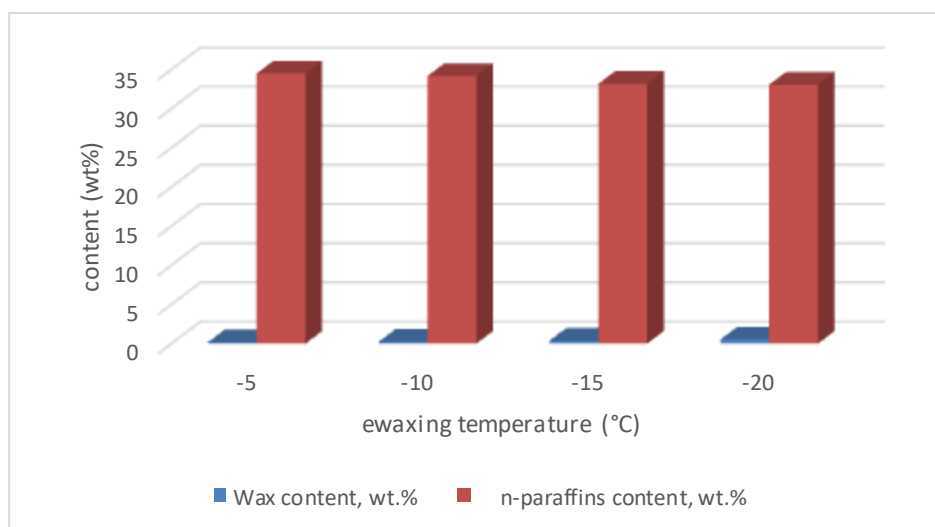


Fig 3.28: Relationship between de-waxing temperature and wax content and n-paraffin content (B).

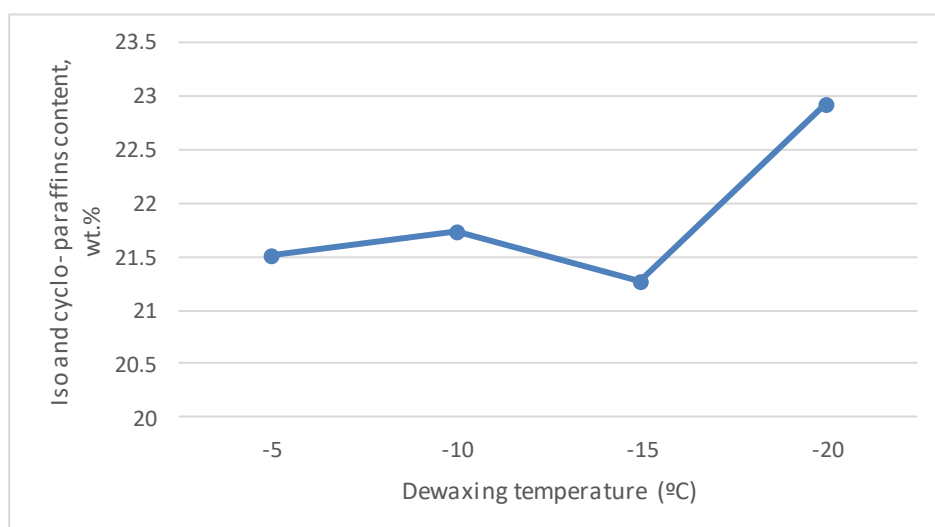


Fig 3.29: Relationship between de-waxing temperature and iso and cyclo-paraffin content (A).

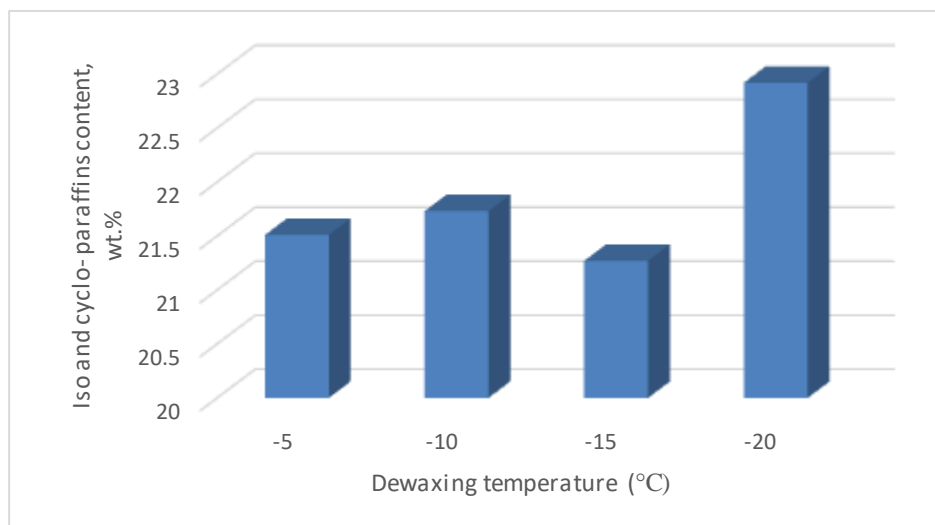


Fig 3.30: Relationship between de-waxing temperature and iso and cyclo-paraffin content (B).

Lowering the de-waxing temperature from -5 to -15 °C decreases the yield (Fig. 3.21 or 3.22) and viscosity index (Fig. 3.25 or 3.26) and increases density, refractive index, kinematic viscosity and mean molecular weight of the de-waxed oils while a considerable improvement in the pour point (Fig. 3.23 or 3.24) is achieved (Table 3.11). Also, data of molecular type composition indicate that decreasing the de-waxing temperature leads to increase the aromatic and sulfur contents of the de-waxed oils. Data of structural group analysis are parallel to the previous results as the percentage of aromatic carbon ($\%C_A$) and aromatic ring (R_A) increase. Moreover, further decrease of de-waxing temperature from -15 to -20 °C, the yield and viscosity index still decrease and the density is slightly increased and a valuable improvement in the pour point is achieved. While, refractive index, kinematic viscosity and mean molecular weight of the de-waxed oils are decreased. Also, data of molecular type composition indicate that decreasing the de-waxing temperature from -15 to -20 °C, leads to decrease the aromatic and sulfur contents of the de-waxed oils. Data of

structural group analysis are parallel to the previous results as the percentage of aromatic carbon ($\%C_A$) and aromatic ring (R_A) decrease. This results may be due to that as more lowering the de-waxing temperature till to reach to -20°C , most of the oil becomes inherent to the wax crystals and the solvent couldn't able to dissolve and all the oil except the low molecular weight oil fractions which causes the decrease in mean molecular weight, refractive index, viscosity and aromatic content.

The efficiency of the de-waxing process is measured by the de-waxing temperature differential. The low value of de-waxing temperature differential means that the process is became more economic from the industrial point of view. The pour points of the de-waxed oils are 11.5 , 15 , 18 and 13.5°C higher than the corresponding de-waxing temperatures (-5 , -10 , -15 and -20°C , respectively). But unfortunately, the obtained yields of the de-waxed oils separated at -5 and -20°C are lower than that separated at -10°C .

3.5 Effect of Crystallization Time:

Table 3.12: Effect of crystallization time on the physical characteristics, molecular type composition and structural group analysis of de-waxed oils obtained using butyl acetate at de-waxing temperature of -10 °C and S/F for dilution and washing 10/1 and 2:1 respectively.

Physical Characteristics	Crystallization Time, h		
	6	12	24
Yield on Sudanese Crude Oil, wt.%	36.22	36.10	36.0
Pour Point, °C	14.5	9.5	5
Density at 20°C	0.8891	0.8909	0.8927
Density at 15.56°C	0.8899	0.8917	0.8935
Specific Gravity at 15.56°C	0.8908	0.8926	0.8943
API Gravity at 15.56°C	27.35	27.04	26.72
Refractive Index at 70 °C	1.4769	1.4774	1.4778
Kinematic Viscosity at 40 °C, mm ² /s	40.49	38.73	36.98
Kinematic Viscosity at 100 °C, mm ² /s	6.80	6.61	6.50
Viscosity Index	125	127	129
Mean Molecular Weight	490	481	480
Sulfur Content, wt.%	0.4313	0.4430	0.4546
Wax Content, wt.%	0.74	0.48	0.23
Total Acid Number, wt.%	0.442	0.553	0.644
Molecular Type Composition			
Saturates Content, wt.%	57.98	56.93	55.90
n-paraffins Content, wt.%	24.20	29.05	34.17
Iso and Cyclo- paraffins Content, wt.%	33.78	27.88	21.73
Aromatics Content, wt.%	42.02	43.07	44.10
Mono-aromatics, wt.%	7.92	9.25	10.60
Di-aromatics, wt.%	34.10	33.82	33.50
Poly-aromatics, wt.%	-----	-----	-----
Structural Group Analysis			
Carbon Distribution Analysis			
% C _A	14.72	14.59	14.43
% C _N	15.70	16.81	18.83
% C _R	30.42	31.40	33.26
% C _P	69.58	68.60	66.74
Ring content analysis			
R _A	0.89	0.87	0.84
R _T	2.16	2.23	2.30
R _N	1.27	1.36	1.46

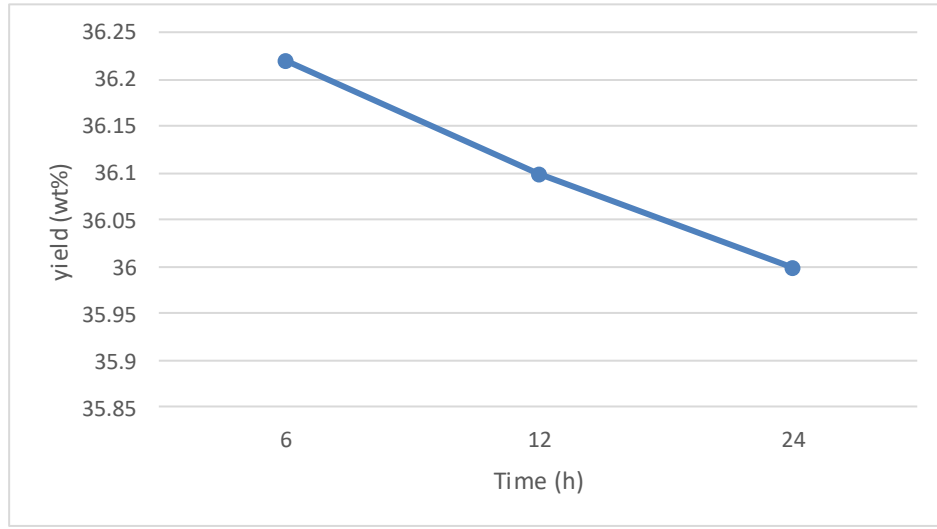


Fig 3.31: Crystallization time vs. yield (A).

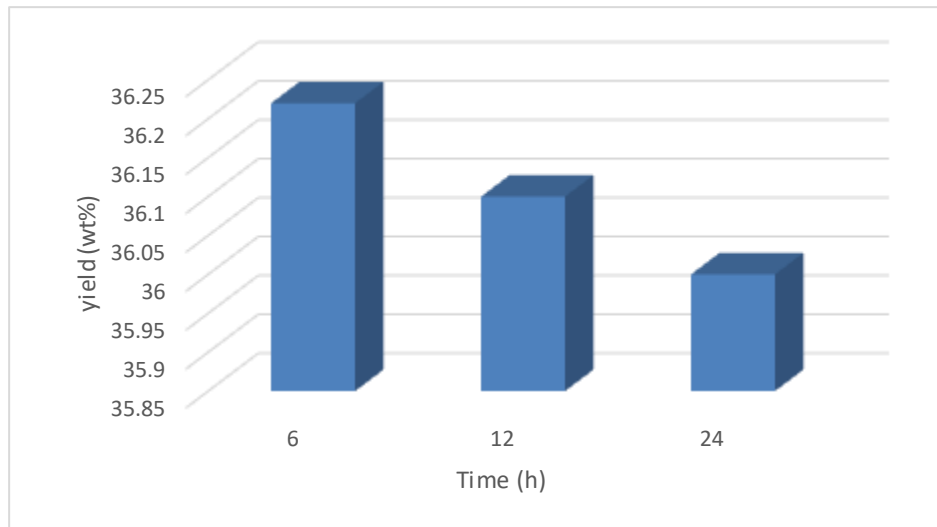


Fig 3.32: Crystallization time vs. yield (B).

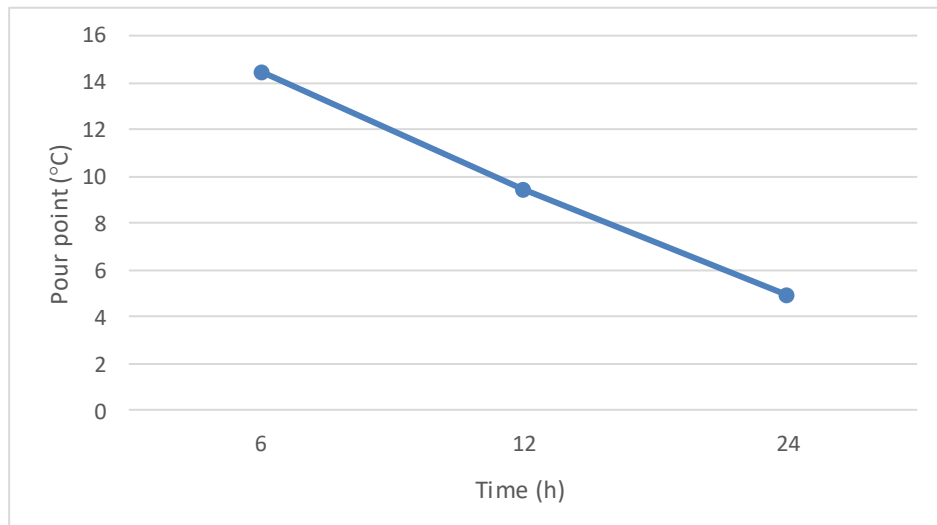


Fig 3.33: Crystallization time vs. pour point (A).

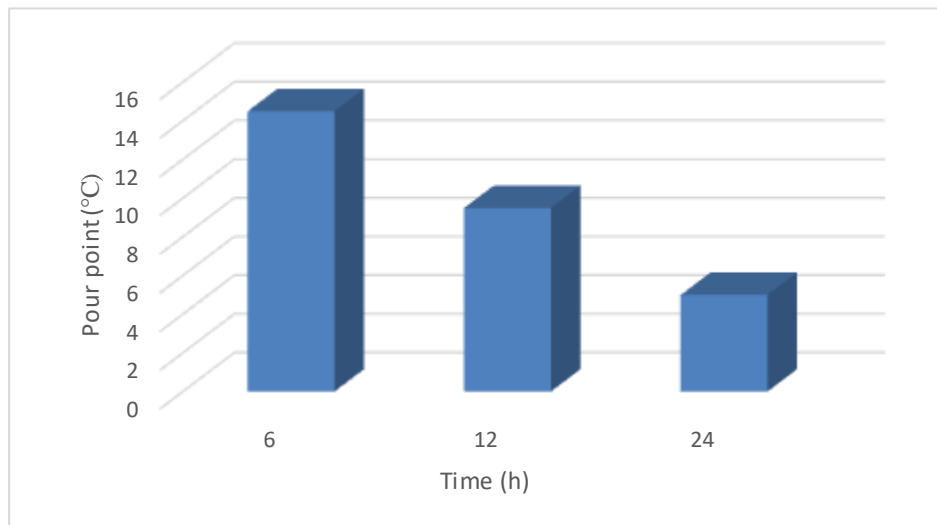


Fig 3.34: Crystallization time vs. pour point (B).

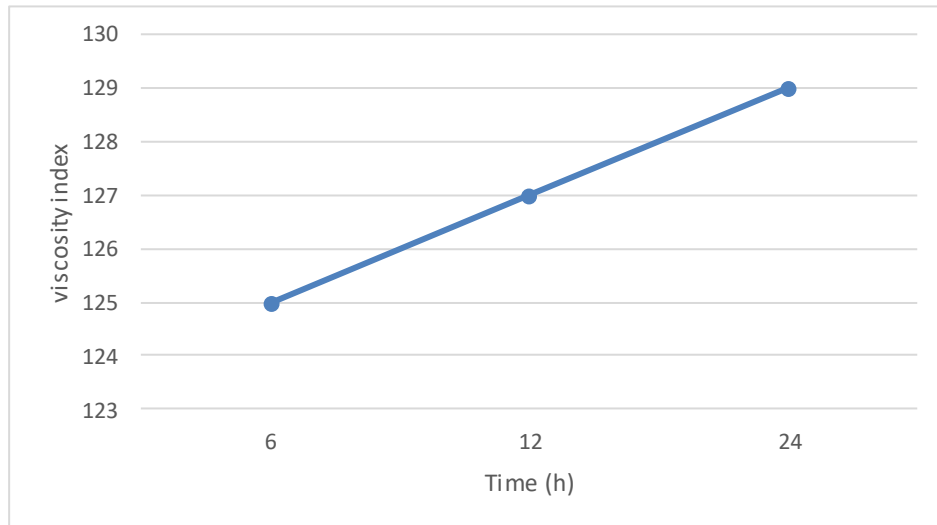


Fig 3.35: Crystallization time vs. viscosity index (A).

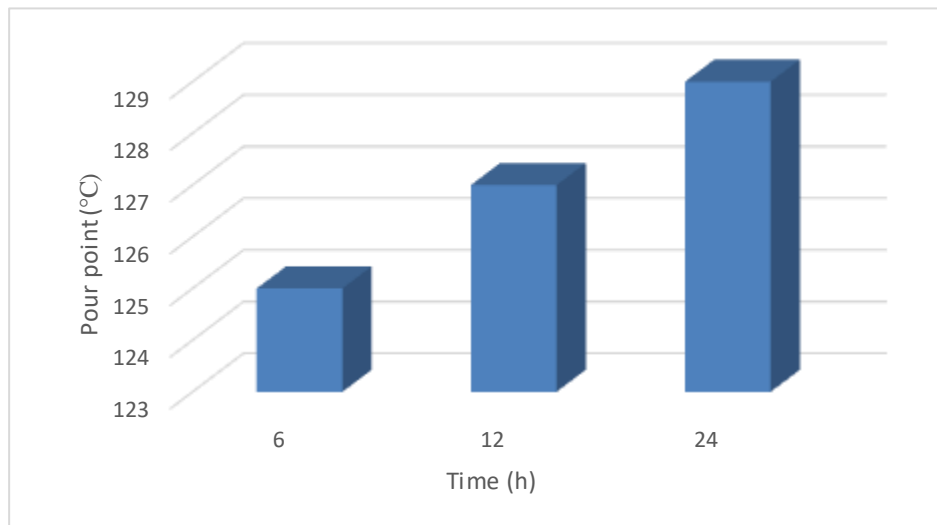


Fig 3.36: Crystallization time vs. viscosity index (B).

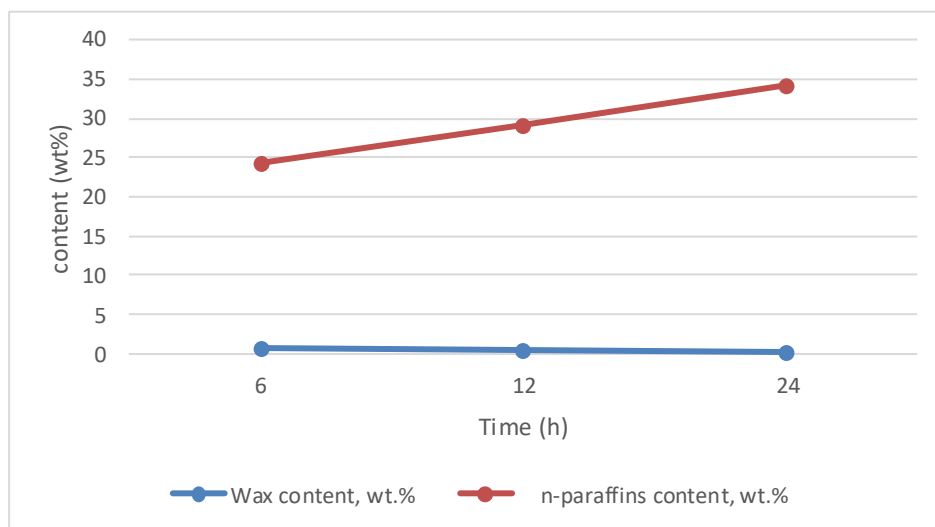


Fig 3.37: Crystallization time vs. wax content and n-paraffin content (A).

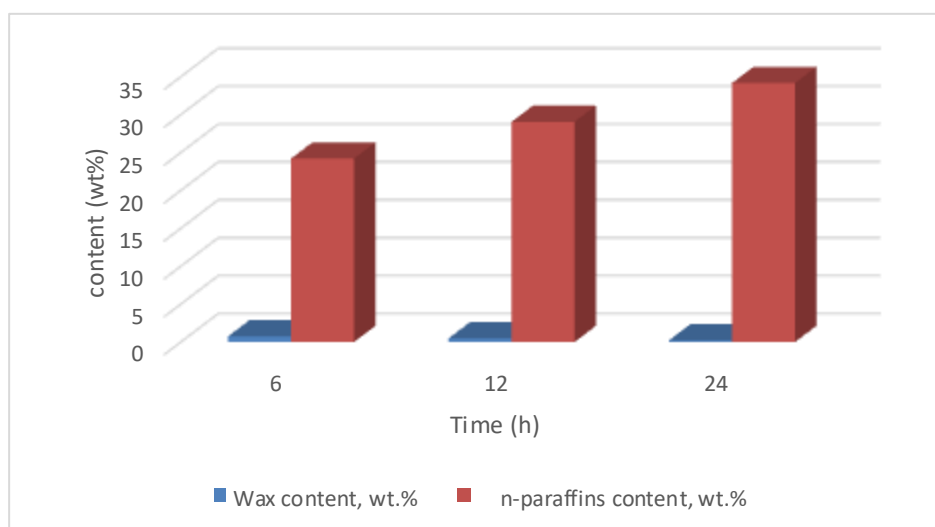


Fig 3.38: Crystallization time vs. wax content and n-paraffin content (B).

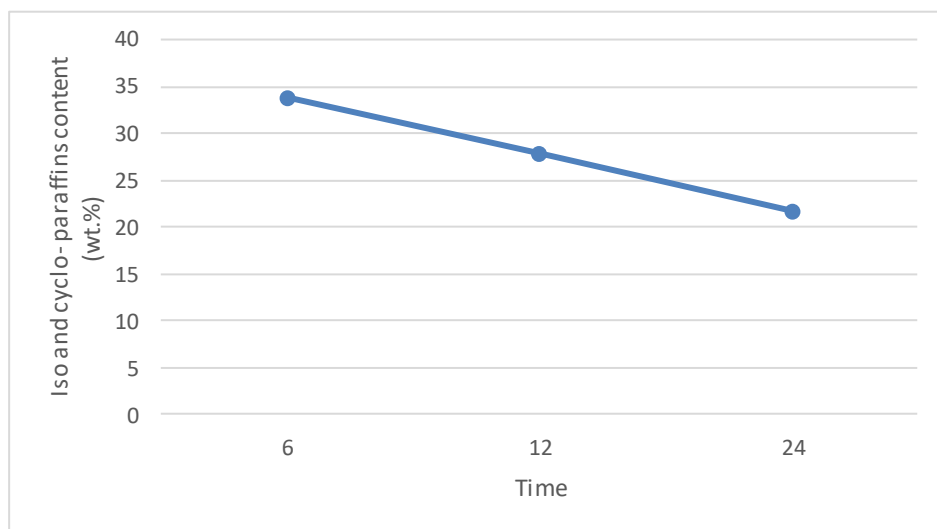


Fig 3.39: Crystallization time vs. iso and cyclo-paraffin content (A).

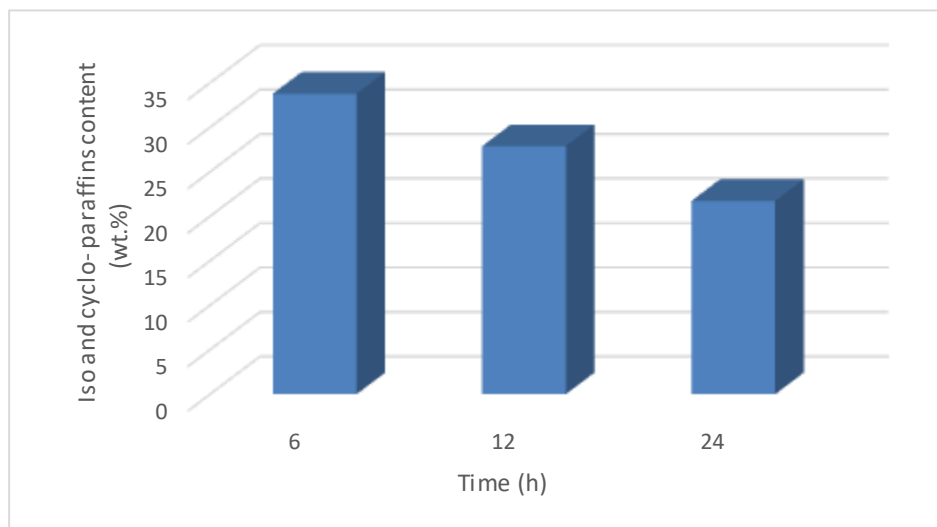


Fig 3.40: Crystallization time vs. iso and cyclo-paraffin content (B).

The effect of crystallization time was studied using BA solvent at de-waxing temperature of -10°C and at dilution solvent ratio of 10:1 by weight. Increasing the crystallization time from 6 to 24h increases density, refractive index and viscosity index (Fig. 3.35 or 3.36) and slight decreases of kinematic viscosity, mean molecular weight and wax content (Fig. 3.37 or 3.38) of the de-waxed oils while a considerable improvement in the pour point is achieved. whereas, it decreases from 14.5 to 5°C upon increasing the crystallization time from 6 to 24h (Table 3.12 and Fig. 3.33 or 3.34). These results can be justified by the fact that, increasing crystallization time enhances the formation and growth of wax crystals, which in turn, resulted in an improved filtration performance. More so, the greater time of crystallization makes the solvent to permeate the oil molecules which have a greater solubility preference for the oil than the wax serves to improve the de-waxing performance.

3.6 Conclusion:

More specifically, it appears that when a high solvent to oil ratio ($S/F = 10/1$ by weight) is used and a higher yield of oil is achieved due to the increase of the solubility of the solvent. Thus, it can be concluded that, BA solvent is selected as the suitable solvent for de-waxing Sudanese crude oil at dilution solvent ratio of 10/1 by weight and at de-waxing temperature of -10°C .

Thus, it can be concluded that the process of de-waxing at de-waxing temperature of -10°C would be economical and is selected for de-waxing of Sudanese crude oil using BA at dilution solvent ratio of 10:1 and de-waxing at crystallization time of 24h would be suitable and is selected for de-waxing of Sudanese crude oil using BA at dilution solvent ratio of 10:1 and at de-waxing temperature of -10°C .

3.7 Recommendations:

A. Recommendations for RAWAT Company

The study recommends that RAWAT Company should:

- Apply crude oil de-waxing in their oil field using the solvent used in this study (Butyl Acetate) in the future.
- Consider running a purification process of the produced wax as it has economic value.
- Study the molecular and physical characteristics of the oil produced from the other fields they run.

B. Implications for Further Research

- Research in de-oiling of waxes produced after the de-waxing process to benefit from the bi-products of this process is required.
- Research in purification of the produced wax and its economic value is essential.
- Research on the use of other de-waxing techniques is needed to broaden the knowledge on the ideal processes of de-waxing for the different petroleum crude oils.

Chapter Four

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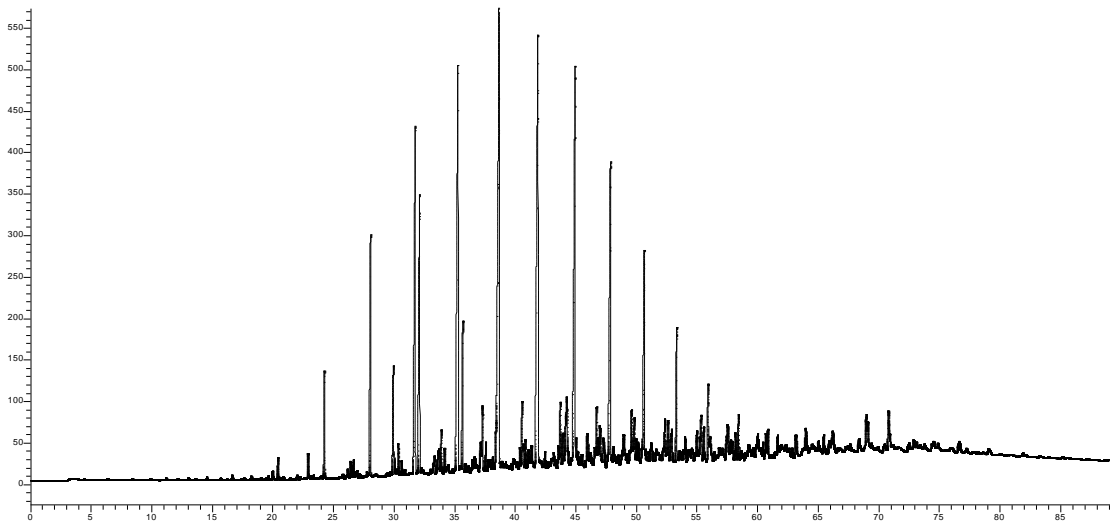
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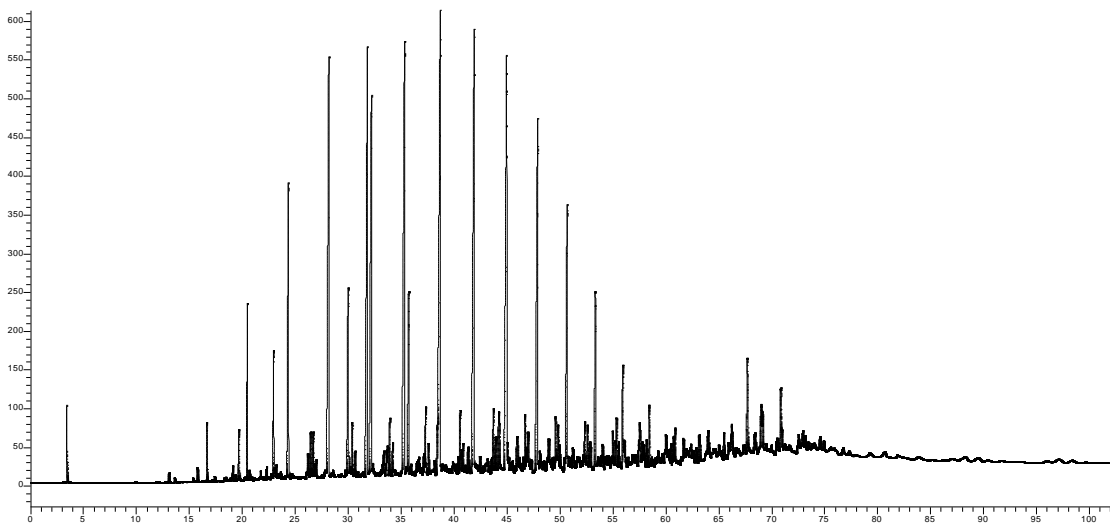
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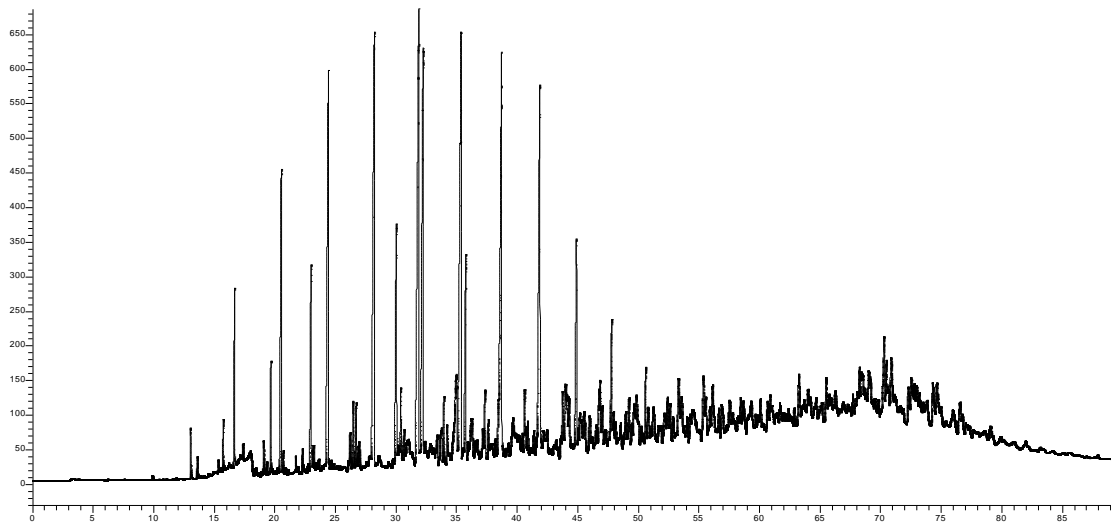
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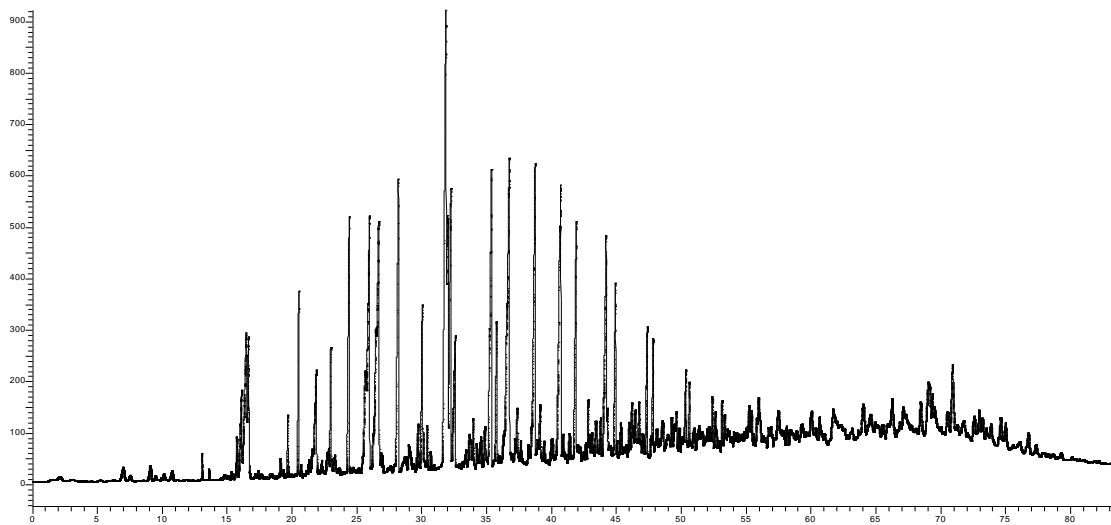
Appendix1- GC graph of de-waxed oil using MIBK (de-waxing temperature - 10°C, S/F 6/1)



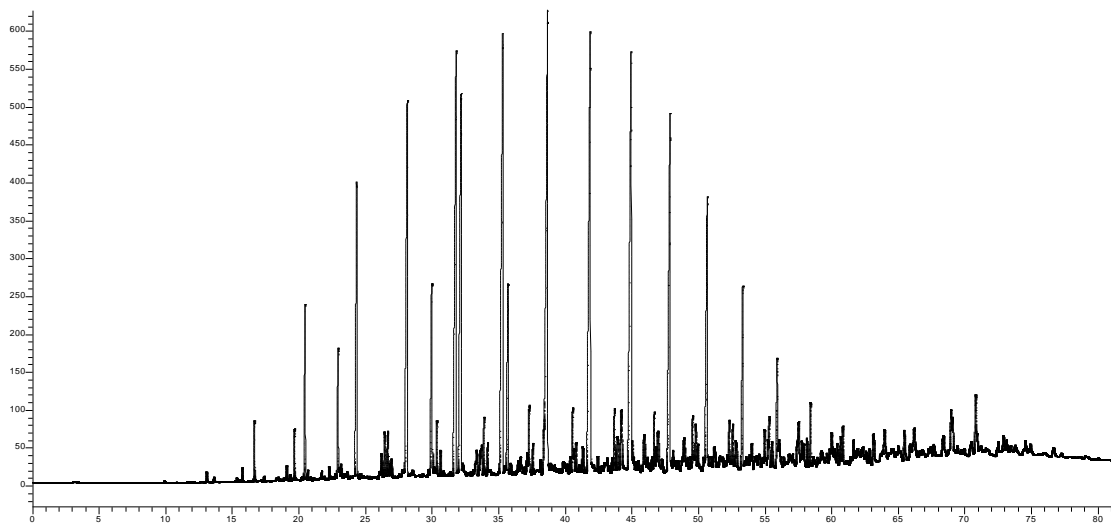
Appendix2- GC graph of de-waxed oil using MIBK (de-waxing temperature - 10°C, S/F 10/1)



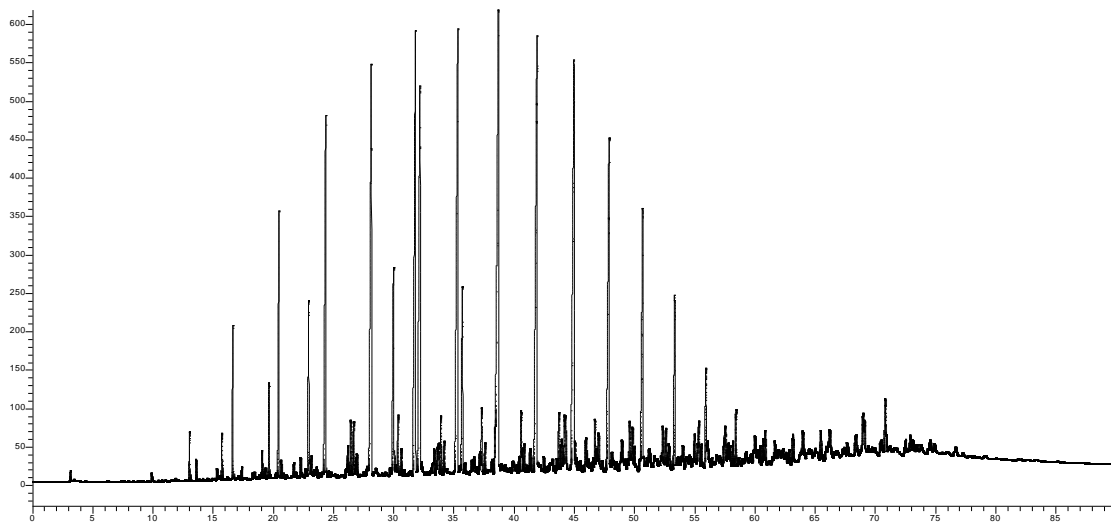
Appendix3- GC graph of de-waxed oil using MEK (de-waxing temperature - 10°C, S/F 4/1)



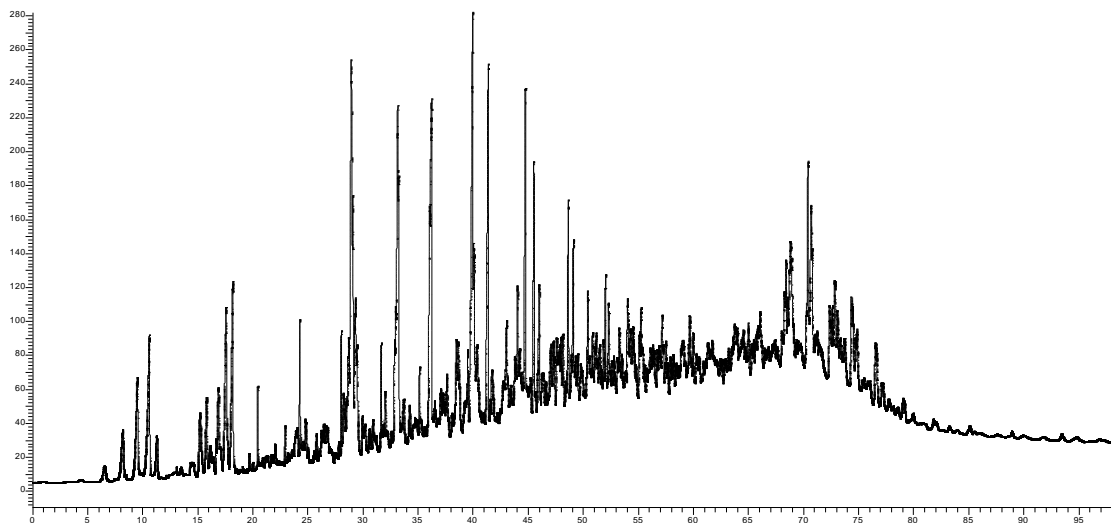
Appendix4- GC graph of de-waxed oil using MEK (de-waxing temperature - 10°C, S/F 8/1).



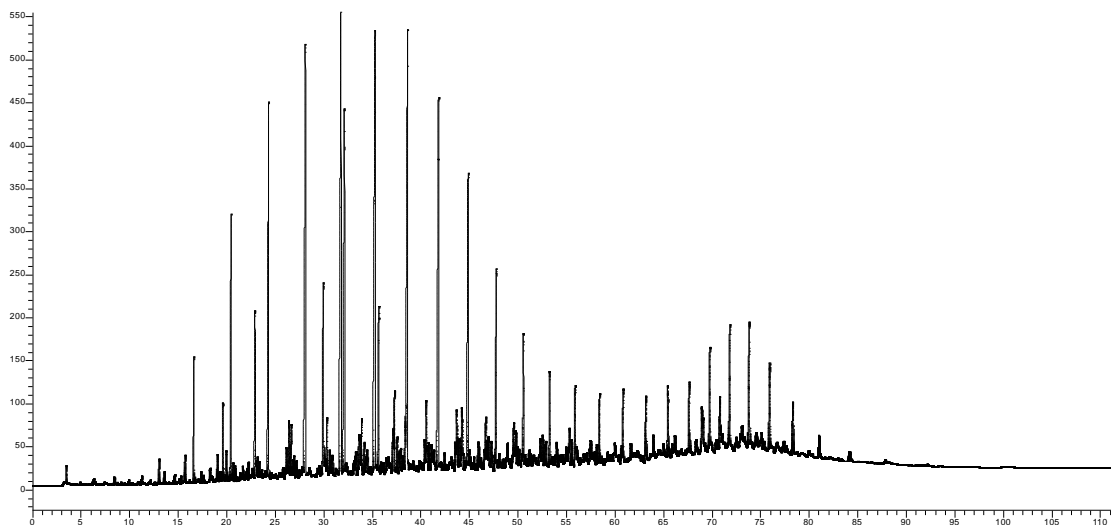
Appendix5- GC graph of de-waxed oil using BA (de-waxing temperature - 10°C, S/F 8/1 and crystallization time 24hrs).



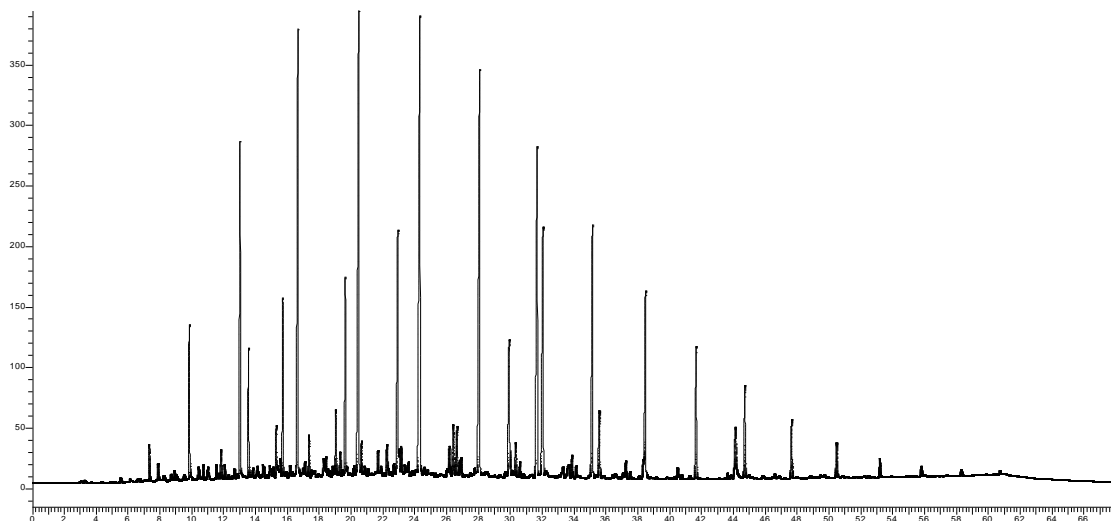
Appendix6- GC graph of de-waxed oil using BA (de-waxing temperature - 10°C, S/F 10/1 and crystallization time 24hrs).



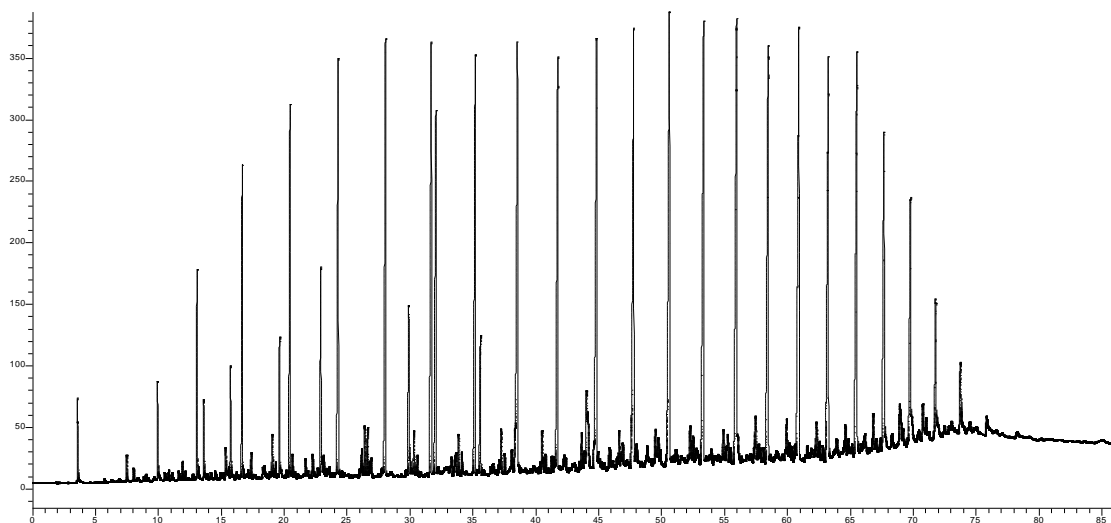
Appendix7- GC graph of de-waxed oil using BA (de-waxing temperature - 10°C, S/F 10/1 and crystallization time 6hrs).



Appendix8- GC graph of de-waxed oil using BA (de-waxing temperature - 20°C, S/F 10/1 and crystallization time 24hrs).



Appendix9- GC graph of de-waxed oil using MTBE (de-waxing temperature - 10°C, S/F 4/1 and crystallization time 24hrs)



Appendix10- GC graph of de-waxed oil using MTBE (de-waxing temperature -10°C, S/F 10/1 and crystallization time 24hrs)