بسم الله الرحمن الرحيم

Sudan University of Science and Technology
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The Effect of Usage on the physicochemical Properties of Lubricant Oils

أثر الاستخدام علي الخواص الفيزيائية والكيميائية لزيوت التزليق

A Dissertation submitted in partial Fulfillment of Requirements of M.Sc degree in Chemistry

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2015

الآيــــة

قال تعالى:

(فتَبَسَّمَ ضَاحِكًا مِّن قوْلِهَا وَقالَ رَبِّ أوْزِعْنِي أنْ أشْكُرَ نِعْمَتَكَ الَّتِي أنْعَمْتَ عَلَيَّ وَعَلَىٰ وَالِدَيَّ وَأنْ أعْمَلَ صَالِحًا تَرْضَاهُ وَأدْخِلْنِي بِرَحْمَتِكَ فِي عِبَادِكَ الصَّالِحِينَ).

صدق الله العظيم

سورة النمل الآية (19)

Dedication

I dedicate this Research to my mother Lila who gives her inspiration me to believe that I was capable of accomplishing this research.

I would like to thank my husband, Fayad, for his support.

Acknowledgement

I would like to acknowledge the inspirational instruction and guidance of ***Dr. Mohammed Elmubarak Osman*** and the initial impetus to study Physical and Chemical Characteristics of Used Lubricant Oils. There is no doubt in my mind that without his continued support and counseling I could not have completed this Research. I would also like to acknowledge the support and assistance of ***Mr. Mohammed Ibn Auf*** who has been very generous in his support of my academic pursuits. Both of them have given me a deep appreciation and love for the beauty and detail of this subject.

Abstract

Study has chemical and physical properties of a sample of use multi-grade engine oils for gasoline engines at different distances 0, 3000, 4000, 5000 km. The results showed a decrease in the total base number, and chemical additives, viscosity at 40,100 °C and flash point. The results showed also an increase in sulphated ash and density.

Physicochemical properties of two samples of multi-grade gasoline engine oils, were characterized before and after 5000 kilometers of operation. Results of used engine oils indicated a decrease in Total Base Number (TBN) a percentage 62.8, 25, 65%, element additives 3, 12%, 119, 25.9 viscosity at 100 °**C** 16.48,13.28%. Presence of Oxidative reaction has been configured by FTIR analyzed.

المستخلص

تمت دراسة الخواص الكيميائية والفيزيائية لعينه من زيوت التزييت المتعددة لمحركات البنزين في مسافات مختلفة 0، 3000، 4000، 5000 كلم. أشارت النتائج إلي انخفاض في الرقم القاعدي الكلي، والمضافات الكيميائية و اللزوجة عندC 40,100 ودرجه الوميض. وأظهرت النتائج أيضا زيادة في الرماد المكبرت والكثافة

كما تمت مقارنه بين الخواص الكيميائية والفيزيائية لعينتين من زيوت التزييت المتعددة لمحركات البنزين قبل وبعد 5000كيلو متر من التشغيل وأوضحت النتائج انخفاض الرقم القاعدي الكلي بنسبه 62.8-و 25.65- % واللزوجة عندC 100 بنسبه 16.48و 13.28 والمضافات الكيميائية بنسبه 3و 12% و11.9و 25. أكدت تقنيه الأشعة تحت الحمراء أكسدت الزيوت المستخدمة.

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Chapter One

Introduction

1. Introduction

The ground begins to rumble, and then shake. The hero of the film – a lean ex-cowboy with a square jaw under his hat and a gorgeous brunette on his arm –reaches out to brace himself against his horse. A smile creases his face as the rumbling grows louder. Suddenly, a gush of black goo spurts into the air and splashes down on him, his side-kick and his best gal. They dance with ecstasy until the music swells and the credits start to roll. Why is our hero so happy? Because he's rich! After years of drilling dry holes in every county between the Red River and the Rio Grande, he finally struck oil.

1.1 What is Petroleum?

Petroleum is, called, a fossil fuel because it is formed from the remains of ancient organisms – primarily one celled plants and animals. Contrary to modern myth, only a tiny fraction (if any) of the molecules in crude oil are from dinosaurs. When these creatures died, their remains accumulated at bottoms of ancient lakes or seas, along with sand and other sediments. Over time, a combination of pressure, heat, and bacterial action transformed the deposits into sedimentary rock.

The incorporated organic matter was transformed into simpler chemicals, such as hydrocarbons, water, carbon dioxide, hydrogen sulfide, and others. The chemicals didn't always stay put. If the surrounding rock was porous, liquids and gases could migrate, either up to the surface or into a reservoir (Fig 1.1) that was capped by impermeable rock or a dome of salt. Today, when petroleum geologists look for oil, they actually are, looking for structures that might be traps for liquid hydrocarbons.

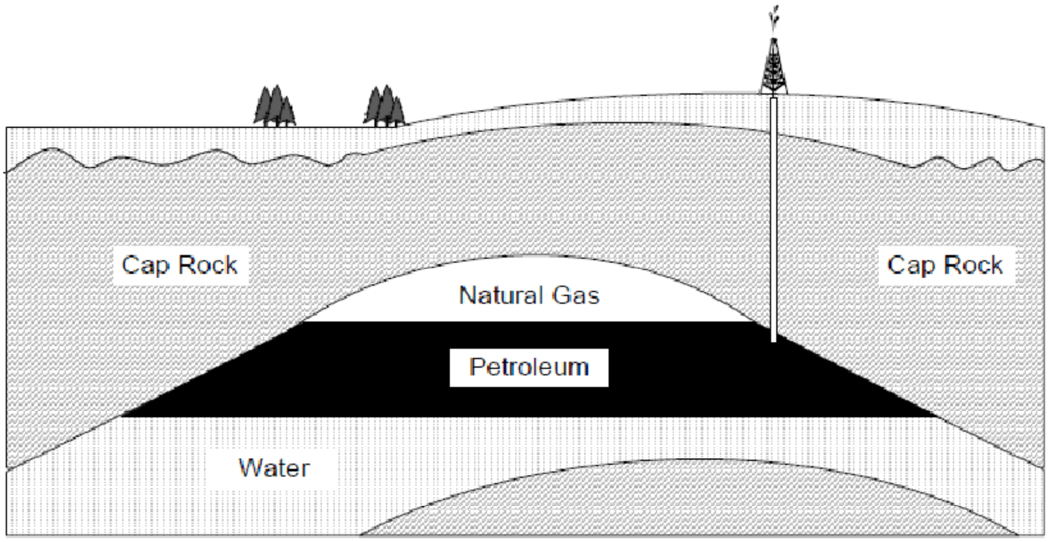


Figure 1.1 Petroleum Reservior

Due to its origin, crude oil is a complex mixture containing thousands of different hydrocarbons. As the name implies, hydrocarbons are chemicals containing hydrogen and carbon. In addition to hydrogen and carbon, most crude oils also contain 1 to 3% sulfur along with smaller amounts of nitrogen, oxygen, metals, and salts. The salts can be removed with a hot-water wash, but the other major contaminants – sulfur, nitrogen, oxygen and metals – are difficult to remove because they are chemically bonded to hydrocarbons. Crude oils from some wells are as clear as vegetable oil. Other wells produce green, brown or black crudes. Some taste sour or smell like rotten eggs. Some flow as easily as water, others don’t flow unless they are heated, and some are so solid to be mined. (Chang, 2006)

1.2 The Chemical Composition of Petroleum

Carbon is present in almost all of the chemical compounds in petroleum. If you’ve ever taken a chemistry class, you know that carbon, more than any other element, binds to itself to form straight chains, branched chains, rings, and complex three-dimensional structures. The most complex molecules are biological – proteins, carbohydrates, fats and nucleic acids, which are present in every living thing, from the smallest bacterium to the largest tree. This is significant here because (as stated above) petroleum was formed from ancient organisms, and its molecules retain certain structural characteristics of the organic compounds from which it is formed

Objectives of The project

1. To study changes of gasoline engine oil properties with running time

2. To study the effects that occurs in the oil of operation, oxidation and external influences.

3. To study the effects of the distances (extended kilometers).

Chapter Two

Literature review

2. Basic Principles of Lubrications

2.1 Meaning of Lubrication

Lubrication is simply the use of a material to improve the smoothness of movement of one surface over another, and the material that is used in this way is called a lubricant. Lubricants are, usually, liquids or semi-liquids, but may be solids, gases, or any combination of solids, liquids and gases. Lubricant oils can be defined as substance introduced between two surfaces in relative motion in order to reduce the friction between them. Lubricants are expected to reduce wear and, often, prevent overheating and corrosion. In most cases dry friction between two covered by two laws which are usually called "Amonton's Laws". The first of these laws is that friction between two solids is independent of the area of contact.

The second law is that friction is proportional to the load exerted by one surface on another. In the 1850 s, small quantities of petroleum oil began to be produced in the U.S.A., Canada, Russia and Romania. The modern petroleum industry was born in 1880. Liquid petroleum has to be distilled and fractionated into a range of products in order to be fully exploited and the heavier of these confined to uses as lubricating oils. It was soon discovered that under reduced pressure, so called vacuum distillation, fractions could be separated without the heavier product being oxidized and deteriorated, and the fractions are reduced as the pressure is lowered, and low temperature is sufficient to separate the mixture˙ (A. RLansdown, 2004).

2.2 Lubricants main functions

The main functions of lubricating oils and other lubricant are: Reducing the friction by putting lubricating oils between moving metal surfaces. Decrease friction. These results in energy conservation and significantly less wear.

2.2.1 Reducing wear

Lubricating oils reduce mechanical wear (caused by abrasion and erosion) and chemical wear (corrosion caused by combustion acids and water). Wear is influenced by various factors, which can be divided into the field of tool, rough part, forming machine and lubricant actual contact area. Possible ways to reduce wear lie in the increase of annealing durability as well as in the hardness of the surface, for example through retrying, and application of mostly wear resistant layers on the tool surface. Reduction can't be achieved by lowering the tool temperature. (Vasily, Raphael, 2005)

2.2.2 Cooling purposes

When oil in the engine flow through oil passageways, it helps cool the engine components by absorbing heat away from the metal part. The circulating hot oil is then returned to the engine crankcase where it is cooled (Edward, 2010).

2.2.3 Removing impurities

lubricants keep engine components clean by preventing the formation of deposits and suspended impurities(dust, combustion residue, engine wear particles) that then build up on the oil filter (Vasily, Raphael, 2005).

2.3 Classification of lubricant oil

Lubricants may be arranged according to the following classification methods:

1. General classification of lubricants

2. Classification of lubricants by application

3. Classification of lubricants by additives (http://www.substech.com/dokuwiki/doku.php?id=classification_of_lubricants)

2.3.1 General classification of lubricants

Lubricants are classified on the basis of their physical state, as follows;

1. Liquid lubricants or lubricating oils,
2. Semi-solid lubricants or grease.
3. Solid lubricants. (V. M. Balsaraf, A.V. Pawar et al, 2010)

2.3.1.1 Liquid lubricant oil

Lubricating oils also known as liquid lubricants and further classified into three categories

(i) Animal and vegetables oils.

(ii) Mineral or petroleum oils.

(iii) Blended oils. (http://cuiet.info/notes/chemistry/Lubricants.pdf).

(i) Animal and vegetable oils:

Animal and vegetable oils are extracted from animal and vegetable sources. They are, typically, triglycerides. The chains of fatty acids are bound with a single molecule of glycerol. Animals and vegetable oils are high in viscosity and provide good lubrication.

Animal and vegetable oil have many disadvantages. They are easily oxidized to form acidic products, they are expensive and they get hydrolyzed easily in the presence of moist air or aqueous mediums. Chemical additives are added to animal and vegetable oils to improve their properties (James, Douglas, 2014)

(ii) Mineral or petroleum oils

Mineral lubricating oils have a variety of physical and chemical properties are now in use. To obtain oils of the required properties, selection of the right crude petroleum source has to be combined with the right manufacturing processes and the use of the right additives in optimum proportions and dosages. (V. Sterpina, 1992).

(iii) Blended oils

Desirable characteristic of lubricating oils can be improved by adding small quantities of various additives. The oils, thus, obtained are known as blended oils or compounded oils. Additives are materials that impart a new or desired property that the lubricating oil, already, possess to some degree. (Devender, Balraj et al, 2008).

2.3.1.2 Semi-solid lubricants or grease

These are neither solid nor liquid. They exist in the gel form like paste or grease. They consist of a soap dispersed throughout a liquid lubricating oil may contain specific additives for specific purposes. These types of lubricants have higher frictional resistance than oil and therefore can support much heavier loads at lower speeds. For examples, greases, vaseline, waxes, creams, etc.

2.3.1.3 Solid lubricant

Lubricants which exist in solid form are called solid lubricants, for example, graphite, molybdenum disulphide, soap stone, wax, mica, chalk, talk etc. These are used in machinery which operates under very heavy load and low speed. Recently some stearates and palmitates of aluminum and mineral acid have also been employed as solid lubricants. Graphite is a more expensive solid lubricant but it is widely used because it is non-inflammable and resists oxidation, even, at higher temperatures. The solid lubricants are used either as such or as a suspended form in oil, grease or water.

Conditions for using solid lubricants

Solid lubricants are used when semi-solid or liquid lubricants are not suitable. Heavy machines are operated under heavy loads and at low speeds. Lubricant or grease are easily contaminated with dust or grit particles etc. semi solid or liquid lubricant are highly combustible (Dr. B. K. Ambasta, 2012).

Poly tetra Fluor ethylene (PTFE)

Poly tetra fluoro ethylene (TFE) is a synthetic fluoropolymer used in various applications including non-stick coatings. Non-stick coating systems often include a special treatment of the substrate. For example, whitford Corporation's Excalibur consists of three layers of PTFE over a metallic substrate which is first grit-blasted to roughen it, then electric-arc sprayed with a proprietary stainless steel alloy. According to Whitford, the irregular surface promotes adhesion of the PTFE and also resists abrasion of the PTFE. (en.wikipedia.org/wiki/motor.oil).

Silicones

Silicones are a group of inorganic polymers, molecules which represents a backbone structure built from repeated chemical units (monomers) containing Si=O moieties. Two organic groups are attached to each Si=O moiety = e.g. methyl + methyl L ($(CH_3)_2$), methyl + phenyl (CH_3 + C_6H_5), phenyl + phenyl ($(C_6H_5)_2$).

The most popular silicon is poly diethylsiloxane (PDMS.). Its monomer is $(CH_3)_2SiO$. PDMS is produced from silicon and methyl L chloride; other examples of silicones are poly methyl phenyl siloxane and poly dipheny siloxane.Viscosity of silicones depends on the length of the polymer molecules and on the degree of their cross-linking. Short non- cross-linked molecules make fluid silicone. Long cross-linked molecules result in elastomer silicone. Silicone lubricants (oils and greases) are characterized by broad temperature range: -100°F to 400°F (73°C to 204°C$^{)}$. (James, Douglas, 2014).

2.3.2 Classification of lubricants by application

- Engine oils
- Gear and hydraulic oils
- Cutting fluids (coolants)
- Turbine oils
- Transformer oils (insulating oils)
- Chain lubricants
- Wire rope lubricants

2.3.2.1 Engine oil

In order to define the viscosity of engine oils, two or three viscosity thresholds were selected to define their flow a minimum viscosity at high temperature. (Theo, Kirsten et al, 2011).

2.3.2.2 Gear and hydraulic oils

Gear and hydraulic are always used in closed application. Nevertheless serious percentages of these oils and up in the environment due to sweating, leaks and accidents. This accounts for the inclusions of gear oils as well as hydraulic oil in LLINCWA (P.van, D.theodori et al, 2003).

2.3.2.3 Cutting fluids (coolants)

The energy used in the cutting process is almost exclusively transformed in heat, which means, depending on the method, that is thermal energy appears in the work piece, the chain and the tool to different extents. During high speed milling, it is possible to discharge energy, almost completely, with the chain (Heinz, 2009).

2.3.2.4 Turbine oils

The ratio between the power output of turbines and oil volume has increased considerably over the years. Consequently, operating temperatures have increased from 100 to 160 °C. Legislated emission regulations and growth in electrical power demand are boosting gas turbines as the most important cogeneration unit. The combined generation of electric power and useful thermal energy, using the normally wasted gas turbines exhaust heat to drive a steam turbine, is called cogeneration or combined cycle gas turbine, CCGT. The conditions under which the lubricant has to function in a gas turbine are even more demanding from thermooxidative and volatility considerations. General electric frame 7 gas turbine oil specification, GEK 32568, exclude the use of 2,6-di-tertiary-butyl-p-cresol, BHT, owing to its volatility under these conditions. With the introduction of cogeneration, the need for a turbine lubricant which simultaneously meets the specifications of both steam and gas turbines will grow. Thus, protecting the lubricant against high-temperature degradation by selecting more thermally stable and less volatile antioxidants has become important. (Dr. Roy, Dr. Stevan etal, 2010)

2.3.2.5 Transformer oils (insulating oils)

Insolating oil forms every significant part of transformer insulation system and has the important functions of acting as an electrical insulation as well as a coolant to dissipate heat losses. The basic raw material for the production of transformer oil is a low viscosity lube termed as transformer oil base stock (Tobs), which is normally obtained by fractional distillation and subsequent treatment of crude petroleum. (Bhel, 2003)

2.3.2.6 Chain lubricants

The chain is probably the most widely used alternative o gears as a means of transmitting power and varying the speed and torque. All types of chain are comprised of the link, pin and bush as the basic elements with, in the case of the inverted -tooth type, an involute tooth operating, on the conforming sprocket tooth, instead of the normal ruler. Chain lubrication, therefore, becomes a matter of lubricating a plain bearing and rolling/ sliding element, the material being steel on steel on each case, and although the speed of the chain as a whole may be high (over 15 m/s), the speed of various elements, relative to each other, are low and the type of lubricant is not critical.

The choice of lubricant of chain drives depend on the method of application of the oil, and on the conditions under which the chain operates. At normal temperatures and under the maximum loading by the manufacturer, straight mineral oil gives adequate lubrication, the viscosity ranging from about 46 cSt to 320 cSt at 40 C. at low chain speeds (say 2.5 m/s) and in open chains, where hand application is adequate, a relatively heavy oil maybe used. At higher speed, up to 7.5 m/s, drip-feed, bath or splash systems should be employed as a rather more positive means of applying the oil. Up to 15 m/s a slinger can be used to throw oil from the bottom of the oil bath on to the chain, while above that speed oil mist or spray is necessary.

If the chain loading is high an EB gear oil maybe necessary, while high temperatures may call for an oil with rust and oxidation inhibition built in. (W. L. Robertson, 1984)

2.3.2.7 Wire rope lubricants

Wire rope forms an important part of many machines and structures. It is comprised of continuous wire strands wound around a central core. There are many kinds of wire rope designed for different applications. Most of them are steel wires made into strands wound with each other. The core can be made of steel, rope or even plastics. Wire ropes (cables) are identified by several parameters including size, grade of steel used, whether or not it is preformed, by its lay, the number of strands and the number of wires in each strand. (Jeffery, 2002)

2.3.3 Classification of lubricants by additives

- Extreme pressure (EP)
- Anti-wear (AW)
- Friction modifiers
- Vapor corrosion inhibitors
- Anti-oxidants
- Anti-foaming agents.

2.3.3.1 Extreme pressure (EP)

Extreme pressure compound are designed to react with metal surface under extreme condition of high load and temperature to prevent welding of the moving parts that would otherwise cause sever damage. Extreme pressure additive occurs form layers on the metals surface by adsorption or chemisotion due to their polar molecules, when hydrodynamic lubricating films are not present and a system runs under boundary lubrication. This can result in increased operating temperatures. Where exposed metal surfaces can become hot. The increase in temperature allows for EP additives to react with the warm metal surface forming tribochemical reaction layers composed of iron phosphids, sulfides, sulfates, oxides and carbide that prevent direct contact between the sliding metals.

The use of EP additives results in amid form of corrosion due to the reaction with metallic surface, for this reason, the additive concentration is an important parameter. (Paradeep, Michael et al, 2013)

2.3.3.2 Anti-wear

When two contacting parts of a machinery start to move and the hydrodynamic lubrication has not yet build up or in the case sever stress and strong forces the lubricant system runs in the area of mixed friction. In this case anti wear (AW) and extreme pressure (EP) additive are necessary in any metal working fluid, engine oil, hydraulic fluid or lubricating grease to prevent welding of the moving part respectively to reduce wear (Theo, Wilfried, 2007)

2.3.3.3 Friction modifiers

Friction modifiers are chemicals used to prevent stick-slip oscillations used and noises acting, directly, on frictional forces. These compounds can be classified into different categories based on their function mechanically working (such as molybdenum disulfide, graphite, PTF), adsorption layers (fatty acid esters amines, imides, long chain carboxylic acids), and friction polymers (including methacrylates, unsaturated fatty acid, and sulfurized olefins).

2.3.3.4 Vapor corrosion inhibitors

Incorporating of Vapor Corrosion Inhibitors in lubricating products provides number of advantages. VCIs when added to lubricants will provide corrosion a protection to machinery during the storage or transportation period and after that the same lubricant can be used in design working applications without spending extra time and money for changing the corrosion protective product for lubricating. Properly chosen combination of VCI and lubricating product also prolong service life of machinery by minimizing the corrosive wear of the equipment. The requirements to the Vapor corrosion inhibitors, which will be added to the lubricants, vary considering the application condition. Usually, these products should be thermostable, should not attack colored metal at high temperatures, and effect physical - chemical properties of lubricant. (Margrita, Kharshan, Alla, 2005)

2.3.3.5 Anti-oxidants

Many lubricants contain anti oxidant additives to delay or minimize the onset of oxidation. Antioxidants or oxygen inhibitors are either natural or artificial additives that have the ability to suppress oxidation. Natural antioxidants such as sulfur or nitrogen compounds can be naturally found in mineral oils. These compounds function by scavenging radicals produced during an oxidation process (Pradeep, Michael etal, 2013).

2.3.3.6 Anti foaming agents

Polydimethylsioxanes, fluorosillicons, acrylates, during the formulation of the oil, blending of all these components gives an extremely wide variety of products described in the classification. Nevertheless, the lubricating greases make up a special product category among them (T.P. Wauquier, 1994)

2.4 Crude oil

The basic chemistry of crude oils like vegetable oil, mineral oil are primarily made of hydrocarbon, that is atoms of carbon and hydrogen bound together to form molecules of different structures. Petroleum or crude oil is a naturally, occurring liquid mixture consisting, primarily, of hydrocarbons and also contains smaller amounts of organic compounds with heteroatom such as sulfur, nitrogen, oxygen and metals. It contains varying amounts of water, inorganic matter, and gas. Nickel and vanadium are present, mostly, in the form of porphyrins and related structures. The distribution, type of compound and molecular weights varies, greatly, with location and the geological formation from which crude oil was obtained.

The hydrocarbons in petroleum are paraffines, naphthenes and aromatics (Julius, A.J. Gruia, 1996).

2.4.1 Paraffins

The lightest paraffin is methane (CH_4) which is the major constituent of natural gas. Paraffins have the general formula C_nH_{2n+2}. The carbon chains in paraffins can be straight or branched. Compounds with the same formula but different structures are called isomers. Straight-chain paraffins are “normal,” while branched paraffins with the same chemical formula are called “iso.”

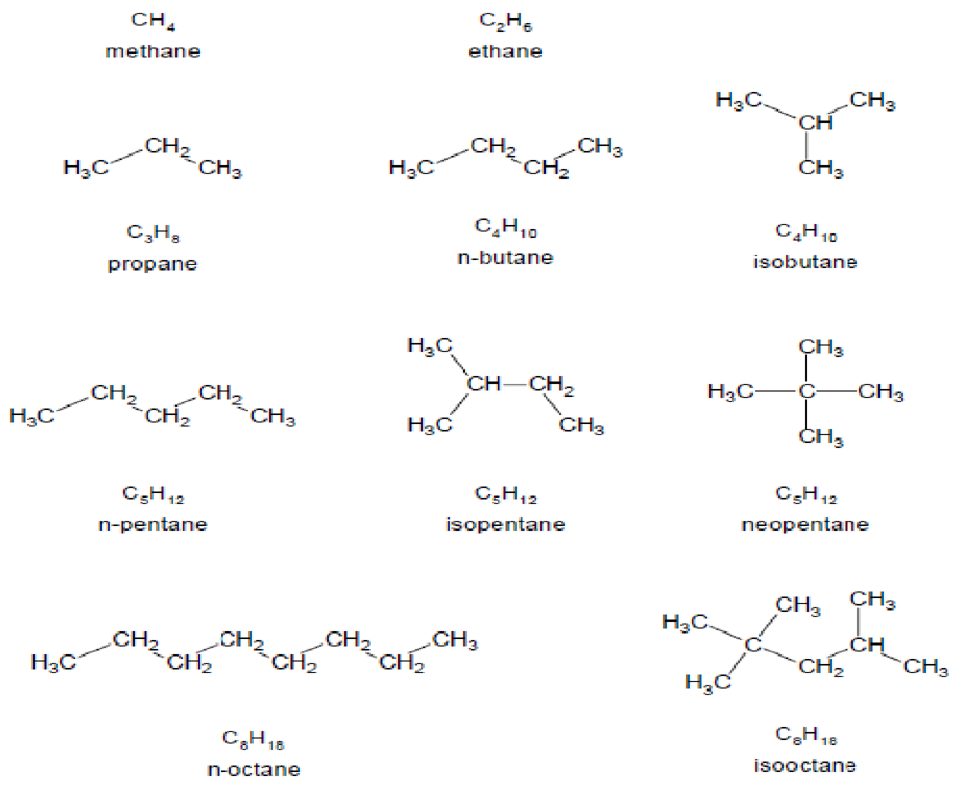


Fig 2.1: Isomers of paraffins

2.4.2 Aromatics and Naphthenes

Aromatics and naphthenes are also found in petroleum. Aromatics contain one or more unsaturated 5 to 6-carbon rings. In naphthenes, carbon rings are saturated with hydrogen. For aromatics with one six-carbon ring, the general formula is CnH2n-6, and for naphthenes with one ring, the general formula is CnH_2n. as shown below.

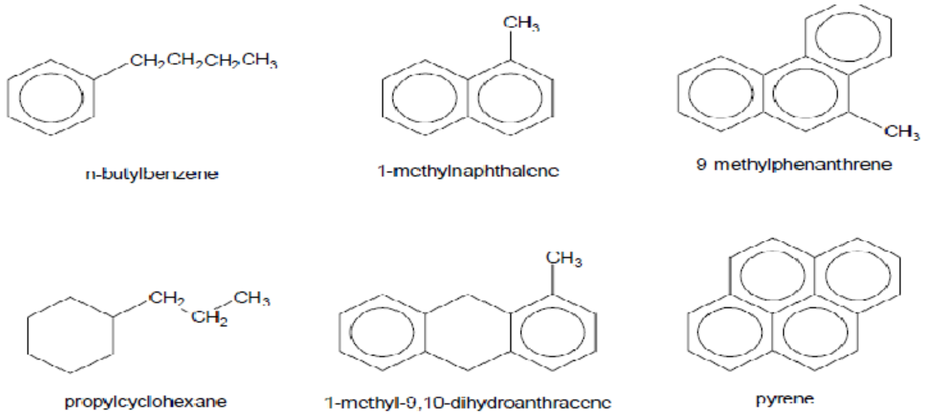


Fig 2.2: Aromatics and naphthenes found in crude oil

Aromatics and naphthenes display significantly different chemical and physical properties. Compared to paraffins and naphthenes with the same carbon number, aromatics are denser and have higher octane numbers.

2.4.3 Olefins

Olefins are not common in natural curde oil due to their high reactivity. However, they are generated by several "cacking" processes in refineries (Ghange , Paul, 2006).

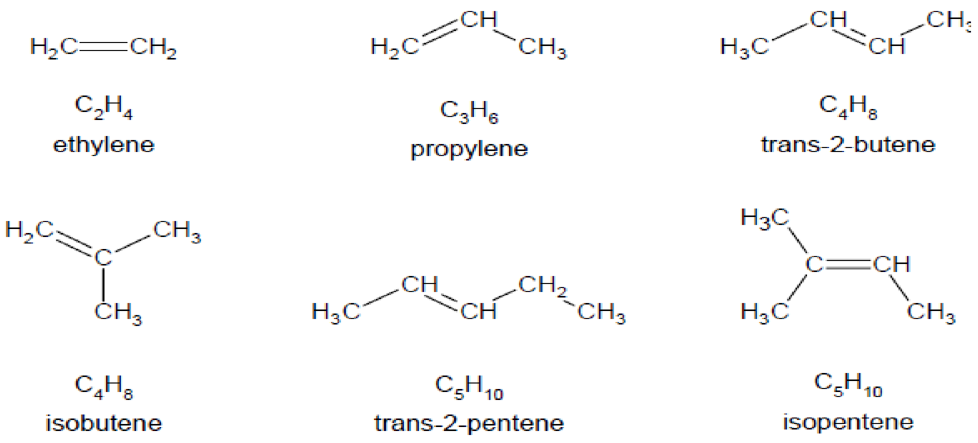


Fig 2.3 Light olefins

2.5 crude oil Products

a. Petroleum gas:

b. Naphtha or Ligroin

c. Gasoline:

d. Kerosene:

e. Lubricating oil

2.6 Lubricant oils

A lubricant (engine oil) can be defined as an oil product that separates the metal parts of an engine, reduce friction and keep it clean. The lubrication system of a engine is intended to avoid the increase of wear, overheating and seizure of rubbing surfaces to reduce the expenditure of power by overcoming mechanical losses in the engine and also to remove wear products of a machine .The oil perform many physical and chemical tasks, any of which if not met, can lead to engine failure. Lubricating oils contain additive packages to aid their performance and extend their useful life. Additives only delay the onset of serious deterioration of the oil and, once consumed, the oxidation of the oil proceeds at an accelerated rate compared to that of the base oil. Degradation results from both physical and chemical changes, internally generated or from extraneous contamination. It should be remembered that lubricants are usually complex blends of chemical additives in a variety of base oils. Since these finished lubricants are, often specifically, designed for particular applications, exposure of lubricants to conditions and component materials for which they are not intended may accelerate lubricant deterioration and result in equipment damage. Lubricant deterioration is the loss of ability of a lubricant to, effectively, perform its intended function. A used oil may become too dirty or viscous for further use. It may become corrosive to system components or form harmful sludges and deposits. Necessary additives compounded into the lubricant may become depleted. Contamination by abrasive or corrosive materials can cause severe damage to equipment. Contaminants, sometimes, act as catalytic agents and accelerate chemical breakdown of lubricants.

Lubricant deterioration is usually a function of time in service, system temperatures, make-up rate, and environmental conditions.

A lubricant can become unsuitable for further service as result of either physical deterioration by direct action of foreign materials. Particulate matter such as core sand, weld spatter, lint, metal chips, and abrasive dust left in a lubricating system, during manufacture and assembly. Foreign contaminants can enter through ineffective seals, dirty oil filler pipes, or make-up with an incorrect lubricant. Internally generated contamination includes wear debris, rust, and sealing materials or chemical deterioration where lubricant oxidation is the most important and most common type of deterioration. When an oil oxidizes, its most unstable constituents combine with oxygen to form acids, resins, varnishes, sludges, and carbonaceous deposits. In addition to increasing the lubricant’s viscosity, which in itself might result in a performance problem, oxidation products can plug small orifices and filters, restrict flow, or cause components to stick. Oxidation products mainly fall into two classes: soluble organic acid compounds and oil insoluble solids, such as gums, resins, varnishes, and asphaltenes. In addition, certain contaminants such as water and metals can act as catalysts and accelerate the oxidation rate. (http://books.google.com/books?id=h4w)

2.7 Comparing gasoline and diesel engine Oils

In the broadest sense, gas and diesel engine oils have the same anatomy or makeup. They are formulated from the blending of base oils and additives to achieve a set of desired performance characteristics. From this simple definition, it starts to diverge, when examining the lubricant's required performance for each engine type. (www.machinery lubrication.com)

2.8 Properties of motor oil

Most motor oils are made from a heavier, thicker petroleum hydrocarbon base stock derived from crude oil with additives to improve certain properties. One of the most important properties of motor oil in maintaining a lubricating film between moving parts is its viscosity. The viscosity of a liquid can be thought of as its "thickness" resistance to flow.

The viscosity must be high enough to maintain a satisfactory lubricating film, but low enough that the oil can flow around the engine parts satisfactorily to keep them well coated under all conditions. The viscosity index is a measure of how much the oil's viscosity changes as temperature changes. A higher viscosity index indicates the viscosity changes less with temperature.

Motor oil must be able to flow at cold winter temperatures to lubricate internal moving parts upon starting up the engine. Another important property of motor oils its pour point, which is indicative of the lowest temperature at which the oil could still be poured satisfactorily. The lower pour-point temperature of the oil, the more desirable the oil is when starting up at cold temperature. Oil is, largely, composed of hydrocarbons which can burn if ignited. Still another important property of motor oil is its flash point, the lowest temperature at which the oil gives off vapors which can ignite. It’s dangerous for the oil in a motor to ignite and burn, so a high flash point is desirable at a petroleum refinery, fractional distillation separates a motor oil fraction from other crude oil fractions, removing the volatile components which ignite more easily, and therefore increasing the oil's flash point.

Another test is to determine the Total Base Number (TBN), which is a measurement of the reserve alkalinity of an oil to neutralize acids. The resulting quantity is determined as mg KOH gram of lubricant. Analogously, total acid number (TAN) is the measure of lubricants acidity.

2.9 Grades of oils

The Society of Automotive Engineers, abbreviated as SAE, has established a numerical code system for grading motor oils according to their kinematics viscosity. SAE viscosity grading include the following: 0,5, 10, 20, 25, 30, 40, 50 and 60. Some of the numbers can be suffixed with the letter "W", designating their "winter" or cold-start, viscosity at lower temperature. Viscosity is graded by measuring the time it takes for standard orifice, at standard temperatures. The longer it takes, the higher the viscosity, and thus higher SAE code. Note that the SAE operates a separate viscosity rating system for transmissions oil which should not be confused with engine oil viscosity. The higher number of a transmission oil (e.g. 75w-140) do not mean that it is necessary higher viscosity than an engine oil.

2.9.1 Single grades oils

For single grades oils, the kinematics viscosity is measured at a reference temperature of 100 °C in units of mm^2/s or the equivalent older non SI units, centistokes (abbreviated cst).

Based on the range of viscosity the oil falls in at that temperature the oil is graded as an SAE number 0, 5, 10, 20, 30, 40, 50, or 60. The higher the viscosity, the higher SAE grade number is. These numbers are often referred to as the weight of motor oil. The reference temperature is meant to approximate the operating temperature to which motor oil is exposed in an engine. The viscosity of the single grade oil derived from petroleum unimproved with additives changes considerably with temperature. As the temperature increases, the viscosity of the oil decreases logarithmically in a relatively predictable manner. In single grade oils, viscosity testing can be done at cold winter (W) temperature (as well as checking minimum viscosity at 100 °C) to grade an oil as SAE number 0w, 5w, 10w, 15w, 20w or 25w. A single grade oil graded at the hot temperature is expected to test into the corresponding grade at the winter temperature; ie a 10 grade oil should correspond a low oil for some applications, such as when the temperature ranges in use are not very wide.

2.9.2 Multi-grade oils

The temperature range the oil is exposed to in most vehicles can be wide, ranging from cold ambient temperatures in winter before the vehicle is started up to hot operating temperatures when the vehicle is fully warmed up into summer weather. A specific oil will have a high viscosity when cold and low viscosity at the engines operating temperature. The difference in viscosities for any single-grade oil is too large between the extremes of temperature to being difference in viscosities closer together, special polymer additives called viscosity index improvers, or VIIS are added to the oil. These additives make the oil multi-grade motor oil. The idea is to cause the multi-grade oil to have the viscosity of the base number when cold, and the viscosity of second number when hot.

This enables on type of oil to be, generally, used all the year and when multi-grades were initially developed, they were frequently described as all-season oil. The viscosity of multi-grade oil still varies logarithmically with temperature, but the shape representing the change is lessened. This shape representing the change with temperature depends on the nature and amount of the additives to the base oil. The SAE designation for multi-grade oils includes two grade numbers, for example; 10w – 30 designates common multi-grade oil, been replaced with a more technical test where a" cold crank in the cold is diminished soon after being put into service. (en.wikipedia.org/wiki/motor oil)

2.10 Base Oil Composition

Crude oil results from physical and chemical processes acting over many million years on the buried remains of plants and animals. Although crude oil is usually formed in fine-grained source rocks, it can migrate into more permeable reservoir rocks and large accumulations of petroleum, the oilfields, are accessed by drilling. Each oilfield produces a different crude oil which varies in chemical composition and physical properties. Some crude oils, ‘crudes’, have a low sulphur content and flow easily, whereas others may contain wax and flow only when heated, yet others contain very large amounts of very highmolecular weight asphalt, (Table 2.1.) Despite the wide range of hydrocarbons and other organic molecules found in crude oils, the main differences between crudes are not the types of molecules but rather the relative amounts of each type that occur in each crude oil source.

Table 2.1 Variation in crude oil properties between sources

Source	North Sea	Indonesia	Venezuela	Middle East
Sulphur content (%)	0.3	0.2	5.5	2.5
Pour point (°C)	–3	39	9	–15
Viscosity at 40°C (cSt)	4	12	19,000	8

2.11 Conventional Base Oil Manufacturing Methods

Very early lubricants were made by the simple distillation of petroleum to recover the lower boiling gasoline and kerosene fractions to give a residue useable as a lubricant. Lubricant quality could be improved by very simple additional processing to remove some of the less desirable components such as asphalt, wax and aromatics. Lubricants of this era relied on the inherent properties of the base oil because virtually no additives were used. Vacuum distillation separated lubricant distillates from crude oil, leaving the asphalt behind in the distillation residue. Wax used to be removed by chilling the lube distillate and filtering in plate and frame presses. Aromatics were reduced by treating the oil with sulphuric acid and separating the acid tar phase. Finally, finishing treatments such as adsorption of acid residues and impurities by activated clays gave further improvement in product quality. These processes were mainly batch operations, labour intensive and characterised by their hazardous nature. They were unsuitable for the great expansion in production capacity which the industry was called upon to supply. New technology developed continuous operations so that plants became much larger and could make more consistent quality products at lower cost. These new process methods were based on the use of solvents: continuous selective solvent extraction for aromatic removal was the process which replaced acid treatment and continuous solvent de-waxing replaced the very labour-intensive cold-pressing technique. Technology has developed further in the last 40 years. Catalytic hydrogenation processes have become the normal method for finishing base oils and a more severe form is used as an alternative to solvent extraction to control aromatics content. With the exception of these newer hydrotreatment processes, all other processes used in modern base oil plants are physical separation techniques, i.e. all the essential constituents of the finished base oil were present in the original crude oil and processing methods are used to concentrate the desirable components by removing the less desirable components as by-products.

2.11.1 Base oil manufacture in a modern refinery

Most base oil plants are integrated with mainstream oil refineries which produce a range of transportation and heating fuel products (fig 2.4). Overall production capacity for lubricant base oils is a very small part of total refinery throughputs, amounting to less than 1.3% in America

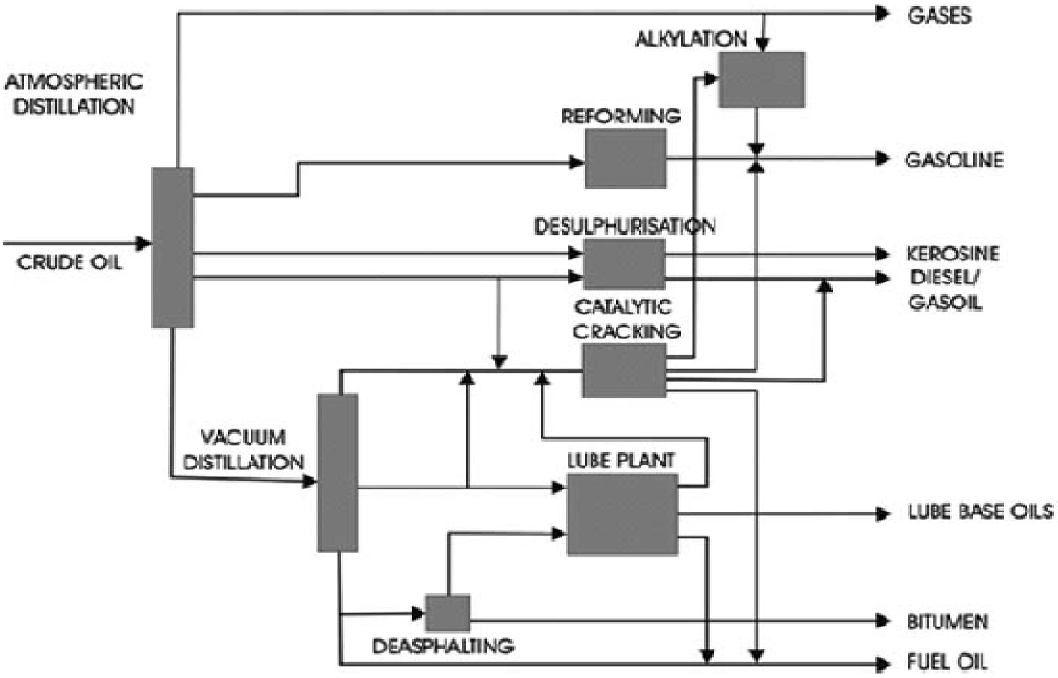


Fig 2.4 Simplified refinery

Since the choice of crude oil is restricted when making base oils, the production of relatively small volumes of base oil makes a large imposition on the crude purchasing requirements of a refinery. If suitable crudes are only available at a premium price, then there is an economic penalty for the refinery. Consequently, in recent years refining companies have given considerable effort to expand the portfolio of crude oil which they can use to make satisfactory base oils, giving more flexibility in crude oil purchasing.

2.11.2 Distillation

The primary process for separating the useful fractions for making lubricant base oils from crude oil is distillation. Crude oil is distilled at atmospheric pressure into components of gases, naphtha, kerosene and gas oil, essentially those boiling below 350 ◦C, and a residue containing lubricant base oil boiling range components. Thermal decomposition increasingly occurs at higher temperatures and further separation by distillation of the atmospheric residue into lubricant base oil is carried out in a vacuum unit (Fig 2.5). Atmospheric residue feedstock is injected with steam and pre-heated in a furnace before entering the lower part of the vacuum column. Inside the column, a variety of different mechanical arrangements are used to assist separation of different boiling range fractions: 1Base Oils from Petroleum

- trays, placed at intervals, with holes, bubble caps or valves to allow rising vapour and falling liquid to contact each other and come to equilibrium,

- packing with randomly arranged rings or other particles, giving a high surface area for liquid/ vapour contact,

- packing with geometrically structured mesh, giving excellent contact and distribution of liquid and vapour.

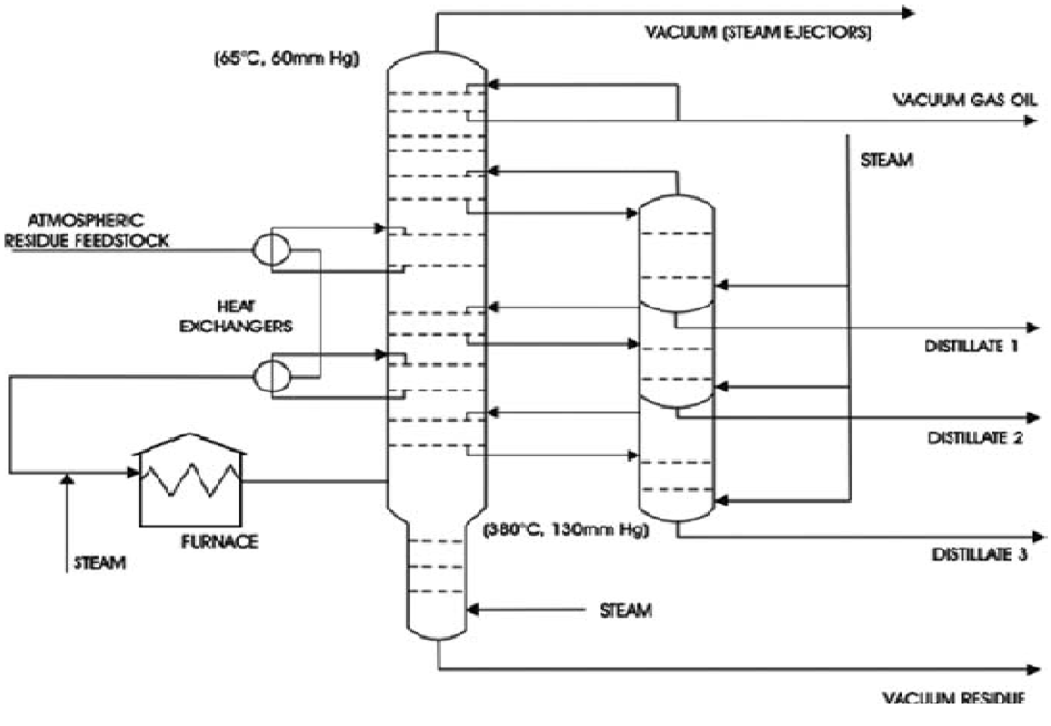


Figure 2.5: Vacuum distillation unit

Vacuum is applied at the top of the column, normally by steam ejectors which use condensing steam to create a vacuum, sometimes by vacuum pumps. Pressure in the flash zone is likely to be in the range of 100–140 mmHg. Injection of superheated steam helps to reduce the partial pressure of hydrocarbons in the flash zone, aiding separation of the heavy distillate from the residue and restricting overheating. From the flash zone the mixture of vapourised hydrocarbons and steam passes upwards and the condensed liquid descends. A temperature gradient is created through the column, from ~140°C near the top to ~360°C at the base by taking several side streams from selected trays at different levels in the column and cooling the streams before re-injection at a higher level. The required lubricant distillates are also withdrawn as sidestreams and are steam stripped to give the best possible separation between each fraction. A residue, typically boiling above 550°C at atmospheric pressure, is drawn from the column base. Distillation provides a limited number of fractions, usually three lubricant distillates, each of which has a viscosity and boiling range defined within a narrow range, and a residue. The quality and consistency of fractionation has considerable impact on all the subsequent process steps. Careful design and operation of the vacuum column should achieve the following desirable results:

– Minimum overlap in boiling range between fractions, noting however that some overlap is inevitable,

– Avoidance of entrained high molecular weight asphaltic components in the heaviest distillate fraction,

– Ability to take a very heavy distillate fraction, rather than losing this material in the distillation residue.

– Flexibility to run different crudes and still achieve design specifications for the properties of each lube fraction.

– Minimum energy usage.

Use of structured packing in past years together with good design of the flash zone region of the column has helped to achieve these aims on modern base oil plants. Re-vamping and modernisation of older columns has also given substantial benefits. The lubricant distillates and residue streams are run to heated intermediate tankage from where they are drawn to feed downstream process units.

2.11.3 De-asphalting

The residue from vacuum distillation is a black, very viscous material containing large amounts of asphaltic and resinous components. When these are removed, a useful high-viscosity base oil fraction, known as bright stock, is left. Low molecular weight hydrocarbons as solvents are effective at dissolving the more desirable compounds whilst leaving the asphaltic material as a separate phase. Liquid propane is by far the most, frequently, used solvent for de-asphalting residues to make lubricant bright stock, (Fig2.6) whereas liquid butane or pentane produces lower grade de-asphalted oils more suitable for feeding to fuel-upgrading units. Liquid propane is kept close to its critical point and, under these conditions, raising the temperature increases selectivity. A temperature gradient is set up in the extraction tower to facilitate separation. Solvent-to-oil ratios are kept high because this enhances rejection of asphalt from the propane/oil phase.

Countercurrent extraction takes place in a tall extraction tower. Vacuum distillation residue enters near the top of the tower, while propane enters near the base. The de-asphalted oil/propane phase, being lower in density, is taken from the top of the tower and the heavy asphalt phase leaves at the bottom. Steam heating coils provide the temperature gradient within the tower. Typical operating conditions are the following:

- Propane/vacuum residue volume ratio between 5–10:1

- Pressure 25–35 bar

- Top temperature 60–80◦C

- Base temperature 30–40◦C

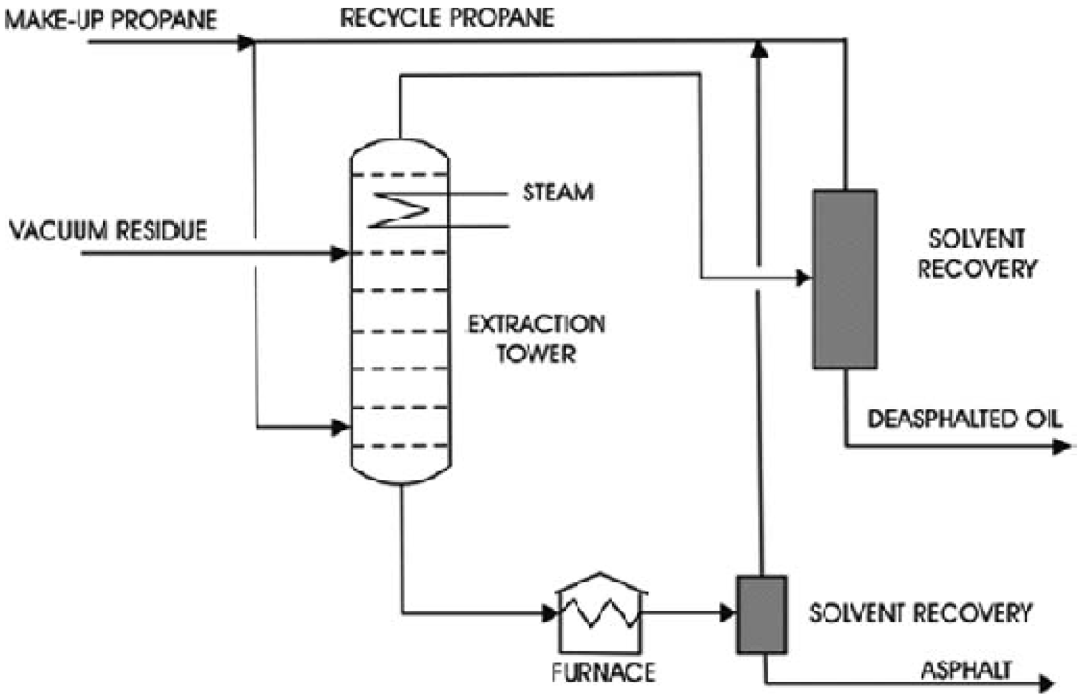


Figure 2.6: De-asphalting unit

2.11.4 Solvent Extraction

Solvent extraction replaced acid treatment as the method for improving oxidative stability and viscosity/temperature characteristics of base oils. The solvent selectively dissolves the undesired aromatic components, the extract, leaving the desirable saturated components, especially alkanes, as a separate phase. Choice of solvent is determined by a number of factors, such as:

- Selectivity, i.e. to give good yields of high-quality raffinate.
- Solvent absorption power, to minimise the solvent/oil ratio.
- Ease of separation of extract and raffinate phases.
- Ease of solvent recovery – its boiling point must be below that of the raffinate extract.
- Desirable solvent properties such as stability, safety, low toxicity, ease of handling and cost.

New plant units and conversions increasingly use N-methylpyrrolidone because it has the lowest toxicity and can be used at lower solvent/oil ratios, which save energy. Solvents used commercially include:

– Sulphur dioxide, historically important but rare nowadays.

– Phenol, now declining in use.

– Furfural, the most widely used.

– N-methylpyrrolidone, increasing in importance.

Each distillate or bright stock stream is processed separately because different process conditions are needed to obtain optimum results for each base oil grade. The main factors in operation of such a plant are the following:

Solvent/oil ratio**:** Increasing the solvent/oil ratio allows deeper extraction of the oil, removing more aromatics and, of course, decreasing the raffinate yield. Over-extraction should be avoided because good lubricant components may be lost.

Extraction temperature**:** Solvent power increases with temperature, but selectivity decreases until feed and solvent become miscible. Clearly, the extreme of complete miscibility must not be allowed. The use of temperature gradients in extraction towers aids selectivity.

Solvent/oil contact**:** The solvent and oil streams must be brought into contact, mixed efficiently and then separated into solvent and raffinate phases. The principal methods used are the following:

– Multi-stage mixing vessels, arranged in series so that flows of solvent and oil run counter-currently,

– Extraction towers packed with ceramic rings or with sieve trays. Flows of solvent and oil are counter-current as described in Section 2.11.3 on the de-asphalting plant. A temperature gradient is maintained within the tower.

– Extraction towers using a vertically mounted ‘rotating disc contact’. The spinning discs alternate with wall-mounted baffles and create a high shear mixing regime around the discs and allow excellent mixing. Rotor speed can be used as a control mechanism.

– Multi-stage centrifugal extractors both mix the incoming solvent and oil streams and separate the raffinate and extract products. They have advantages of small size and small hold-up volume.

2.11.5 Solvent De-waxing

The material which crystallises out of solution from lubricant distillates or raffinates is known as wax. Wax content is a function of temperature. As the temperature is reduced, more wax appears. Sufficient wax must be removed from each base oil fraction to give the required low-temperature properties for each base oil grade. Naphthenic feedstocks, of course, are relatively free of wax and do not normally require de-waxing. The molecular types within the wax fraction change as the boiling range of the feedstock increases. Linear alkanes crystallise easily in the form of large crystals and these are the predominant constituent of wax in the lighter distillates. Isoalkane waxes form smaller crystals and these predominate in the heavier fractions. In addition, as the temperature of de-waxing decreases, the molecular composition of the wax which crystallises out of solution also changes; the highest melting point components crystallise first. Different grades of wax can be separated from different viscosity feedstocks at different temperatures.

The original de-waxing method involved cooling the waxy oil and filtering with large plate and frame presses. Pressures up to 20 bar were applied to the wax cake to force the oil out. However, the process had severe drawbacks, being very labour intensive and oils of high viscosity could not be filtered at low temperatures. Filtration efficiency was greatly improved by diluting the oil with solvents such as naphtha, but selectivity for wax removal was reduced. Improved solvent systems have been developed to give better de-waxing performance. Important factors in the choice of solvent are the following:

– Good solubility of oil in the solvent and low solubility of wax in the solvent.

– Small temperature differences between the de-waxing temperature and the pour point of the de-waxed oil.

– Minimum solvent/oil ratios.

– Formation of large wax crystals, which are easily filtered.

– Ease of solvent recovery, i.e. low boiling point.

– Desirable properties such as stability, safety, low toxicity, ease of handling and cost.

Solvents in commercial use include propane, methyl isobutyl ketone and also mixed solvents such as methyl ethyl ketone/toluene or methylene dichloride/ dichloroethane. Using paired solvents helps to control oil solubility and wax crystallisation properties better than using a single solvent. A simplified flow scheme for a modern solvent de-waxing plant (fig 2.7). Solvent and oil are mixed together, then, progressively, chilled to the required temperature for filtration, which will be several degrees lower than the desired pour point. The rate of chilling influences the size and form of the wax crystals and the subsequent ease of filtration. Chilling takes place in special heat exchangers with mechanically driven scrapers to keep the pipe walls clear of solidifying wax, aid heat transfer and ensure that the oil/wax/solvent slurry remains mobile. Filtration is carried out on large rotary drum filters with suction applied to the inside of the, horizontally, mounted drum which, slowly, rotates with the lower part of the drum immersed in the chilled slurry. As oil passes through the filter cloth, a layer of wax (about 0.5 cm thick) builds up on the cloth and is, later, removed by a scraper blade or blown off by inert gas as the drum rotates.

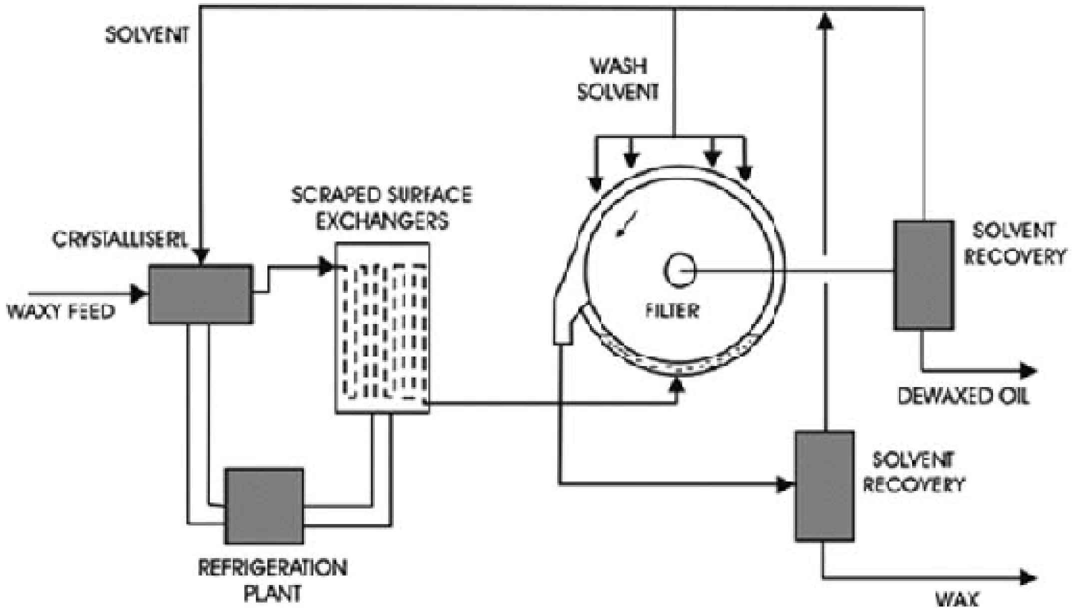


Figure: 2.7 Solvent de-waxing

2.11.6 Finishing

Despite the intensive series of process steps carried out so far, trace impurities may still be present in the base oil and a finishing step is needed to correct problems such as:

- Poor colour.
- Poor oxidation or thermal stability.
- Poor demulsification properties.
- Poor electrical insulating properties.

These undesirable components tend to be nitrogen-, oxygen- or, to a lesser extent, sulphur-containing molecules. In the past, selective adsorbents such as clay or bauxite were used to remove impurities but these processes were messy and gave waste disposal problems.

Hydrofinishing has almost completely taken over now and differs from all process steps described previously because it is not a physical separation procedure. It depends on the selective, catalysed hydrogenation of the impurities to form harmless products under relatively mild conditions. Yields of finished base oil are high (at least 95%) and costs are quite low. Hydrofinishing should be effective for removing organonitrogen molecules because they are, largely, responsible for poor colour and stability of base oils, while organosulphur molecules should be retained because they tend to impart natural oxidation stability to the base oil. (Dr.Roy, Dr.stevan et al, 2010).

Chapter Three

Material and Methods

Materials and Methods

3.1 Materials

1.Samples:

1- Petronas samples (fresh and used) 4 samples [0km, 3000 km,4000km, and 5000 km].

2- Petromin samples (fresh and used) 2 samples [o km and 5700 km].

Samples of multigrade gasoline engine oil SAE 20 W 50 API SL/CF (fresh and used) were investigated. Samples were withdrawn from car engine, directly, by suction. The cars monitored are in good, Mechanical, working conditions.

3.2 Methods

ASTM methods, were used to determine physicochemical properties of oils.

3.2.1. Determination of flash point

The specimen was filled to inside mark in the cup of the tester and closed with the lid. It was heated at slow constant rate. An ignition source was directed into the cup at regular intervals, the flash point was then recorded.

3.2.2. Determination kinematic viscosity

The viscosity was determined using ASTM D445, standard, method. A viscometer tube was filled with the sample of oil and placed on a viscosity bath maintained at 40 ^{0}C, the time needed by the sample to flow under gravity was recorded, the same procedure was repeated in a temperature 100 ^{0}C. The viscosity was calculated by multiplying the time in seconds by the viscometer factor.

3.2.3. Determination of total base number

The TBN was determined using ASTM D4739 standard method 10 g of the oil sample was dissolved in 125 ml of the solvent (chloroform-isopropane-toluene). The mixture was then titrated against 0.1M KOH.

3.2.4. Determination of density and relative density

The density was determined using ASTM D4052 standard method. A specific volume was withdrawn with a syringe, a small volume (approximately 0.7 ml) of liquid sample was introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube was used in conjunction with calibration data to determine the density of the sample, and the reading was recorded.

3.2.5. Determination of sulfated ash

The sulfated ash was determined using ASTM D874, standard, method. According few drops of sulfuric acid was added to 10g of the sample and then burnet on the flame in the crucible. Only ash and carbon remain ignited at 700 to 750 ^{0}C in muffle furnace for 30 min, the crucible was allowed to cool to room temperature and then weighed.

3.2.6. Determination of additive elements in fresh oil

The additive elements were determined using ASTM D4951, standard method. A sample portion is weighted and diluted by mass with mixed xylenes. An internal standard is combined with the dilution solvent. The solutions are introduced to the ICP instrument by pump; the concentrations of elements in the sample are calculated.

3.2.7. Color D1500

The degree of the color was recorded using the comparative color box.

3.2.8 Determination of element composition

Ten g of the oil sample was heated on flame and then ignited at 775 ^{0}C in furnace for 30 min. The crucible was cooled and the ash dissolved in 1:1 diluted hydrochloric acid. The volume was completed to 50 ml. The elements concentration was determined using atomic absorption spectrophotometer.

3.2.9. Ash ASTM D482

Ten g of the sample was burnt on the flame in crucible and then ignited at 775 ^{0}C in furnace for 30 min. The crucible was allowed to cool to room temperature and then weighed.

3.2.10. Carbon residue

Ten g of the sample was burnt on the flame in crucible and then ignited in 550 ^{0}C in a furnace for an hour; the crucible was allowed to cool to room temperature and then weighed.

Chapter Four

Results and Discussion

Result and discussion

4.1 Discussion

Table 4.1 Figure (4.1), (4.2) show the variations of viscosities of oils at 40^0C and 100°C before and after use. The results show that there is minor decrease and increase is viscosity of used oils. Decrease in viscosity may be due to fuel dilution. The increase of viscosity can be attributed to the oxidation of lubricants, contamination of solid particles and wear products sample 3 after (4000) use. (Susan A.Arendt, 2006)

Figure (4.4), (4.5) show flash point and sulfated ash. Flash point measurement show a slight decrease except sample 4 (5000). The decrease in flash point may be due to contamination of the fuel, but increase of flash points is associated with solids. The results for ash contents of all oils have increased. The increase in sulfated ash for used engine oils may be due to oxidation of oils.

Figure (4.6) shows that changes of Total Base Number values is largest in the new oils, and decrease by longer service time due to formation of acids. Low TBN value indicates that working life of oil is near the end.

Figures (4.7), (4.8) show the variation in density and API gravity. The increase in value of specific gravity of used engine oil is due to the presence of oxidation products (water and acids), heavy metals (Fe, Cu, Pb and Ni), and combustion products (sludge, and varnish). Decrease in API gravity indicates reduce of oil quality.

Table (4.1) physicochemical properties of new and used gasoline engine oil

Drain interval SAE 20 W 50 API SM		**New(0 km)**	**3000Km**	**4000Km**	**5000Km**
Test ASTM	**Test Method**	**Results**			
Appearance	**Visual**	**Clear**	**Dark brown**	**Dark brown**	**Dark**
V at 40 ^{0}C mm^2/s	D-445	169.6	109.9	123	115.3
Vat100 ^{0}C mm^2/s	D-445	17.53	13.98	15.12	14.64
Viscosity Index	D-2270	112	112	127	129
Flash Point ^{0}C	D-93	230	187	175	176
TBN mg KOH/g	D 4739	8.08	4.79	5.07	2.97
Water content	Crackle	-ve	-ve	-ve	-ve
Density at15^{0}C g/ml	D 4052	0.8864	0.8888	0.8885	0.8889
Specific gravity		0.8872	0.8896	0,8893	0.8897
API degree		27.99	27.56	27.61	27.54
Sulfated ash % wt	D 874	0.946	0.95	0.953	0.956
Insoluble Volume %	IP 316/93	0.94		in range	Max 2
Ca p.pm	AdditiveD-4951	2350	1736	2330	2271
Zn p.pm	AdditiveD-4951	1667	1063	1189	1472
P	Additive D-4951	1428	930	1053	1238
Cu p.pm	Wear D-4951	0.00	0.1130	1.436	1.096
Fe p.pm	Wear D-4951	0.6253	0.7758	13.06	25.17
Mg	Wear D-4951	101	697	202.9	222.8
Cr		0.514	0.0471	1.023	0.4646
Al p.pm	Wear D-4951	<0.0055	<0.0055	5.401	12.13
Si p.pm	Pollutant D4951	0.0086	<0.0086	<0.0086	<0.0086
Pb p.pm	Pollutant D4951	0.1012	0.1027	0.3007	0.4708

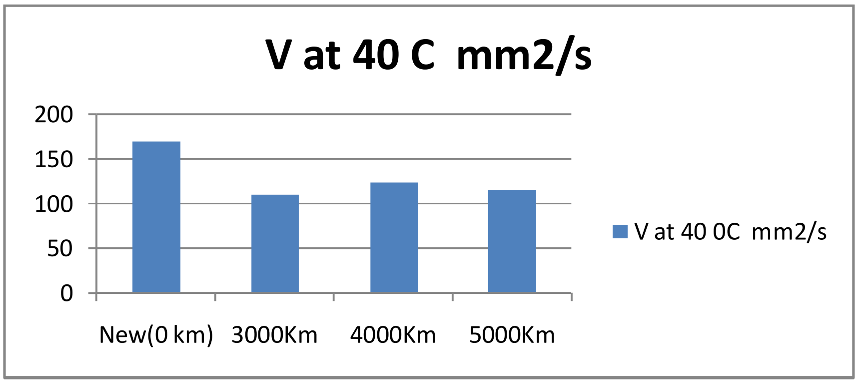


Fig 4.1 the change of viscosity at 40 ^{0}C with usage

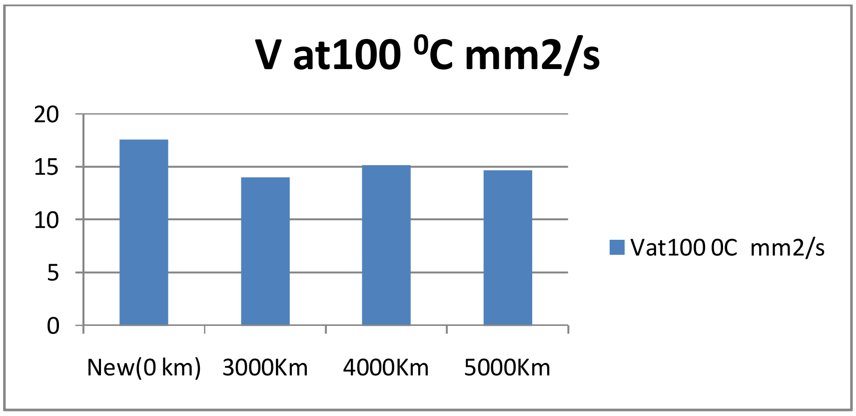


Fig 4.2 the change of viscosity at 100 with usage

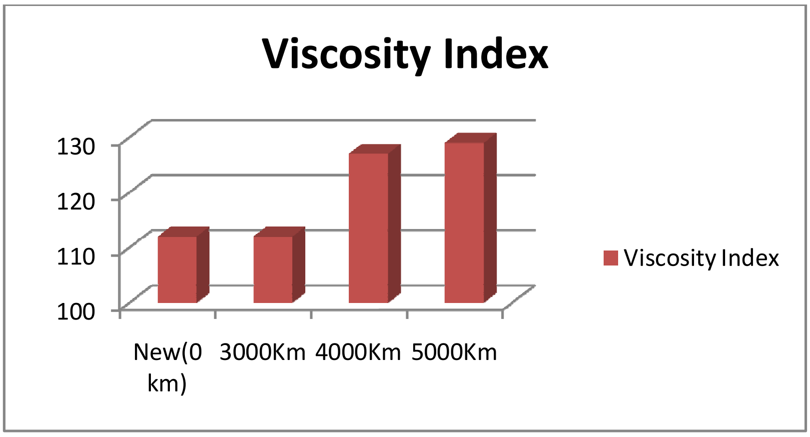


Fig 4.3 the change of viscosity index with usage

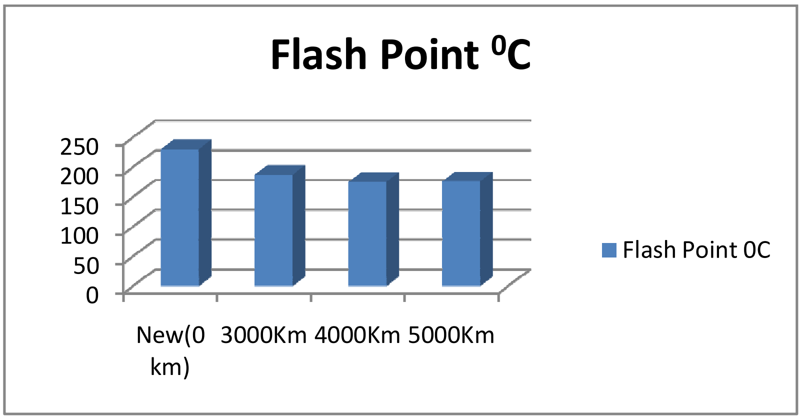


Fig 4.4 the change of flash point with usage

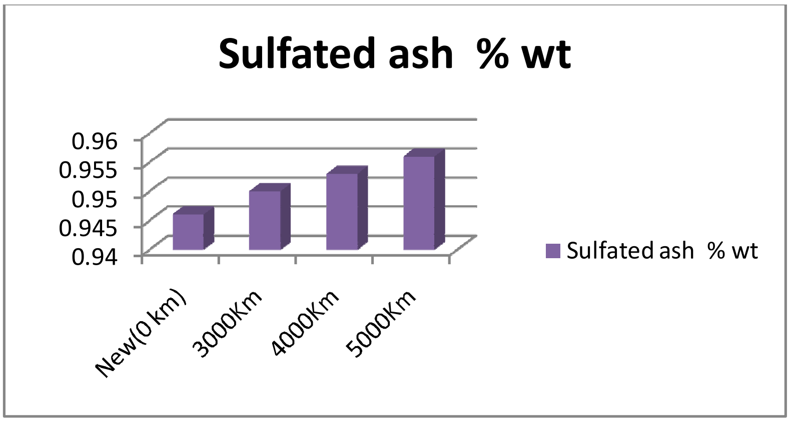


Fig 4.5 the change of sulfated ash with usage

in the usage

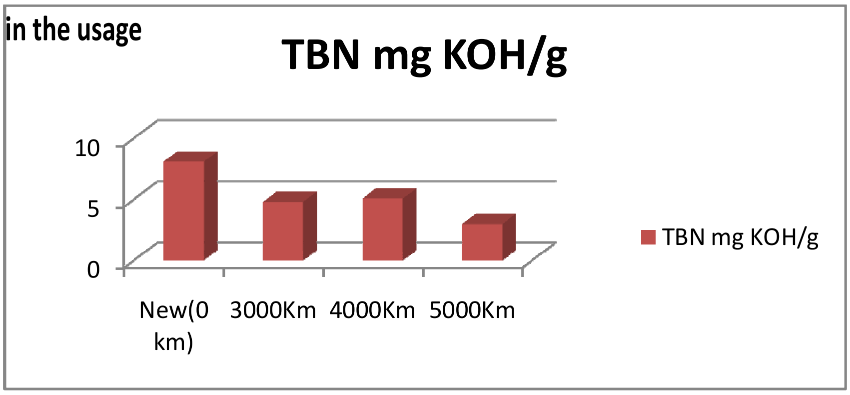


Fig 4.6 the change of TBN with usage

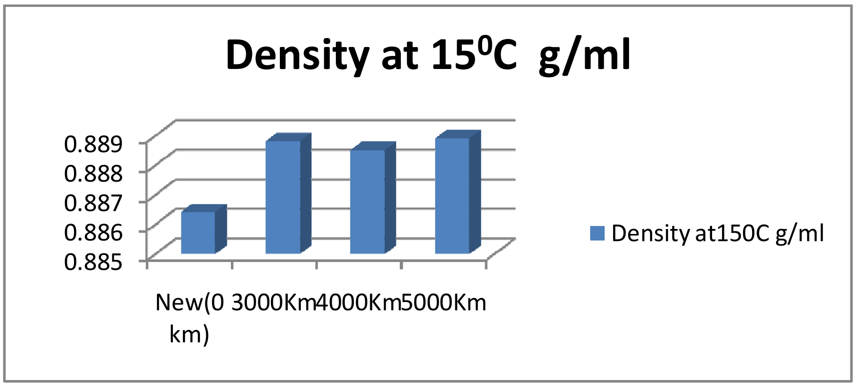


Fig 4.7 the change of density with usage

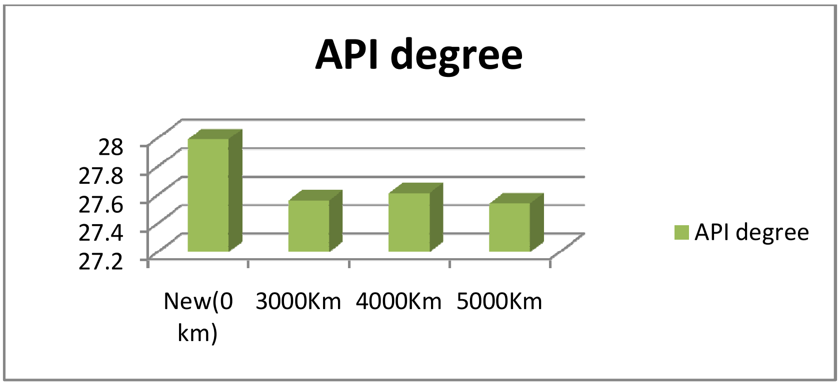


Fig 4.8 the API degree with usage

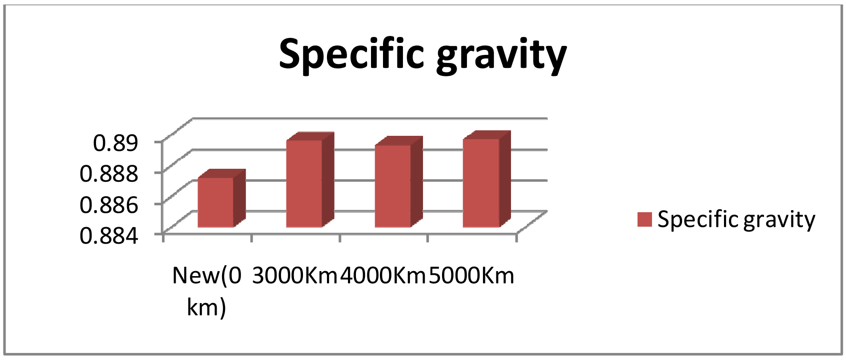


Fig 4.9 the specific gravity with usage

Figure (4.10) show decrease in the additive elements. The figures show the additives degraded and some of the resulting degradation products are absorbed by the filter, which result in lowering of the concentrations of the corresponding elements in the oil (Ca, Zn, Mg and P).

figures (4.11) and (4.12) shows a slight increase in wear and contaminant elements (Fe, Cu, Al), (Pb and Si) indicating that wear in the engine tribomechanical systems of all samples is within the allowed limits (Simon A.Watosn, 2010). Figure (4.10) show decrease in the additive elements. The figures show the additives degraded and some of the resulting degradation products are absorbed by the filter, which result in lowering of the concentrations of the corresponding elements in the oil (Ca and Zn).

Figures (4.11), (4.12) show the variation in API gravity and density. The increase in value of specific gravity of used engine oil is due to the presence of oxidation products (water and acids), heavy metals (Fe, Cu, Pb and Ni), and combustion products (sludge, and varnish). Decrease in API gravity indicates reduce of oil quality.

Table (4.2) show the change of properties of two different oils after 5000km.

Table(4.3) show motor oil physicochemical and allowed deviation values.

Table (4.3) figures (4.13), (4.14) and (4.15) show the variation of physicochemical properties of fresh and used oils(viscosity, Total Base Number, additive and wear elements). The viscosity is decrease in the order of 16.4% and 13.28 % respectively. The results indicate the composition of the elements, Ca, and Zn were increased slightly in the order of 3% and 11.9 % respectively for Petronas and 12 % and 25.9 % respectively for Peromin. All above results are in allowed limits table(4.4). The decrease of additives in Petromin oil is larger than Petronas oil. The measurement of TBN show decrease of 62.8 % for petronas oil. That means the oil is degraded and must be changed.

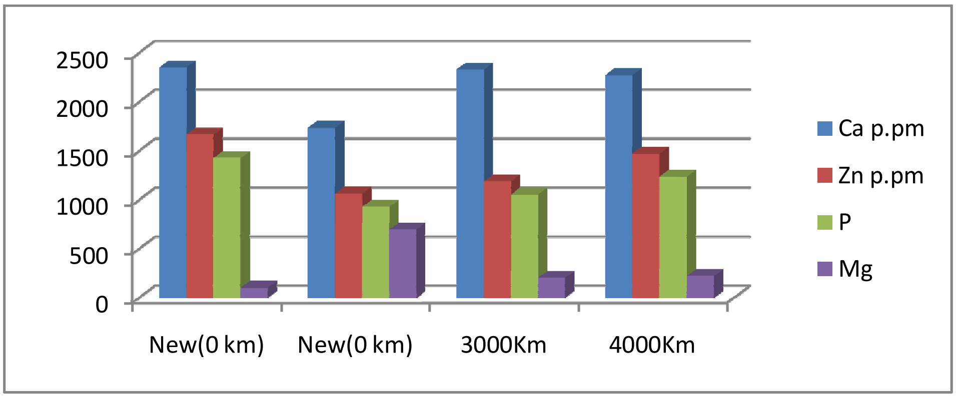


Fig 4.10 the change of the additive element Ca, Zn, P, Mg with usage

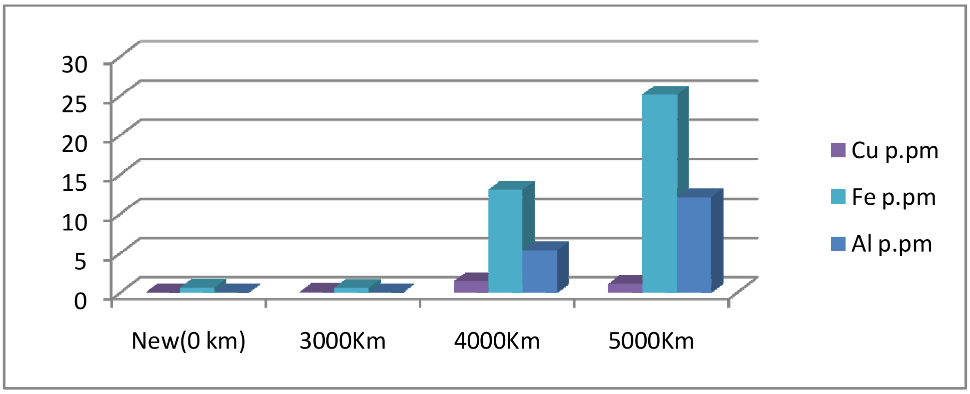


Fig 4.11 the change of the wear element Cu, Fe, Al with usage

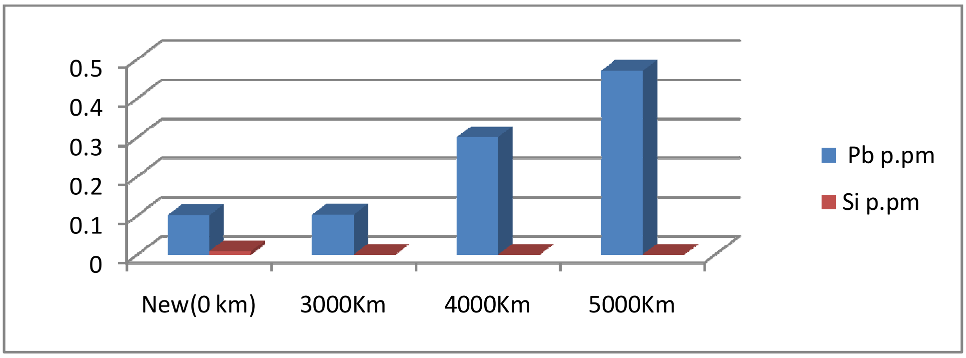


Fig 4.12 the change of the contaminate element Pb, Si with usage

Table 4.2 The change of properties of two different oils after 5000km

SAMPLES	PETRONAS			PETROMINE		
Test method	0 km	5000 km	Change %	0 km	5700 km	Change %
Vat100 ^{0}C mm^2/s	17.53	14.64	16.48%	19.2	16.65	13.28%
TBN mg KOH/g	8.08	3	-62.8%	7.6	5.65	25.65%
Ca p.pm	2350	2271	3 %	2374	2085	12 %
Zn p.pm	1667	1472	11.9 %	1180	873.2	25.9%
Cu p.pm	0.04	1.4	97.14	0.1161	0.4173	72.18
Fe p.pm	0.5	2.5	80	2	5.002	60.01
Si p.pm	0.011	0.01	9.09	9.14	8.14	10.9
Pb p.pm	0.1	0.471	87.7	1	1.05	47.61

Table 4.3 Motor oil physicochemical and allowed deviation values

Oil analysis test	Maxi allowed variation
Viscosity	± 20 %
Viscosity index	± 5
TBN	Degradation to 50 %
Iron (Fe) ppm	100
Silicon ppm	30
Copper ppm	50
Pb ppm	100

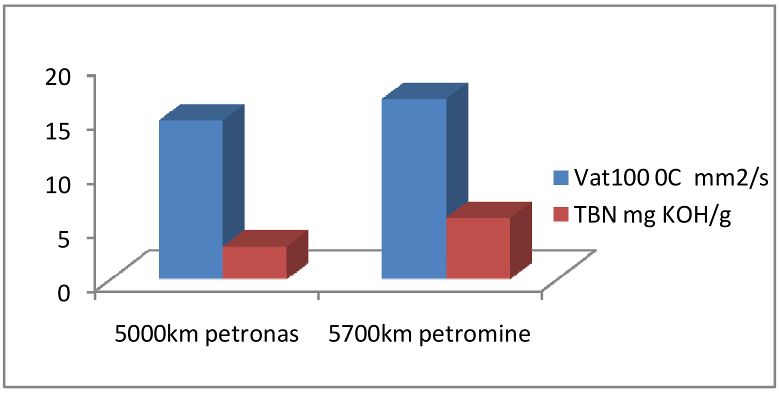


Fig 4.13 the change in viscosity and TBN for petronas and petromin

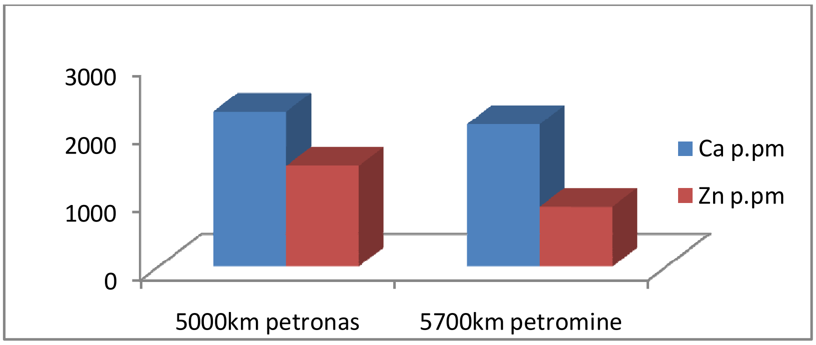


Fig 4.14 the change in additives for petronas and petromin

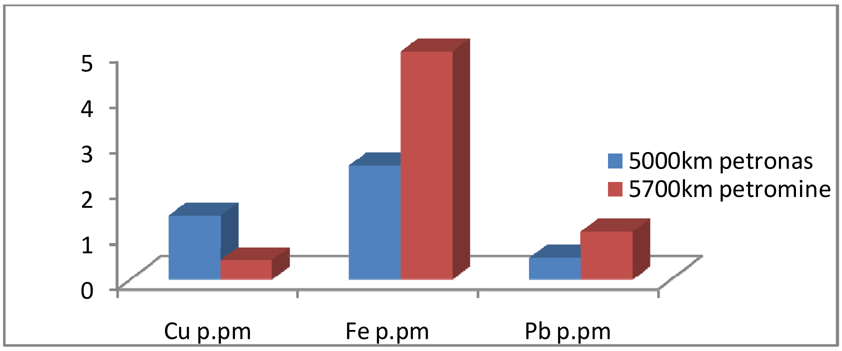
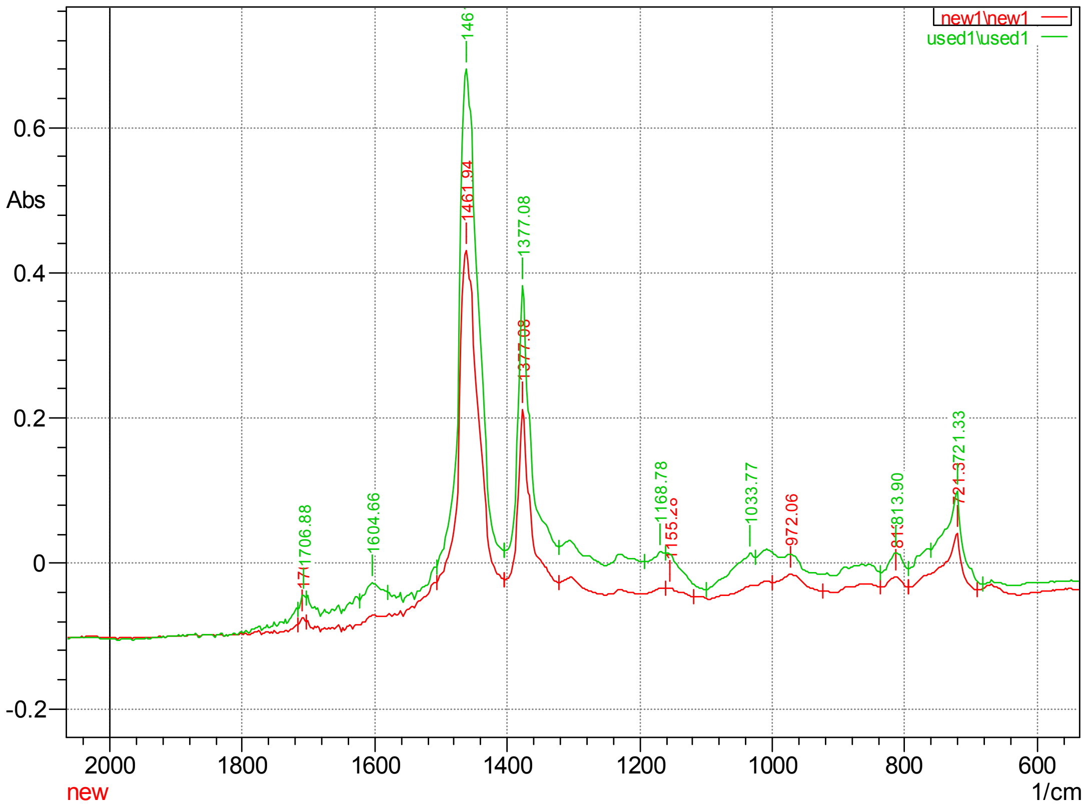


Fig 4.15 the change in wear element for Petronas and Petomin

Table (4.4) Parameters and spectral location cm $^{-1}$

Parameters	Spectral location	Result
Soot	1980 cm $^{-1}$	1.33
Oxidation	1720 cm $^{-1}$	3.33
Sulfation	1150 cm $^{-1}$	8.893

Figure 4.16 show the IR spectrum of new and used engine oil the products of oxidation process caused by oxygen weren't monitored in the area of 1720 cm $^{-1}$, soot was monitored at 1980 cm $^{-1}$ nitration (organic nitrate) were monitored at 1630 cm^{-1} and products of suffocation occurred in the region of 1150 cm $^{-1}$Neil Robinson. (Michael Carry, 2007).



Parameters and spectral location cm $^{-1}$

Conclusion

- The Results indicate a decrease in Total Base Number (TBN), Ca, Mg, and Zn in used engine oils. And show negligible changes in corrosion elements (iron, and copper), slight increase indicate to extended machine life.
- Analysis of the degradation oils by FTIR method enables to determine both the current condition and the operating life of the oil.
- A decrease in the total base number (TBN) as a result of the oxidation processes was observed in most samples accompanied by the expected depletion of the additives content. Minor wear was also observed which is related to the frictional processes.
- Minor or no significant changes were observed in flash points and viscosity indicating that no significant penetration of fuel into the lubrication system.
- In some oils all the above mentioned changes were not significant suggesting a better oil quality and/or a better additives formulation.
- Oxidation, nitration and sulfation components are not reported as concentration values, because there are many different chemical compounds formed that contribute to the measured absorption.
- Petronas oil is suitable for Sudan environmental conditions because it contains appropriate antioxidant additives which act against oxidation promotion by high temperature.
- Multi-grade oil can be used in new models, because is suitable for both cold and hot weather (for all seasons) and for long distances at high speeds.

- Used oil can be treated to produce base oil (reduce environmental pollution).

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