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the Award of Master Degree in Industrial Chemistry

Titled

Recycling of Used Engine Oil

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2019
DECLARATION

I, Student of Faculty of Pure and Applied Sciences, International University of Africa, hereby declare that I have completed the research on “Recycling of Used Engine Oil” in partial fulfillment of the requirements for the award of Master Degree in Industrial Chemistry. The information submitted is true and original to the best of my knowledge.

Name: Elamin Osman Elamin

Signature
Dedication

To my Mother..
To my Father..
To my Wife..
To my Children..
To my Brothers and Sisters..
& my Friends..

Elamin
Acknowledgement

I am greatly indebted to my supervisor Dr. Azhari Hamid Noor for his help, guidance, support and encouragement which was the real motivation for me to complete this work.
ABSTRACT

Lubricating oils are made from base oil and mixing of certain other chemicals (additives) for improving their certain properties. Engine oil is used to lubricate moving parts of engine, reducing friction, protecting against wear, and removing contaminants from the engine. Moreover, act as a cleaning agent, as an anticorrosion and cooling agent. This research effort focuses on comparative study of re-refined used engine oil by extraction of composite solvent and single solvent methods. Composite solvent was made-up of (ethanol, isopropyl alcohol and toluene) and isopropyl alcohol used as single solvent. Extraction had been carried out at two different temperatures (40 and 60 °C) and solvent to oil ratios of (1:1) and (2:1). Different properties such as viscosity; calcium and zinc content and total base number in order to know the degree of treatment of regenerated oil and waste oil were analyzed. The regenerated oil compared with virgin base oil (SN 500) by using Fourier Transform Infra-Red (FTIR) technique in order to know the correlation between them. On the basis of experimental work, it was found that the calcium and alkalinity contamination which are came from additive of detergent, zinc which is came from additive of anti-wear were decreased for both composite and single solvents. The results from the viscosity, viscosity index, and FTIR spectrum were improving at different degrees when compared with virgin SN 500, but the best results observed when used an isopropyl alcohol as single solvent and extraction temperature of 40 °C. Regenerated oil can be improving further process of metal removal by using metal adsorption agent, such as zeolite. Therefore, in future, may warrant more investigation on parameters such as other solvents and temperatures in order to compare with current studied parameters.
الملخص

تصنف زيوت التشحيم من زيوت الأساسي وخلطها ببعض المواد الكيميائية الأخرى (المضافات) لتحسين خصائصها المعنوية. يستخدم زيت المحرك لزيت الأجزاء المتحركة من المحرك، مما يقل الاحتكاك والحماية من التآكل وإزالة الملوثات من المحرك. علاوة على ذلك، يعمل كعامل منظف، كعامل مضاد للتآكل و كعامل تبريد. يركز هذا الجهد البحثي على دراسة مقارنة إعادة تكرير زيت المحرك المستخدم بطريقة الاستخلاص بخلط من المذيبات مرة و مذيب واحد مرة أخرى. يتكون خليط المذيبات من الإيثانول وكحول الأيزوبروبيل والتوتولوين؛ تم استخدام الكحول الآيزوبروبيل كمذيب واحد. تم إجراء الاستخلاص عند درجتي حرارة مختمفتين (40 و 60 درجة مئوية) و نسب المذيبات بالنسبة للزيت هي (1: 1) و (2: 1). تم تحليل الخصائص المختلفة للزيت المكرر والزيت المستخدم، مثل اللزوجة، محتوى الكالسيوم والزنك والرقم القيادي لمعرفة درجة المعالجة. تم مقارنة الزيت المكرر بزيت الأساس البكر (SN500) من أجل معرفة العلاقة بينهما باستخدام تقنية الإشعة تحت الحمراء Fourier Transform Infra-Red (FTIR). من العمل التجريبي، وجد أن ثلث الكالسيوم والقلوية التي تأتي من واحدة من المواد المضافة تعمل كمنظف، والزنك الذي يأتي من مادة مضادة للتآكل قد انخفض لكل من خليط المذيبات والمذيب الواحد. من نتائج اللزوجة، ومعامل اللزوجة، وطيف الإشاعة تحت الحمراء، هناك تحسن بدرجات مختلفة عند مقارنتها مع زيت الأساسي البكر، ولكن شهدت أفضل النتائج باستخدام كحول الأيزوبروبيل كمذيب منفرد عند درجة حرارة إستخلاص 40 درجة مئوية. يمكن تحسين الزيت المكرر من خلال عملية إضافية لإزالة المتبقي من المعادن الثقيلة باستخدام عامل إمتصاز المعادن، مثل الزيوليت. لذلك، في دراسات مستقبلية، قد يستدعي إجراء مزيد من التحقيق حول ظروف الاستخلاص مثل استخدام مذيبات أخرى ودرجات حرارة مختلفة من أجل مقارنة مع الظروف التي تم دراستها حاليا.
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<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Material</td>
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<tr>
<td>AW</td>
<td>Anti-Wear</td>
</tr>
<tr>
<td>BN</td>
<td>Base Number</td>
</tr>
<tr>
<td>EP</td>
<td>Extreme Pressure</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infra-Red</td>
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<tr>
<td>ICP-AES</td>
<td>Inductively Coupled Plasma Atomic Emission Spectrometry</td>
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<tr>
<td>MEK</td>
<td>Methyl Ethyl Ketone</td>
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<tr>
<td>PAG</td>
<td>Poly Alkylene Glycol</td>
</tr>
<tr>
<td>PAO</td>
<td>Poly Alpha Olefin</td>
</tr>
<tr>
<td>PCB</td>
<td>Poly Chlorinated Biphenyl</td>
</tr>
<tr>
<td>SAE</td>
<td>Society of Automotive Engineers</td>
</tr>
<tr>
<td>SG</td>
<td>Specific Gravity</td>
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<tr>
<td>UOPs</td>
<td>Universal Oil Products</td>
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<tr>
<td>VI</td>
<td>Viscosity Index</td>
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<td>ZDDP</td>
<td>Zinc Diphenyl Dithio Phosphate</td>
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LIST OF SYMBOLS

cSt  Centistoke (Unit of Kinematic Viscosity)
°C  Degree Celsius (Unit of Temperature)
mgKOH/g  Milligram Potassium Hydroxide Per Gram Sample (Unit of Base Number)
mL  Milliliter (Unit of Volume)
ppm  Part Per Million (Unit of concentration)
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CHAPTER ONE
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1.1. Lubricating Oils and Their Function

The most important petroleum fraction is lubricating oil that is use in almost all vehicles and machines. A lubricant performs many diverse functions, which help protect and prolong the life of the equipment. These include the following:

1.1.1. Lubrication (reduce friction and wear): Lubricant helps reduce friction and wear by introducing a lubricating film between mechanical moving parts, such as gears and bearings. Essentially, the presence of a lubricating film minimizes the metal-to-metal contact and reduces the force necessary to move one surface against the other, thereby reducing wear and saving energy.

1.1.2. Cooling (heat transfer): Lubricant acts as a heat sink and dissipates the heat away from the critical moving parts of the equipment, thereby decreasing the possibility of the machine component deformation and wear. The heat is either frictional heat that results from the metal surfaces rubbing against one another, such as in gears, or is conducted and radiated heat, which is due to the close proximity of the parts to a combustion source, such as the combustion chamber in an automobile engine.

1.1.3. Cleaning and Suspending: Lubricant facilitates smooth operation of the equipment by removing and suspending potentially harmful products, such as carbon, sludge, and varnish, and the other materials, such as dirt and wear debris. This lubricant function is important in operations that involve high operating temperatures, as in the case of an internal combustion engine or a transmission. This is because in these applications the lubricant gets oxidized to form deposit precursors that can separate on hot surfaces and get converted into deposits.

1.1.4. Protection: Lubricant prevents metal damage due to oxidation products, corrosion, and wear. It achieves this by forming a physical film on metal surfaces that is impervious to oxygen, water, and acids, or by forming physical and chemical films by additives, such as rust and corrosion inhibitors, extreme-pressure (EP) additives, and anti-wear agents, that are present in the lubricant (Minami 2017; Rizvi, 2009).

1.2. Lubricant Deterioration

As mentioned above, the main requirement of engine lubrication oil is to lessen the wear on the engine parts, reduces corrosion, clean, improves sealing and to reduce the heat from the engine. If this oil is not frequently changed, dirt and sludge can
develop on the engine and this old and impure oil won't properly lubricate the engine moving parts such like new lubrication oil does. Dirty oil can cause the serious damage, and if it continues as bad enough, it can be even an engine replacement happens in the near forthcoming period (Rammohan, 2016).

Lubricants lose their effectiveness during use, due to degradation. The degradation rate depends upon operation severity, time in service, system temperatures, make-up rate, and the environmental conditions. Lubricant degradation may result from both physical and chemical factors, some of which are a result of extraneous contamination (Rizvi, 2009). Used oil is any petroleum based or synthetic oil that has been used. During normal use, impurities such as dirt, metal scrapings, water or chemicals can get mixed in with the oil or be generated in it due to thermal degradation or oxidation. Therefore, the oil quality gradually decreases to a level that, the used oil should be replace by a new one (Haider et al., 2013).

Used oil creates environmental pollution if not disposed properly; there is a possibility that substances that it may contain enter natural cycles through the food chain via water, soil and air. In this way, used oil pose risk to human health and impedes the growth of plants and their ability to take up water as sometimes used oil contained hydrocarbons, heavy metals, polychlorinated biphenyl (PCBs) and other halogenated compounds detergents and lubrication additives. Used lubricating oil must be disposed of properly, if burnt as a low-grade fuel, harmful metals and other pollutants may be released into air (Haider et al., 2013).

In addition to the environmental problems, improper used oil disposal is simply a waste of a valuable resource. Every gallon of used motor oil not recovered results in the need to drill for more oil and in some cases it results in increases in oil import. Today, however, most of the crude petroleum produced throughout the world contains very little of the special hydrocarbon chains necessary for motor oil. As a result, refining crude petroleum to produce virgin lube oil is an elaborate, complex, and expensive process that requires nearly three times as much energy as re-refining used oil (Haider et al., 2013).
1.3. **Objectives of the Study**

1. To recover base oil from used engine oil by solvent extraction process
2. To characterize the recovered base oil
3. To compare the properties of recovered base oil with the virgin oil

1.4. **Scope of the Study**

This study effort focuses on comparative study of re-refined used engine oil SEA 40 by extraction of composite and single solvent methods. Composite solvent was made up of ethanol, isopropyl alcohol and toluene; isopropyl alcohol was used as single solvent. Extraction had been carried out at two different temperatures (40 and 60 °C) and solvent to oil ratios of (1:1) and (2:1). The characterization of regenerated base oil it was included tests of kinematic viscosity at (40 and 100 °C), viscosity index, base number, zinc and calcium content and compared to the virgin base oil by using FTIR with correlation criteria 90%.

1.5. **Significance of the Study**

The presents various parameters of how the solvents used could effectively treat and remove contaminants from the used engine oil, which can help in improvement of used oil re-refining process, which is consider as one of important processes because, the recycling of used oil reduce dependence on base oil imports saving foreign exchange, prevent ground water contamination and pollution, and eliminate improper burning of waste oil as fuel, which generate toxic fumes and air pollution. Moreover, the results obtained from this study could be part of literature which adding knowledge in the field.
CHAPTER TWO
LITERATURE REVIEW
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LITERATURE REVIEW

2.1 Tribology

Tribology is the science of “Tribein.” The word comes from the same Greek root as “Tribulation.” A faithful translation defines tribology as the study of rubbing or sliding. The modern and broadest meaning is the study of friction, lubrication, and wears (Ludema, 1996).

2.2 Lubrication Regimes

When we talk about lubrication, we usually imply liquid lubrication that is by the use of lubricating oil, which is normally a blend of oil and additives that perform various functions. Lubrication efficiency of an oil depends not only upon its properties, such as composition, consistency, flow properties, and surface activity, but also on the needs of the tribological system. Lubrication environments, often called lubrication regimes. The primary functions of a lubricant are to minimize friction between the surfaces in contact, prevent wear, and remove frictional heat. Tribological parameters that usually define a lubrication environment are friction, lubricant viscosity, and the equipment speed and load.

The relationship of the coefficient of friction (μ) and the oil film thickness to lubricant viscosity (Z), equipment speed (N), and equipment load, or pressure (P). The ratio of ZN/P is related directly to the oil film thickness but inversely to the coefficient of friction (μ). This implies that high lubricant viscosity (Z), high equipment speed (N), and low equipment load (P) will allow the formation of a thick lubricant film, and hence the equipment will encounter little or no friction. Depending upon the lubricating environment, lubrication regimes can be dividing into fluid-film, boundary, mixed-film, and hydrostatic types.

2.2.1 Fluid-Film Lubrication

Fluid-film lubrication, also known as hydrodynamic lubrication, is the most desirable type. This type of lubrication depends upon the viscosity of the lubricant and is effective only when the load in the contact zone is low.
2.2.2. **Boundary Lubrication**

Boundary lubrication represents the opposite extreme of the lubrication environment spectrum. Under this kind of lubrication, high loads and very slow speeds produce extreme pressures that can lead to the lack of effective lubrication. The film thickness in this regime is in the order of 0.0 –2.0 µm only, and hence maximum metal-to-metal contact occurs. If not controlled, the resulting dry metallic friction will cause catastrophic wear, and ultimately will lead to total seizure. Reactive chemicals called anti-wear and extreme pressure agents provide protection in this kind of lubrication environment.

2.2.3. **Mixed-film Lubrication**

Mixed-film lubrication falls between the two extremes mentioned above and contains characteristics of both the fluid film and the boundary lubrication. There are regions of no metal-to-metal contact and of extensive metal-to-metal contact.

2.2.4. **Hydrostatic Lubrication**

Unlike the other types of lubrication discussed above, hydrostatic lubrication has the advantage of not depending upon the motion of the surfaces. Hence, this type of lubrication is invaluable in applications that involve little or no surface movement. This lubrication regime is characterizing by the lack of wear, low friction, high load capacity, and the ability to dampen vibration (Rizvi, 2009).

2.3. **Source of Lubrication and Base Oil:**

In terms of volume, base oil is the most important component in lubricants. The average base oil fraction is more than 95% in lubricant formulations. Some lubricant series, such as hydraulic or compressor oils, contain base oil concentrations as high as 99%. With growing requirements for environmentally compatible high-performance lubricants, base oils will play a major role in the development of new high-performance lubricants. To achieve excellent lubricant performance, the base oil itself must have good tribological properties (Gao et al., 2015). Base oil is derived from three sources: petroleum (mineral oil), synthetic, and biological, i.e., plant or animal in origin.
2.3.1. *Mineral Base Oil*

A vast majority of lubricants are based on mineral oils, which is because of their low cost, ready availability, and overall adequate performance. Since the base fluid makes up the bulk of the lubricant, its properties greatly impact the properties of the lubricant. The properties of a mineral base stock depend on its source, viscosity, and the degree of refining. As stated before, mineral base stocks or oils are classified on the basis of the predominant hydrocarbon type present in their composition, that is, as paraffinic, naphthenic, and aromatic, or bright stocks. Unfortunately, the hydrocarbon-based classification is not clear cut but is vague because these base stocks are manufactured based on viscosity and not on structural composition. Hence, neither base stock is purely paraffinic, naphthenic, or aromatic, but is a blend of all three types of hydrocarbons.

While each type of hydrocarbons has its own advantages and disadvantages, the quality of base oil is primarily determine by its viscosity index, low-temperature properties (pour point), and volatility (flash point). In terms of the chemical composition, the aromatics in the base stocks are usually undesired and a relatively lower amount of linear, or normal, paraffins is preferred. This is because aromatics have a low viscosity index (VI) and impart oxidative instability to the base stock. On the other hand, normal paraffins have good VIs, but they have high pour points because of the tendency to crystallize at low temperatures to form network structures. Incidentally, branched paraffins also have good VIs and reasonable pour points, but they are somewhat more volatile than their unbranched counterparts. Hence, the base oil manufacture has the primary objectives of lowering the amount of the aromatics and improving the pour point. These objectives are achieved by either removing the aromatics via solvent extraction or by converting them into naphthenes through hydrotreating. Normal paraffins are removed through dewaxing.

2.3.2. *Synthetic Base Oil*

These man-made (synthetic) base oils possess certain advantages over mineral base oils, which make their use more suitable in lubricants that are employed in applications that experience temperature extremes or operating conditions, or both. Synthetics have a number of advantages or disadvantages over the mineral oils which pertain to the following properties (Rizvi, 2009).
1. Thermal stability
2. Oxidation stability
3. Viscosity-temperature behavior
4. Tribological properties (lubricity and load-carrying properties)
5. Corrosion resistance
6. Volatility
7. Biodegradability
8. Toxicity
9. Compatibility with other materials
10. Miscibility with mineral oils
11. Solvency (additive solubility)
12. General availability and only in certain viscosity grades
13. Cost

Of the total worldwide synthetic base stock volume, three classes of materials represent over 80% were:
- Polyalphalifene PAO (45%)
- Esters, including dibasic ester and polyol esters (25%)
- Polyalkleneglycol (PAG) (10%).

Other smaller volume synthetic base stocks include alkylaromatics, such as alkylbenzenes and alkynaphthalenes, polyisobutylene, phosphate esters and silicone fluids. Among these synthetic base stocks, with the exception of phosphate esters and silicones, the starting materials all derived from basic petrochemicals - ethylene, propylene, butenes, higher olefins, benzene, toluene, xylenes, and naphthalenes. As expected, the major producers of PAO, esters, PIB and alkylaromatics are integrated petroleum companies that supply conventional mineral oil base stocks and petrochemicals as well as various synthetic base stocks. PAG, phosphate esters and silicone fluids are manufactured by chemical companies that produce these fluids on a much larger scale mainly for other applications. Their use as lubricant base stocks is only a fraction of the total market. (Wu et al., 2007).

a. **API Base oil categories**

The American Petroleum Institute (API) has categorized base oils into five categories. The first three groups are refined from petroleum crude oil. Group IV base oils are full synthetic (polyalphaolefin) oils. Group V is for all other base oils not
Table 2.1: API Base Oil Categories

<table>
<thead>
<tr>
<th>Base Oil Category</th>
<th>Sulfur (%)</th>
<th>Saturates (%)</th>
<th>Viscosity Index</th>
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<tr>
<td>Group I</td>
<td>&gt; 0.03</td>
<td>and/or</td>
<td>&lt; 90</td>
</tr>
<tr>
<td>Group II</td>
<td>≤ 0.03</td>
<td>and</td>
<td>≥ 90</td>
</tr>
<tr>
<td>Group III</td>
<td>≤ 0.03</td>
<td>and</td>
<td>≥ 90</td>
</tr>
<tr>
<td>Group IV</td>
<td>All Polyalphaolefins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Group V</td>
<td>All others not included in the above groups</td>
<td></td>
<td></td>
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b. Base Oils Compatibility and Additive Solubility

While inter-compatibility of the mineral oil-derived lubricants is not a problem, the inter-compatibility of the synthetics is and so is their compatibility with the mineral oils. This is because not all synthetics are compatible with mineral oils or with one another. This is because of the polarity difference among them. Besides compatibility, the polarity of the base oil plays an important role in many other applications. For example, blends of polar esters with nonpolar polyalphaolefins or paraffinic base oils have better viscometrics, as well as good lubricating ability.

The ability to dissolve additives, or solvency, of a base stock is a related problem. Most additives, except some viscosity improvers or some pour point depressants, contain hetero atoms, nitrogen, oxygen, sulfur, and phosphorus. Their presence makes these additives highly polar in a manner similar to that of the esters and PAGs, therefore raising the question of compatibility. While polar base stocks are quite compatible with the most classes of additives, PAOs sometimes have difficulty in keeping the additives dissolved. This is overcome by co-blending with either a mineral oil, an ester, and or an alkyl aromatic (Rizvi, 2009).

2.3.3. Biological (Natural) Base Oils

There has been a great deal of renewed interest in the use of oils from sources that are easy to replenish; such as animal fats and vegetable oils, to formulate lubricants. In addition to the advantage of continuous supply far into the future, these oils possess other properties that are important in their own right. A high degree of biodegradability and ongoing uncertainty over the crude oil supply and its price.
Lubricants from the mineral base oils are not always compatible with the environment; hence, the disposal of mineral oil-based used lubricants poses a problem.

Animal fats and vegetable oils occur in nature and are therefore biodegradable. As a result, the disposal of lubricants containing them is of less concern. Interest in biodegradable lubricants, such as those derived from the natural oils, has historically been in response to the environmental concerns, particularly relating to the effects of the oil entering the soil and the fresh water. Therefore, the lubricants used in agriculture, forestry, and marine applications are formulated by the use of biodegradable and nontoxic synthetic and natural ester base stocks (Rizvi, 2009).

2.4. Lubricant Additives

Additives are chemical compounds added to lubricating oils to impart specific properties to the finished oils. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life (Abo-Hatab et al., 2018; Trivedi et al., 2015).

2.4.1. Polar Additives

Additive polarity is defined as the natural directional attraction of additive molecules to other polar materials in contact with oil. In simple terms, it is anything that water dissolves or dissolves into water. A sponge, a metal surface, dirt, water and wood pulp are all polar. Things that are not polar include wax, Teflon, mineral base stock, a duck’s back and water repellents.

It is important to note that additives are also sacrificial. Once they are gone, they’re gone. Think about the environment you work in, the products you produce and the types of contaminants that are around you daily. If you are allowing into your system contaminants that additives are attracted to, such as dirt, silica and water, the additives will cling to contaminants and settle to the bottom or will be filtered out and deplete your additive package (Noria, 2018).

2.4.2. Additive Dosage

When using oil additives, more is not always better. As more additive is blended into the oil, sometimes there isn’t any more benefit gained, and at times the performance actually deteriorates. In other cases, the performance of the additive
doesn’t improve, but the duration of service does improve. In addition, increasing the percentage of a certain additive may improve one property of an oil while at the same time degrade another. When the specified concentrations of additives become unbalanced, overall oil quality can also be affected. Some additives compete with each other for the same space on a metal surface. If a high concentration of an anti-wear agent is added to the oil, the corrosion inhibitor may become less effective. The result may be an increase in corrosion-related problems (Noria, 2018).

2.4.3. **Types of Lubricant Additives**

Practically all types of lubricating oil contain at least one additive, and some oils contain several different types of additives. The amount of additive used varies from a few hundreds of a percent to 30% or more. Over a period of many years, oil additives were identified that solved a variety of engine problems: corrosion inhibition, ability to keep particles such as soot dispersed, ability to prohibit acidic combustion products from plating out as varnish on engine surfaces, and ability to minimize wear by laying down a chemical film on heavily loaded surfaces. In addition, engine oil became specialized so that requirements for diesel engine oils began to diverge from requirements for gasoline engines, since enhanced dispersive capability needed to keep soot from clumping in the oil of diesel engines (Ahmed and Nassar, 2011). The more commonly used additives will discuss in the following sections.

a. **Anti-oxidants**

One of the most important aspects of lubricating oils is that with maximum stability of oxidation. Exposure of hydrocarbons to oxygen and heat will accelerate the oxidation process. The internal combustion engine is an excellent chemical reactor for catalyzing the process of oxidation. Also, the engine's metal parts, such as copper and iron, act as effective oxidation catalysts. Thus, engine oils are probably more susceptible to oxidation than any other lubricant application. However, any lubricating oil exposed to air and heat will eventually oxidize. Antioxidants are the key additive that protects the lubricant from oxidative degradation, allowing the fluid to meet the demanding requirements for use in engines and industrial applications. Several effective antioxidants classes have been developed over the years and have seen use in engine oils, automatic transmission fluids, gear oils turbine oils, compressor oils,
greases, hydraulic fluids, and metal-working fluids. The main classes of oil-soluble organic and organometallic antioxidants are the following types:

1. Sulfur compounds
2. Phosphorus compounds
3. Sulfur-phosphorus compounds
4. Aromatic amine compounds
5. Hindered phenolic compounds
6. Organo-alkaline earth salt compounds
7. Organozinc compounds
8. Organocopper compounds

b. **Rust and Corrosion Inhibitors**

These additives reduce or eliminate internal rust and corrosion by neutralizing acids and forming a chemical protective barrier to repel moisture from metal surfaces as shown in Figure (2.1). Some of these inhibitors are specific to protecting certain metals. Therefore, an oil may contain several corrosion inhibitors. Again, they are common in almost every oil and grease. Metal deactivators are another form of corrosion inhibitor (Noria, 2018).

![Figure 2.1: Mechanism of Rust inhibitors](image)


c. **Viscosity Index Improvers**

Viscosity index improvers are very large polymer additives that partially prevent the oil from thinning out (losing viscosity) as the temperature increases. These additives are used extensively when blending multi-grade engine oils such as SAE
5W-30 or SAE 15W-40. They are also responsible for better oil flow at low temperatures, resulting in reduction in wear and improved fuel economy. In addition, VI improvers are used to achieve high-VI hydraulic and gear oils for improved start-up and lubrication at low temperatures. To visualize how a VI-improver additive functions, think of the VI improver as an octopus or coil spring that stays coiled up in a ball at low temperatures and has very little effect on the oil viscosity. Then, as the temperature rises, the additive (or octopus) expands or extends its arms (making it larger) and prevents the oil from thinning out too much at high temperatures.

VI improvers do have a couple of negative features. The additives are large (high molecular weight) polymers, which makes them susceptible to being chopped or cut up into small pieces by machine components (shearing forces). Gears are notoriously hard on VI-improver additives. Permanent shearing of the VI-improver additive can cause significant viscosity losses, which can be detected with oil analysis. A second form of viscosity loss occurs due to high shearing forces in the load zone of frictional surfaces (e.g., in journal bearings). It is thought that the VI-improver additive loses its shape or uniform orientation and therefore loses some of its thickening ability. The viscosity of the oil temporarily drops within the load zone and then rebounds to its normal viscosity after it leaves the load zone. This characteristic actually aids in the reduction of fuel consumption. There are several different types of VI improvers (olefin copolymers are common). High-quality VI improvers are less susceptible to permanent shear loss than low-cost, low-quality VI improvers (Noria, 2018).

d. Anti-wear (AW) Agents

The additives are typically using to protect machine parts from wear and loss of metal during boundary lubrication conditions. They are polar additives that attach to frictional metal surfaces. They react chemically with the metal surfaces when metal-to-metal contact occurs in conditions of mixed and boundary lubrication. They are activated by the heat of contact to form a film that minimizes wear as shown in Figure (2.2). They also help protect the base oil from oxidation and the metal from damage by corrosive acids. These additives become “used up” by performing their function, after which adhesive wear damage will increase. They are typically phosphorus compounds, with the most common being zinc dialkyldithiophosphate (ZDDP).
There are different versions of ZDDP, some intended for hydraulic applications and others for the higher temperatures encountered in engine oils. ZDDP also has some anti-oxidant and corrosion-inhibition properties. In addition, other types of phosphorous-based chemicals are using for anti-wear protection (Noria, 2018).

### e. Extreme Pressure (EP) Additives

These additives are more chemically aggressive than AW additives. They react chemically with metal (iron) surfaces to form a sacrificial surface film that prevents the welding and seizure of opposing asperities caused by metal-to-metal contact (adhesive wear). They are activated at high loads and by the high contact temperatures that are created. They are typically used in gear oils and give those oils that unique, strong sulfur smell. These additives usually contain sulfur and phosphorus compounds (and occasionally boron compounds). They can be corrosive toward yellow metals, especially at higher temperatures. Therefore, should not use in worm gear and similar applications where copper-based metals are used. Some chlorine-based EP additives exist, but they rarely used due to corrosion concerns.

Anti-wear additives and extreme pressure agents form a large group of chemical additives that carry out their function of protecting metal surfaces during boundary lubrication by forming a protective film or barrier on the wear surfaces. As long as the hydrodynamic or elastohydrodynamic oil film is maintained between the metal surfaces, boundary lubrication will not occur and these boundary lubrication additives will not be required to perform their function. When the oil film does break
down and asperity contact is made under high loads or high temperatures, these boundary lubrication additives protect the wearing surfaces (Noria, 2018).

f. **Detergents**

Detergents perform two functions. They help to keep hot metal components free of deposits (clean) and neutralize acids that form in the oil. Detergents are primarily used in engine oils and are alkaline or basic in nature. They form the basis of the reserve alkalinity of engine oils, which is referred to as the base number (BN). They are typically materials of calcium and magnesium chemistry. Barium-based detergents were used in the past but are rarely used now. Since these metal compounds leave an ash deposit when the oil is burned, they may cause unwanted residue to form in high-temperature applications. Due to this ash concern, many OEMs are specifying low-ash oils for equipment operating at high temperatures. A detergent additive is normally use in conjunction with a dispersant additive.

g. **Dispersants**

Dispersants are mainly found in engine oil with detergents to help keep engines clean and free of deposits. The main function of dispersants as shown in Figure (2.3) is to keep particles of diesel engine soot finely dispersed or suspended in the oil (less than 1 micron in size). The objective is to keep the contaminant suspended and not allow it to agglomerate in the oil so that it will minimize damage and can be carried out of the engine during an oil change. Dispersants are generally organic and ash less. As such, they are not easily detectable with conventional oil analysis. The combination of detergent/dispersant additives allows more acid compounds to be neutralized and more contaminant particles to stay suspended. As these additives perform their functions of neutralizing acids and suspending contaminants, they will eventually exceed their capacity, which will necessitate an oil change (Noria, 2018).
h. Anti-foaming Agents

The chemicals in this additive group possess low interfacial tension, which weakens the oil bubble wall and allows the foam bubbles to burst more readily as shown in Figure (2.4). They have an indirect effect on oxidation by reducing the amount of air-oil contact.

Some of these additives are oil-insoluble silicone materials that are not dissolved but rather dispersed finely in the lubricating oil. Very low concentrations are usually required. If too much anti-foaming additive is added, it can have a reverse effect and promote further foaming and air entrainment (Noria, 2018).

i. Friction Modifiers

Friction modifiers are typically use in engine oils and automatic transmission fluids to alter the friction between engine and transmission components. In engines, the emphasis is on lowering friction to improve fuel economy. In transmissions, the focus is on improving the engagement of the clutch materials. Friction modifiers can be thought of as anti-wear additives for lower loads that are not activated by contact temperatures (Ahmed and Nassar, 2011).
j. **Pour Point Depressants**

   The pour point of oil is approximately the lowest temperature at which oil will remain fluid. Wax crystals is that form in paraffinic mineral oils crystallize (become solid) at low temperatures. The solid crystals form a lattice network that inhibits the remaining liquid oil from flowing. The additives in this group reduce the size of the wax crystals in the oil and their interaction with each other, allowing the oil to continue to flow at low temperatures (Noria, 2018).

k. **Demulsifiers**

   Demulsifiers are molecules that aid the separation of oil from water usually at low concentrations. They prevent formation of water and oil mixtures. Demulsifiers typically have limited solubility in the oil phase and migrate to the oil/water interface when the oil is mixed with water. Demulsifiers are surfactants that are important in breaking the emulsion system (Al-Sabagh et al., 2011).

l. **Emulsifiers**

   Emulsifiers are used in oil-water-based metal-working fluids and fire-resistant fluids to help create a stable oil-water emulsion. The emulsifier additive can be thought of as a glue binding the oil and water together, because normally they would like to separate from each other due to interfacial tension and differences in specific gravity.

m. **Biocides**

   Biocides are often adding to water-based lubricants to control the growth of bacteria.

n. **Tackifiers**

   Tackifiers are stringy materials used in some oils and greases to prevent the lubricant from flinging off the metal surface during rotational movement (Noria, 2018).

2.4.4. **Lubricant Additives Depletion**

   Most of these additives get consumed and depleted by:

   - Decomposition or breakdown,
   - Adsorption onto metal, particle and water surfaces, and
   - Separation due to settling or filtration.
The adsorption and separation mechanisms involve mass transfer or physical movement of the additive. For many additives, the longer the oil remains in service, the less effective the remaining additive package is in protecting the equipment. When the additive package weakens, viscosity increases, sludge begins to form, corrosive acids start to attack bearings and metal surfaces, and/or wear begins to increase. If oils of low quality are used, the point at which these problems begin will occur much sooner (Noria, 2018).

2.5. Used lubricating oils

Used oil – as its name implies – is any petroleum-based or synthetic oil that has been used. During normal use, impurities such as dirt, metal scrapings, water or chemicals can get mixed in with the oil or be generated in it due to thermal degradation or oxidation. Therefore, the oil quality gradually decreases to a level that the used oil should be replaced by a new one. Disposing the used oil off in nature creates an intense dangerous pollution. But by proper recovery and refinement of it, a lot of valuable product can be obtained. This article studies one of the best methods of used oil re-refining and compares its product specifications with those of virgin base oil. (Bridjanian and Sattarin, 2006).

The largest source for used oil in developing countries is lubricating oils from motor vehicles, combustion engines and gear boxes. Apart from that, minor amounts are generated from hydraulic systems, transformers and other diverse industrial applications. Due to increase of the automotive traffic in developing countries the amount of used oil from motor vehicles increased steadily in the past (Yash, 2015).

2.5.1. Used Engine Oil

Engine oil lubricants make up nearly one half of the lubricant market and therefore attract a lot of interest. The world lubricant use by product type is showing in Figure (2.5). The principal function of the engine oil lubricant is to extend the life of moving parts operating under many different conditions of speed, temperature, and pressure. At low temperatures the lubricant is expected to flow sufficiently in order that moving parts are not starved of oil. At higher temperatures they are expected to keep the moving parts apart to minimize wear. The lubricant does this by reducing friction and removing heat from moving parts. Contaminants pose an additional problem, as they accumulate in the engine during operation. The contaminants may be
wear debris, sludge, soot particles, acids, or peroxides. An important function of the lubricant is to prevent these contaminants from doing any damage (Ahmed and Nassar, 2011)

![Figure 2.5: World lubricant use by product type](image)

The majority of used engine oil is generated in small quantities at a great number of places, e.g. garages, small workshops and private premises. There are few major generator of waste oil like railways, large truck fleet operators and large industries.

After a certain period of useful life, the lubricating oil loses its properties and cannot be used as such in machinery. Buildup of temperature degrades the lubricating oil, thus leading to reduction in properties such as: Viscosity, Specific gravity, etc. Dirt and metal parts worn out from the surfaces are also deposited into the lubricating oils. With increased time of uses, the lubricating loses its lubricating properties as a result of over reduction of desired properties and thus must be replaced with fresh one. It is surprising to know that base oil never gets spoiled, it only gets dirty. Lubricating oil becomes unfit for further use for two main reasons: accumulation of contaminants in the oil and chemical changes in the oil. The main contaminants are listed below:

- Combustion products $\text{H}_2\text{O}$

   Water: Fuel burns to $\text{CO}_2$ and $\text{H}_2\text{O}$. For every liter of fuel burnt, a liter of water is created. This normally passes out through the exhaust when the engine is hot, but when cold it can run down and collect in the oil. This leads to sludge formation and rust. Soot and carbon: These make the oil go black. They form as the result of
incomplete combustion, especially during warm-up with a rich mixture. Lead: Tetraethyl lead, which used to be used as an anti-knock agent in petrol, passes into the oil. Typical used engine oil may have contained up to 2% lead, but today any lead comes from bearing wear and is likely to be in the 2 - 12 ppm range. Fuel: Unburnt gasoline or diesel can pass into the lubricant, again especially during start-up.

- **Abrasives**

  Road dust: This passes into the engine through the air-cleaner. Composites of small particles of silicates, wear metals, iron, copper and aluminum are released due to normal engine wear.

- **Chemical products**: Oxidation products: Some of the oil molecules, at elevated temperatures, will oxidize to form complex and corrosive organic acids (Yash, 2015). One of the main concerns with lubricating oil relates to used oil management for both industrial and engine oils, although the environmental impact of gasoline and diesel engine oils is the most critical. If efficient management systems are in place, most used oil should not reach the environment, so, the major question is how to dispose of collected used oil. The first option lies in burning it as a fuel, the second in recycling. The latter allows recovery of mineral base oils, which are valuable constituents of crude oil (Kajdas, 2000).

### 2.5.2. Used oil recycling

Waste oil is a pollutant but valuable from an energy conservation point of view. It is not always an economic resource but it helps to keep the environment clean if it is re-refined properly. To minimize the incidents of hazardous disposal, it is necessary to use modern treatment procedures and recovery technologies for disposing of the produced waste materials. The used oil creates environmental pollution problems if not disposed after proper pretreatment. To decrease environmental pollution from waste oils, it is necessary to increase the collection and processing of the oils, in order to extract useful materials and to convert the harmful wastes into harmless substances (Khawaja and Aban, 1996).

### 2.5.3. Treatment Technologies

The idea of recycling used lubricating oil was presented in the year of 1930. Initially the used lubricating oils were burnt to produce energy, and later these oils were re-blended to engine oils after treatment. Due to the increasing necessity for
environmental protection and more stringent environmental legislation, the disposal and recycling of waste oils has become very important. The recycling of waste lubricating oils can be accomplish through three basic methods, which are reprocessing, re-refining and destruction (Yash, 2015).

- **Solvent extraction**

  One of reprocessing techniques is solvent extraction, which involves the use of a solvent to selectively extracting the lubricating oil from an oil-contaminated mixture. Lubricating oil consists of base oil and additives that help to impart certain characters of the oil such a viscosity and this, should be rejected by the solvent.

  A solvent should also dissolve the base oil and precipitate other substances to form sludge. The polarity of solvent with respect to that of the lubricating oil contaminants also influences solubility. A solvent has good dissolving efficiency when its polarity is similar to that of oil pollutants. A good solvent should dissolve base oil and precipitate other substances to form sludge. The efficiency of the extraction solvents can also be related to the various interactions between the solvent and oil molecules, due to the size of the main carbon chain and the solvent molecules configuration. The increase in recovery with increase in solvent carbon chain length as carbon atoms lose hydrogen ions and act as a carrier medium for the oil molecules (Diphare et al., 2014).

2.6. **Previous studies**

Previous studies have shown that different types of solvents either composite or single can be used in different ratios as follow:

- Solvent extraction blends {toluene, butanol and methanol (A)}, {toluene, butanol and ethanol (B)} and {toluene, butanol and isopropanol (C)} was evaluated experimentally, oil to solvent proportions from 1:1 to 1:3 were analyzed for mixture blend (C). The results confirm solvent mixture (A) gave good efficiency with the highest percent sludge removal. The maximum percent of sludge removal improves with the increase of solvent to oil ratios. The physical properties of the recycle oil were measured. The results show the in the properties of recycling oil and have good efficiency (Osman et al., 2018).
Various data on the performance of the three solvents chosen were (MEK, propan-2-ol, a composite mixture of 75% MEK and 25% propan-2-ol) studied and compared based on certain parameters are presented and discussed. From the results obtained, it was observed that Methyl Ethyl Ketone (MEK) had the best performance because it gave the highest sludge removal and closest properties to the fresh lubricating base stock. Furthermore, it was also determined that increase in temperature improved the quality of oil obtained up till 50°C above this temperature poorer quality of oil was observed. But above of all the factors investigated, it was concluded that solvent to oil ratio has a greater effect on the quality of oil produced after treatment (Oladimeji et al., 2018).

On comparative study of re-refined engine oils by extraction of composite solvent, single solvent, and acid treatment methods. Composite solvent was made up of butanol, propane and butanone; propane was used as single solvent. Different properties of refined oil and waste oil were analyzed, such as cloud and pour point, flash point, specific gravity, ash content, viscosity, moisture ratio and acid value. On the basis of experimental work, it was found that the iron contamination decreased from 50 ppm to 13 ppm for composite solvent; for propane solvent it decreased up to 30 ppm and 15 ppm for acid treatment. Results from the flash point, pour point, viscosity, specific gravity, and ash percentage was improved at different degrees, but the best results were seen by using the composite solvent with having drawback of expensiveness (Abro et al., 2013).

In this work the action of some solvents (2-propanol, 2-butanol, 2-pentanol, methyl ethyl ketone, and methyl n-propyl ketone) on both yield and quality of the recovered oil has been investigated. The quality has been assessed through the measurement of metallic, polymeric, and oxidation compound concentrations in the extracted oil. Experimental results have shown that extraction yields increase with increasing solvent/oil ratios up to a point at which they stabilize. When comparing alcohols and ketones it has been found that yields obtained with solvents of equal numbers of carbon atoms are similar and increase with increasing solvent molecular weight for both families. On the other hand, metallic and oxidation compound removal was similar for alcohols and ketones of equal numbers of carbon atoms, but alcohols were more efficient than ketones when polymeric additive elimination was considered. All
these results may be attribute to the combined effect of factors such as the system viscosity, the detergent-dispersant additive concentration, and the difference between the solubility parameters of the system components (Rincon et al., 2005).

- The composite solvent 2-propanol, 1-butanol and butanone have two alcohols that make a binary system reasonably effective. This work also attempts to study the performance of the composite solvent in the extraction process for recovering waste lubricating oil. The key parameters considered were vacuum pressure, temperature and the weight ratio of solvent to waste lubricating oil. The performance was investigated on the PSR (Percentage Sludge Removal) and POL (Percent Oil Loss). The best results were obtained using composite solvent 25% 2-propanol, 37% 1-butanol and 38% butanone by a solvent to oil ratio of 6:1 at vacuum pressure 600 mmHg and distillation temperature 250 °C. The vacuum distilled oil pretreated with the composite solvents was matched to the standard base oil 500N and 150N, found in close agreement and could be used for similar purpose (Durrani et al., 2011).

- Solvent extraction technique is one of the cheapest and most efficient processes experienced in recycling of used lubricating oils. In this paper, the performance of three extracting solvents (2-propanol, 1-butanol, and methyl-ethyl-ketone (MEK) in recycling used oil was evaluated experimentally. The effect of the most critical parameters (type of solvent, solvent to oil ratio, and extraction temperature) was investigated. The results show that MEK achieved the best performance with the lowest percent oil losses, followed by 2-propanol and 1-butanol, and as the extraction temperature increases the percent oil losses decreases (Elbashir et al., 2002)
CHAPTER THREE
MATERIALS AND METHODS
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MATERIALS AND METHODS

3.1. Materials

- Used oil SAE 40 was obtained from oil monitoring lab of Fuchs Lubricants – Sudan, which received from customer for after sales service.
- Isopropyl alcohol (99%) which manufactured by PARK Scientifc Ltd., Ethanol (96%) manufactured by VWR Prolabo Chemicals and Toluene (99%) manufactured by CARLO ERBA REAGENTS.

3.2. Methods

- Solvent Extraction

The used oil subjected to filtration before treatment. This was done using a Buchner funnel. Quantity of 200 mL of used oil was mixed with a combination of solvents of Toluene, Isopropyl alcohol and Ethanol (1:1:1), by solvent to oil ratio 1:1. The whole mixture in a beaker was placed on a magnetic stirrer with heater and stirred for 45 minutes at 40 °C. Then it was allowed to stand for 24 h in closed container. Same step was repeated by heating the mixture to 60 °C. Same steps were employed by solvent to oil ratio 2:1. The same method was done by using an isopropyl alcohol as single solvent. Now, the eight containers of samples given labels as sample 1 to sample 8. The clear surface oily layer as shown in Figure (3.1), which containing solvents and oil was transferred to simple distillation unit in order to separate the solvents from the regenerated base oil. All the above experiments carried out in the lab of chemistry at Faculty of Pure and Applied Science, International University of Africa, Sudan.
Figure 3.1: Separation of clear oily layer in all samples after 24 Hrs.

- Testing of Recycled Oil
  The recovered base oil has been tested for the kinematic viscosity at 40 °C and 100 °C, base number, metal content, as follow:

  Viscosity has been tested by using Stabinger viscometer, model SVM 3000, that shown in Figure (3.2) which manufactured by Anton Paar Company, as per test method ASTM D 7042. About 3 mL of oil sample was introduced into the measuring cells, which are at a closely controlled and known temperature (40 and 100) °C. The dynamic viscosity and density were determined directly, and the kinematic viscosity is calculated by dividing the dynamic viscosity by the density.
Base Number (BN) has been tested by potentiometric perchloric acid titration as per test method (ASTM D-2896), the Figure (3.3) illustrated Metrohm titrino plus 848 which used as automatic titrator as follow. About 0.5 g of each sample of recovered oil was dissolved in 60 mL of an essentially anhydrous mixture of chlorobenzene and glacial acetic acid and titrated with a solution of perchloric acid in glacial acetic acid. A glass combination electrode (indicator and a reference electrodes) was used, which is connected to titrator.
The meter readings are plotted against the respective volumes of titrating solution, and the end point is taken at the inflection in the resulting curve. The BN value was calculated automatically from the equation \( BN = V \times N \times 56.106 / S \) which inserted before into device’s test method, where \( V \) is volume of \( \text{HClO}_4 \) solution used to titrate the sample to the inflection point on the titration curve, \( mL \), \( N \) is normality of \( \text{HClO}_4 \) solution, and \( S \) is sample weight, \( g \).

Calcium and zinc content has been tested for used engine oil and all samples of regenerated base oil in order to check the degree of treatment by using inductively coupled plasma – optical emission spectrometry (ICP-AES) according to test method ASTM D-4951, the Figure (3.4) shown an ICP of GBC company, model name (Integra XL) which was used for metal analysis. The test was carried out as follow: A sample portion is weighed and diluted by volume with kerosene. Calibration standards are prepared similarly. The solutions are introduced to the ICP instrument by peristaltic pump. By comparing emission intensities of elements in the test specimen with emission intensities measured with the calibration standards, the concentrations of elements in the sample are calculated.

![Figure 3.4: ICP-OES for Metal Test](image)
Fourier Transform Infra-Red (FTIR) of Perkin Elmer Co., model (Spectrum Two) which shown in Figure (3.5) was used to show that how similar a regenerated oil samples spectrum is to previously collected reference virgin base oil (SN 500) spectrum as follow. The spectrum of regenerated oil was selected, then click on compare option in FTIR software, the reference spectrum was selected. The compare process reports the similarity between spectra as their correlation, value between 1(a perfect match) and 0 (wholly unrelated).

Figure 3.5: Fourier Transform Infra-Red

All this tests have been carried out in quality control Lab at Fuchs Lubricants Plant, Khartoum, Sudan.
CHAPTER FOUR

RESULTS AND DISCUSSION
CHAPTER FOUR

RESULTS AND DISCUSSION

The Table (4.1) illustrated the effects that they would have on the solvent extraction process and the data are presented in subsections.

### Table 4.1: Effects on the extraction process

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Total Qty, mL</th>
<th>Qty of clear Oily layer Obtained, mL</th>
<th>Percentage of clear Oily layer Obtained</th>
<th>Qty of Oil obtained after distillation, mL</th>
<th>Percentage of Oil obtained from 200 mL used oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:1</td>
<td>2:1</td>
<td>1:1</td>
<td>2:1</td>
<td>1:1</td>
</tr>
<tr>
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<td>0.0</td>
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<td>300</td>
<td>50.0</td>
<td>23</td>
<td>11.5</td>
</tr>
</tbody>
</table>

The Table (4.1) show the samples of used oil and solvent mixture which numbered from 1 to 8, the quantities of clear oily layer which obtained from every mixture, the percentage of clear oily layer from every mixture and the quantity and percentage of oil obtained from the 200 mL used oil.

#### 4.1. Effect of Solvent to Oil ratio

Figure (4.1) shows effect of solvent to oil ratio and indicate that, increasing the solvent to oil ratio is the increase in the percentage recovery of the oil and all previous studies confirm this observation, sample 6 gave the greatest oil recovery followed by sample 8 then samples 2 and 4, which indicate that, isopropyl alcohol was gave oil recovery percentage better than combination of it with ethanol and toluene. Previous
study determined that methyl ethyl ketone as single solvent can give greatest sludge formation and oil recovery percentage better than isopropyl alcohol.

![Figure 4.1: Effect of Solvent to Oil ratio](image)

From observation the oil recovery was increase with increasing solvent to oil ratio this is because at lower solvent to oil ratios the base oil might be saturated in the extraction phase leading to low oil recovery and greater oil losses.

4.2. Effect of Extraction temperature

Figure (4.2) shows effect of extraction temperature on recovery percentage, no important difference in recovered oil percentage when increase the temperature from 40 °C to 60 °C, just can be observed that increase in temperature up to 60 °C reduce percent of oil when use the Isopropyl alcohol as single solvent, it might be due to the increase in temperature that enhance the rate of solvent vaporization. Previous study determined that increase in temperature improved the quality of oil obtained up till 50 °C above this temperature poorer quality of oil was observed.
4.3. Comparison of Degree of Treatment Between the Different Samples

4.3.1. Additive Metal Removal

The metal content of base oil is a very important parameter as the metal content in an oil sample as it can increase the rate of corrosion of the metal parts it is in contact with. The metal content of oil mainly comes from the additives added to the oil. Calcium comes mainly from detergents and dispersants and Zinc is introduced to base oil in the form of additives packaged as anti-oxidant, corrosion inhibitor, and anti-wear.

Figure (4.3) and appendix (1) shows the effect of solvent extraction in calcium removal and observed that, sample 6 gave better removal tendency for the calcium, followed by sample 8 then samples 5 and 7, and lastly sample 2, then sample 4, which indicate that, the extraction by Isopropyl alcohol as single solvent gave better calcium removal than the combination of it with ethanol and toluene. Also observed that the calcium removal increase with increasing solvent to oil ratio, and decrease with increasing the temperature from 40 °C to 60 °C.

![Figure 4.2: Effect of temperature on recovery Percentage](image_url)
Figure 4.3: Effect of Solvent extraction in Calcium removal

From the Figure (4.4) and appendix (1) observed that, samples 2 and 4, were gave better zinc removal tendency, which indicate that the mixture of isopropyl alcohol, ethanol and toluene have a great removability for the zinc content, it might be due to high solubility of the zinc compounds such as Zinc Diphenyl Dithiophosphate (ZDDP) in isopropyl alcohol as single solvent.

Figure 4.4: Effect of Solvent extraction in Zinc removal

4.3.2. Alkalinity Removal

Figure 4.5 shows effect of extraction on BN. The internal combustion engine oils were formulated with a highly alkaline base additives package to neutralize the acidic products composition. The base number (BN) is a measure of this package and it may be used as an indication for the engine oil’s replacement time. This is because
BN depletes with time in service. Higher oil BN values are more effective at neutralizing acids for longer periods of time. The rate of consumption of the additives is an indication of the projected service life of the oil.

![Base Number, mgKOH/g](image)

**Figure 4.5:** Effect of Extraction on BN

As shown in Figure (4.5) the removal of alkaline material increase with increase of solvent to oil ratio and decrease when increase temperature from 40 to 60 °C, and isopropyl alcohol was gave better effect than combination of it with ethanol and toluene.

### 4.4. Recovered Oil vs. Virgin Base Oil

Table 4.2, illustrate the comparison between recovered oil with virgin base oil – SN500, in the term of kinematic viscosity at (40 and 100 °C) and viscosity Index.

**Table 4.2:** Properties of Recovered Oil vs. Virgin Base Oil

<table>
<thead>
<tr>
<th>Properties</th>
<th>Test Method</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Sample 7</th>
<th>Sample 8</th>
<th>Virgin SN 500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic Viscosity @ 40 °C, cSt</td>
<td>ASTM D-7042</td>
<td>NA</td>
<td>92.83</td>
<td>NA</td>
<td>86.51</td>
<td>90.52</td>
<td>83.94</td>
<td>85.77</td>
<td>84.38</td>
<td>91.70</td>
</tr>
<tr>
<td>Kinematic Viscosity @ 100 °C, cSt</td>
<td>ASTM D-7042</td>
<td>NA</td>
<td>10.83</td>
<td>NA</td>
<td>10.30</td>
<td>10.33</td>
<td>10.03</td>
<td>10.31</td>
<td>10.08</td>
<td>10.62</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>ASTM D-2270</td>
<td>NA</td>
<td>100</td>
<td>NA</td>
<td>100</td>
<td>95</td>
<td>99</td>
<td>101</td>
<td>99</td>
<td>98</td>
</tr>
</tbody>
</table>

**Note:** No data for sample 1 due to no oil has been extracted, no data for sample 3 due to insufficient quantity of regenerated oil
4.4.1. Viscosity

The type of viscosity measured is the kinematic viscosity. It is the ratio of dynamic viscosity to density. In addition, it is affected by pressure and temperature. Like the general definition of viscosity as temperature increases, viscosity decreases and vice-versa the same also applies to kinematic viscosity. The effect of the different Extraction’s parameters on oil viscosity can be seen in Figures (4.6) and (4.7), and was compared to the viscosity of an unused lube base stock.

**Figure 4.6:** Effect of Extraction on Oil Viscosity @ 40 °C

**Figure 4.7:** Effect of Extraction on Oil Viscosity @ 100 °C
From the Figures (4.6 and 4.7) observed that, sample 2 and sample 5 were gave greatest effect then followed by sample 7; which indicate that the viscosity of the oil decreases as solvent to oil ratio increases this is because the sludge removed from the treated oil contains aromatic compounds, aromatic compounds with high molecular weights have been removed, leaving behind paraffinic compounds of relatively lower viscosity. When used mixture of isopropyl alcohol, ethanol and toluene the viscosity of recovered oil has been poorer with increase temperature from 40 to 60 °C. But this variation in viscosity is not consider as big problem because in lubricants formulation the viscosity is adjustable property it can be controlled by using viscosity improver or mixing the low viscosity base oil with another highest in viscosity.

4.4.2. **Viscosity Index**

Viscosity index (VI) is a value that indicates the effect of temperature on the kinematic viscosity of an oil sample. This test is usually done using viscosity values attained at 40 and 100 °C. A table where viscosity values and reference series are listed is used in calculating the viscosity index value. The accuracy of this method is dependent on the accuracy of the kinematic viscosity value determination. The variation in VI between the different samples of regenerated oil and virgin SN 500, that shown in Table (4.2), it might be due to contamination of samples with traces of extraction solvent.

4.4.3. **Comparison by using FTIR Spectra**

Figure 4.8 shows the spectrum of FTIR correlation coefficients of the samples. From the data from FTIR observed that, sample 6 spectrum was gave the greatest correlation coefficient to the spectrum of virgin base oil followed by sample 5, then sample 2, which indicate that at 40 °C the extraction by using isopropyl alcohol as single solvent is better than combination of it with the toluene and ethanol, oil components wise. Also data observed that samples 7 and 8 were gave the poorer correlation coefficient with virgin base oil and the main differences in the fingerprint area (below 1400 cm⁻¹). The increase of temperature from 40 to 60 °C might be lead to transfer undesired components to the extraction phase.
Sample 2 Details:

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Best Hit</th>
<th>Description</th>
<th>Correlation</th>
<th>Correlation Criteria</th>
<th>Pass / Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 2</td>
<td>SN 500_001.sp</td>
<td>Fresh Base Oil</td>
<td>0.93988</td>
<td>0.90</td>
<td>Pass</td>
</tr>
</tbody>
</table>

Sample 2 Spectra:

Sample 4 Details:

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Best Hit</th>
<th>Description</th>
<th>Correlation</th>
<th>Correlation Criteria</th>
<th>Pass / Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 4</td>
<td>SN 500_001.sp</td>
<td>Fresh Base Oil</td>
<td>0.906146</td>
<td>0.90</td>
<td>Pass</td>
</tr>
</tbody>
</table>

Sample 4 Spectra:
### Sample 5 Details:

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Best Hit</th>
<th>Description</th>
<th>Correlation</th>
<th>Correlation Criteria</th>
<th>Pass / Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 5</td>
<td>SN 500_001.sp</td>
<td>Fresh Base Oil</td>
<td>0.94395</td>
<td>0.90</td>
<td>Pass</td>
</tr>
</tbody>
</table>

#### Sample 5 Spectra:

![Sample 5 Spectra](image)

### Sample 6 Details:

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Best Hit</th>
<th>Description</th>
<th>Correlation</th>
<th>Correlation Criteria</th>
<th>Pass / Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 6</td>
<td>SN 500_001.sp</td>
<td>Fresh Base Oil</td>
<td>0.974129</td>
<td>0.90</td>
<td>Pass</td>
</tr>
</tbody>
</table>

#### Sample 6 Spectra:

![Sample 6 Spectra](image)
Sample 7 Details:

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Best Hit</th>
<th>Description</th>
<th>Correlation</th>
<th>Correlation Criteria</th>
<th>Pass / Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 7</td>
<td>SN 500_001.sp</td>
<td>Fresh Base Oil</td>
<td>0.877217</td>
<td>0.90</td>
<td>Fail</td>
</tr>
</tbody>
</table>

Sample 7 Spectra:

Sample 8 Details:

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Best Hit</th>
<th>Description</th>
<th>Correlation</th>
<th>Correlation Criteria</th>
<th>Pass / Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 8</td>
<td>SN 500_001.sp</td>
<td>Fresh Base Oil</td>
<td>0.898278</td>
<td>0.90</td>
<td>Fail</td>
</tr>
</tbody>
</table>

Sample 8 Spectra:

**Figure 4.8** Spectrums of FTIR correlation coefficients of the samples
CHAPTER FIVE
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CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

The yields of base oil obtained by extraction of used engine oil with composite solvents (isopropyl alcohol, ethanol and toluene) or isopropyl alcohol as single solvent increased with increasing of solvent to oil ratio. The isopropyl alcohol as single solvent and temperature at 40 °C were gave best results of yield and quality of regenerated base oil.

5.2. Recommendation

Regenerated oil can be improving by further process of metal removal by using metal adsorption agent, such as zeolite. From the data of previous studies and this research methyl ethyl ketone is better than isopropyl alcohol, and can be used as single solvent for extraction and optimization in future studies.
REFERENCES


Haider S.W., Shahzad M.A., and Usman M., 2013. *Re-refining of Used Lubricating Oil*. Research, National University of Sciences and Technology (NUST), H-12, School of Chemical and Materials Engineering (SCME), Islamabad.


Appendices
Appendices

Appendix 1: Calcium and Zinc Content (Wt. %)

<table>
<thead>
<tr>
<th>Metal Type</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Sample 7</th>
<th>Sample 8</th>
<th>Used Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>NA</td>
<td>0.025</td>
<td>NA</td>
<td>0.027</td>
<td>0.048</td>
<td>0.037</td>
<td>0.046</td>
<td>0.036</td>
<td>0.058</td>
</tr>
<tr>
<td>Ca</td>
<td>NA</td>
<td>0.087</td>
<td>NA</td>
<td>0.114</td>
<td>0.052</td>
<td>0.030</td>
<td>0.052</td>
<td>0.044</td>
<td>0.511</td>
</tr>
</tbody>
</table>

Note: No data for sample 1 due to no oil has been extracted, no data for sample 3 due to insufficient quantity of regenerated oil.

Appendix 2: Base Number for Recovered Oil and Used Oil, (mgKOH/g)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample 2</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Sample 7</th>
<th>Sample 8</th>
<th>Used engine oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBN value</td>
<td>3.47</td>
<td>4.05</td>
<td>2.87</td>
<td>1.67</td>
<td>3.14</td>
<td>2.22</td>
<td>16.14</td>
</tr>
</tbody>
</table>

Note: No data for sample 1 due to no oil has been extracted, no data for sample 3 due to insufficient quantity of regenerated oil.