Re-refining of semi synthetic used engine oil 20W-50 and improvement of its Tribological behaviour using carbon nanotube

MSc Dissertation

Prepared by

Student name: Gabriel Mwendenda Kabamba

Student number: 1808300

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School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa

Supervisor(s): Doctor Diakanua Nkazi

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DECLARATION

I, Gabriel Mwendenda Kabamba, hereby declare that the work provided in this dissertation is to the best of my knowledge original except where cited and has never been submitted at this university or any other post-graduate institution.

Signature of candidate……………………on this ……….day of ……………………………

DEDICATION

I dedicate this work to

My dear and wonderful wife Theresa Kasongo for her support during the journey of this research project.

My children Luboya, Mariana and Jolieuse; anything is possible if you work hard.

My parents, Kashinga Luboya and Mariana Mulubula Tshala, your guidance and moral support to study engineering will always be remembered.

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ABSTRACT

Machines and Automobiles usage decrease the capability of lubricants, and favor water contamination, variation of heat and damage of solid surfaces. The impurities generated during the lubricant's degradation are unsaturated, phenolic, aldehyde, acidic compounds, metals, gums, and other asphaltic compounds. Poisonous metals waste such as zinc, chromium, copper, Tin, arsenic, lead, barium, cadmium and magnesium are found in some used lubricants and unfortunately disposed into environments and freshwater sources such as rivers, lakes, dams, and streams.

In this project, re-refining of SAE 20W-50 through solvent extraction followed by precipitation and modification of lubricant tribological behaviour using CNT's was investigated. Multistage filtration (with screen filtration varied from 100 to 200 micrometers, followed by soil filtration) was employed to remove solid impurities at atmospheric pressure. The filtrate was dissolved in various solvent (n-butanol, butan-2-ol, and t-butanol) at various temperatures (from 30 to 65^{0}C). The mixture was cooled to different temperatures from 10 to 30^{0}C, and then ethanolamine was added as precipitant. The oil-solvent ratios and ethanolamine were also investigated.

The filtration system was able to remove solid and suspension particles and the color of the filtrate changed from dark black to brown. The high viscosity index of 124 was observed with oil extracted using butan-2-ol, which indicates better resistance of oil to change in temperature. Better dissolution and primary precipitation were observed at temperature of 50^{0}C. The use of Butan-2-ol favors the refining of the used lubricant. The sludge removal by addition of ethanolamine increased with the increasing in oil-solvent ratio to an optimum of 1:4. The sludge removal was better with a ratio of 1:5 (ethanolamine: oil-solvent).

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LIST OF ABBREVIATIONS

HHV	High Heating Value
KWh/kg	Kilowatt hour per kilogram
MWCNTs	Multi-walled carbon nanotubes
Kg/m3	Kilogram per cubic meter
O_2	Oxygen
H+	Hydrogen ion
CP	Cathodic Protection
As_2O_3	Arsenic Trioxide
Na_3AsO_4	Sodium Arsenate
Bi	Bismuth
Sb	Antimony
Ca	Calcium
Mg	Magnesium
Zn	Zinc
SO_2	Sulfur Dioxide
Na_2NO_2	Sodium Nitrite
PCB'S	Polychlorinated Biphenyls
5W-40	5: viscosity at 0^oC; W: For Winter; 40: Oil viscosity at 100^0C
VIS	Motor Brand
TAN	Total Acid Number
KOH/g	Potassium Hydroxide per gram

ML	Mililiter
(Wt %)	Weight Per cent
TBN	Total base number
Cu	Copper
Mg	Magnesium
Cr	Chrome
Sn	Tin
Pb	Lead
Fe	Iron
Zn	Zinc
CNTS	Carbon Nanotubes
SAE	Society of Automotive Engineers
20W-50	20W indicates how quickly the engine will start in cold weather; 50 relate to the viscosity thick
Eg	Example
ACE	Associated Chemical Enterprises
G/ml	Gram per litter
$C_4H_{10}O$	Butanol
$C2H_7NO$	Ethanolamine
Mm^2/s	Square millimetre/second
Max	Maximum
ETA	Ethanolamine
NS	No Separation

Ni	Nickel
Ppm	Parts per million
Pb	Boiling Point
Ph.D.	Philosophiae Doctor
Rpm	Number of revolution per minute
Kg/l	Kilogram per litter
T_2	Temperature number two
T_1	Temperature number one
VI	Viscosity index

LIST OF SYMBOLS

>	Greater-Than
&	And
%	per cent
/	Slash
@	At
^{0}C	Degree Celsius

CHAPTER 1. BACKGROUND AND MOTIVATIONS

This chapter outlines the importance of this research. It pinpoints the problem statement, justification and objectives of the research.

1.1 Introduction

Lubricants are one of the most important fractions of petroleum, which decrease rubbing between surfaces in moving parts of engines, gearboxes and hydraulic systems. Automobiles and machines usage decrease the efficiency of lubricants due to water contamination, variation of heat and damage to solid surfaces. The impurities generated during the degradation are unsaturated, phenolic, aldehyde and acidic compounds; metals, gums and other asphaltic compounds. Poisonous metals waste such as zinc, chromium, copper, Tin, arsenic, lead, barium, cadmium and magnesium are found in some used lubricants and unfortunately disposed into environments and freshwater sources such as rivers, lakes, dams and streams. Hamawand et al. (2013) (cited in Mekonnen (2014)) and Algayyim *et al.*, (2018) indicated that recycling polluted materials will have a vital positive effect on the environment and will be an advantage in the way of reducing lubricant costs. To avoid alteration of the properties the engine, lubricant oil life usage should be controlled. Re-refining of used engine oil is crucial prior re-usage.

Recent research focused on the use of Nano-materials as a lubricant additive, which improved the thermo-physical properties of oil (Afrand, Najafabadi, & Akbari, 2016). Low concentration of functionalised Nano-materials reduced the friction at a higher temperature (± 160 ^{o}C) and well distributed in the lubricant compared to conventional friction reducers (Which are not soluble in oil-based lubricants) (Sudeep et al. (2013); Arumugam *et al.*, (2018).Charanpahari et al. (2013) and Arumugam *et al.*, (2018) stated that MWCNTs functionalised with anionic surfactant enhanced the tribological performance of the lubricant oil, and improved the bearing load capacity, friction reduction and anti-wear properties

1.2 Problem Statement

Waste disposal of used engine oil into the environmental affects aquatic and earth living bodies life, and generally disrupt the natural cycle of the earth systems. This becomes a major environmental concern for policymakers. A several techniques have been used for re-refining of used engine oil. In acid clay process sulphuric acid has been used to eliminate the asphaltic materials from used lubricant oil. These methods produces enormously acid tar unhygienic which are deflect to discharge at the environment that’s one of the raisons why it cannot be accepted in the moment. In other processes, propane extraction procedure, the virgin oil has been recovered from the used oil using liquefied propane. Nevertheless those processes are expensive because it needs propane in liquefied form, moreover as propane is flammable and hazardous material consequently, these processes are considered as potentially dangerous (Gul et al., 2014; Abu-Elella *et al.*, 2015).

In this project, n-butanol, t-butanol, 2-butanol and ethanolamine were used for solvent extraction to re-refining used motor oil. The method is cost effective and allows high recovery over other conventional regeneration methods of used engine oil. The used solvents can be retained in higher amount under reasonable experimental circumstances. The oil treated with this technique could then be used again as motor engine oil.

1.3 Research Questions

1. How the alcohol structures affect the purification process of used engine oil?
2. How the ethanolamine affects the residues removal process at various temperatures?
3. What parameters affect re-refining of used engine oil?
4. To what extent MWCNTs functionalized with anionic surfactant enhance Tribological behavior of re-refined engine oil?

1.4 Research Aim and Objectives

The aim of this research project is to investigate the re-refining process of semi synthetic used engine oil 20W-50 using various butanol structural isomers as solvent and ethanolamine as precipitant, and the effect of multi wall carbon nanotube functionalised with anionic surfactant as tribological behaviour modifier of re-refined engine oil. To achieve this aim, the following objectives should be investigated:

- The effect of butanol structure isomers (n-butanol, butan -2-ol and tert-butanol) as solvent for the extraction process;
- The effect of process temperature for solvent extraction and sludge removal;
- The effect of solvent- lubricant ratio and ethanolamine-solution (solvent- lubricant) ratio on the sludge removal efficiency.

CHAPTER 2. LITERATURE REVIEW

2.1. Introduction

Chapter 2 is a review of the literature relating to the nature and function of lubricating oil as it expands the processes of refining the oils. It is critical also to have a good working relationship with respect to effective recycling of lubricants. In pursuit of this, the review will also look at various elements, which will result in a reduction in the number of cases. It is important to begin this review by providing an understanding of lubricating oil.

2.2. Lubricating oil

According to Jonathan et al (1993) cited in Mariamawit (2016) and Elkhaleefa (2016) cited in Abu-Elella *et al.* (2015), 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. In short a lubricant functions to lubricate machinery and should be applied to the required engines and machines to perform that function.

Lubricants were at one time exclusively animal or vegetable oils or fats, but modern requirements in both nature and volume have petroleum as the main source of lubrication. Lubricating oil can be produced by modern methods of refining from crude which ranges from thin easily flowing spindle oils to tank cylinder oils as demonstrated by Billet (1999) and Abu-Elella *et al.* (2015).

Lubricating oil is a highly specialized product, carefully developed to perform many essential functions of which are the following:

- Permit easy starting of the engine,
- Reduce friction,
- Protecting machinery against rust and corrosion,
- Lubricating of engine parts etc. (Idumeh, 2000).

A lubricant is an important resource that cannot be disposed of randomly due to the presence of pollutants contained in it and accumulated while it serves to protect machinery. In response to economic efficiency and environmental protection, there is a growing trend of regeneration and reuse of waste lubricants (Hsu and Liu 2011; Jafari and Hassanpour, 2015). This fully demonstrates that lubricants are a critical part of the modern mechanical equipment and that their management is an essential element towards good and sustainable business and industrial practices.

Lubricants can be derived from mineral oil, animal and vegetable oils, or synthetic base oil. Lubricating oil is mainly used for lubricating mechanical equipment, so to reduce friction and abrasion between machine parts. It can reduce noise and be used for cooling, but it is damaged after use because of oxidation and pollution. Developed countries and industrialized countries tend to have a higher demand for lubricating oil (Hsu and Liu 2011; Jafari and Hassanpour, 2015). With this growing demand, there is also a need for better processing and limiting pollution.

2.3. Lubricating oil Properties

Sufficient knowledge of the viscosity, temperature, pressure, density, specific gravity, the relationship of lubricating oils is essential in building an understanding of efficacious ways of managing used oils. An understanding of the properties of lubricating oils is necessary to assist in posting effective recycling options. Of critical importance is the viscosity and temperature of the oil.

2.3.1 Oil viscosity and temperature

By definition, the viscosity of a liquid represents a measure of its resistance against the flow, more precisely, a measure of the frictional forces between its moving molecules. It follows from this definition that the viscosity of a liquid represents a measure of its resistance against the flow, more precisely, a measure of the frictional forces between its moving molecules. For a given liquidity, the viscosity will be governed by the forces between, and the flexibility of its molecules (Roelands, 1966; Epelle *et al.*, 2017). Viscosity has the essential constructional property of oils employed in hydrodynamic lubrication. In general, however, viscosity does not simply assume a uniform level throughout, a hydro dynamically created oil film (Roelands, 1966; Epelle *et al.*, 2017). This, therefore, implies that the measurement of viscosity is particularly important when large volumes of the substance are involved.

Viscosity modifiers (controlling the temperature dependence of the oil's viscosity, i.e., the so-called "viscosity index", or VI), antioxidants, detergents, and anti-corrosives (Cairns and Haycock 1996). It also represents one of the important parameters characterizing the deterioration of engine oil (Roelands, 1966; Epelle *et al.*, 2017). Viscosity for individual oils can be further modified by changing the temperature of the oil: increasing temperature decreases viscosity and vice versa. Westfield et al. (2017) demonstrated during their experiments on the effects of lubricants on Piston Ring Friction that viscosity decreases with increasing temperature.

2.3.2 Lubricant Density and Specific Gravity

In engineering calculations, lubricant density is significant and occasionally offers a simple way of identifying lubricants. Specific gravity or density is frequently used to characterize crude oils. It gives a rough idea of the quantity of gasoline and kerosene present in the oil. The oil density, however, is often confused with specific gravity.

Specific gravity is defined as the ratio of the mass of a given volume of oil at temperature ‘T_1’ to the mass of an equal volume of pure water at temperature ‘T_2’. Density, on the other hand, is the mass of a given volume of oil [kg/m3]. The density of a typical mineral oil is about 850 [kg/m3] and, since the density of water is about 1000 [kg/m3], the specific gravity of mineral oils is typically 0.85 (Chia-Yu, 2008).

2.3.3 Degradation of lubricating oil

Commonly, the chemical and physical fluid properties of lubricants change due to their fact of being used. It is extensively known that oxidation is the main mechanism that degrades the lubricant. Lubricant oil degradation under operating conditions is a problem that involves meaningful economic losses. Many studies have also shown that Oxidation is the primary agent of degradation and has caused deterioration of the oil produced in the base oil (Bowman and Stachowiak, 1996; Keskin and Kok, 2001; Gamlin et al., 2002; Amanam and Kovscek, 2017; Santos et al., 2017).

2.3.4 Oxidation

The most essential and known form of chemical breakdown of motor oil and its additives is oxidation which is the reaction between an organic compound and oxygen. This continuous reaction between motor oil and oxygen is taking place inside the engine. The by-products of this reaction are very acidic compounds. These compounds are the source of corrosion of engine components and some deposits that can cause the malfunction of the engine over a period of time. They are also less stable than the pristine hydrocarbon (engine oil) (Mekonnen, 2014).

2.3.5 Thermal degradation

The degradation of the motor oil is observed when it is heated over a certain temperature which is known as thermal degradation. This operation changes the physical properties of the oil such as viscosity. For this oil to gain back the original properties it has to go through the refining process. This process consists of eliminating the products that decrease the oxidation resistance. Thermal degradation increases proportionally with the temperatures. In order for an oil to offer appropriate service at high operating temperatures extremely refined oils with a lot of anti-oxidants ought to be employed. The less highly refined lubricant is preferred for average service. Thermal degradation can considerably have an effect on volatility and evaporation rate of lubricating oil in addition to changes on viscosity and oxidation, and also augment carbon residue (Mekonnen, 2014).

The degradation of a liquid lubricant is often going together with detrimental changes in its physical and chemical properties that can harmfully influence its performance (Santos et al., 2004). This alteration makes the management of the resultant properties complex and their tendency to pollute makes it critical to search for ways to ease their impact. There has been growing interest to understand the details of oxidative degradation processes with respect to the oil composition or types. The following paragraph provides an insight of a form of degradation known as corrosion.

2.3.6 Corrosion

Corrosion is the deterioration of the material such as metal and its properties due to chemical reactions between it and the environment. When lubricants are used for a certain period of time they deteriorate they are unsuccessful to fulfil their purpose. The by-products coming from their degradation result in corrosion. Therefore, the following paragraph will provide some possible corrosion inhibitors capable of maintaining the performance of the lubricant.

2.3.6.1. The effect of corrosion inhibitors on lubricating oil

Nathan (1965) pointed up the following variety of corrosion inhibitors:

- **Nonoxidizing anions**

Nonoxidizing anions comprise species that require oxygen to passivate a metal. Passivation is a process in which metals or other materials are made unreactive by changing the surface layer or coating the surface with a thin inert layer. Characteristic chemistries include silicate, carbonate, phosphate, tungstate, and molybdate as agents to passivate in the process of inhibiting corrosion.

- **Cathodic inhibitors**

Cathodic inhibitors operate by delaying the reduction of O_2 or H+ or selectively precipitate onto cathodic areas. Cathodic protection (CP) is a method employed to manage the corrosion of a metal surface by transforming it in the cathode of an electrochemical cell. A simple technique of protection joins the metal to be protected to a more simply corroded "sacrificial metal" to play the role of the anode.

- **Hydrogen poisons**

Hydrogen poisons mostly operate in acidic medium to hold back the hydrogen reduction reaction by reducing its production at the cathode and precipitating a layer of the poisoning metal. Hydrogen poisons include As_2O_3 or Na_3AsO_4), Bi, or Sb etc. Unluckily, they also promote hydrogen absorption in steel and can cause hydrogen embrittlement if not cautiously managed.

- **Cathodic precipitates**

Cathodic precipitates reduce the corrosion rate where the metal is exposed by producing insoluble hydroxides of metals such as Ca, Mg, or Zn. They are used in neutral or alkaline solutions.

- **Oxygen scavengers**

Oxygen scavengers decrease corrosion by holding excess oxygen in the system. Characteristic aqueous oxygen scavengers are used in water treatment. They include hydrazine, SO_2, $NaNO_2$, and Na_2SO_3. There are also some organic antioxidants which could also be considered in this category, they based on alkylated diphenylamine or alkylated phenols that are employed in lubricating oils to scavenge oxygen.

- **Mixed (or organic) inhibitors**

Mixed inhibitors are organic materials which are absorbed on a metal surface to prevent both anodic and cathodic reactions. These materials are the characteristic corrosion inhibitors employed in lubricating oils. They are hard to remove by chemical reaction or mechanical action than the monolayer films created by the anodic and cathodic inhibitors.

2.3.6.2 Effect of oil contaminants

1) Soot Contaminant

The literature has shown that wear of many engine components was increased by Soot-contaminated lubricants. An engine's valve train has confirmed to be the most extremely affected because of the thin oil-film thicknesses involved in many of its sharing contacts. The film thicknesses made in such contacts was small than the diameter of the soot particles contained within the lubricant.

Green, and Lewis (2008) and Amanam and Kovscek, (2017) observed the effects of soot-contaminated engine oil on wear and friction. Abrasion was the dominant wear mechanism identified. However, at very high soot contamination levels more serious starvation wear occurs, which could lead to engine failure as contacts may end up operating unlubricated. They similarly indicated that soot contamination affects the properties of lubricants unfavourably, in particular increasing the viscosity, which in turn increases contact friction, leading to a reduction in engine efficiency.

2) Water

Mohamed (2016) has found that water can facilitate corrosion and could, therefore, be set aside from the lubricant. Nevertheless, water cannot be avoided by contaminating the lubricant. Once the water amounts in the oil exceed a certain limit, the only alternative left is to drain the oil or to extract water from oil. In the case of large lubrication systems, the water sinks to the bottom of the oil tank owing to its big density and can be let out through a drain cock. However, it needs a good water extraction from the lubricant.

The Water contaminating oil leads to gear surface corrosion and, in the limit, destroy a gear completely. Considering industrial gear oil with just one-percent water content can decrease bearing life by up to 90 percent (Mohamed 2016) and contamination can quickly escalate.

3) Liquid contaminants:

Literature has shown that lubricating oil is diluted by Liquid contaminants such as unburned fuel from engines and possibly decreases their viscosity beyond a safe load. The lubricant with heavier oil contamination augments oils viscosity and interferes with the oil circulation. This affects the lubricating value and heat transfer capacity (Awaja & Pavel, 2006; Owolabi *et al.*, 2017).

According to Mekonnen (2014), the motor oil pollution furthermore causes deterioration of the lubricant oil. Common contaminant sources comprise dirt; sand and dust from the air, soot, unburned fuel in the oil, water from the condensation of the combustion process, metallic wear particulates that the filter of oil cannot trap and hold, corrosion by-products and additive elements that have degraded. In addition, dirt, sand and dust can continue to enter the engine and, to generate more wear debris, associated with other contaminants and cause more damage than they would when they are individuals. The table 2-1 shows typical contaminants found in used oils.

2.3.7 Contamination

According to Mekonnen (2014), contaminants are the major cause of oil deterioration. The most common contaminant sources are dirt, sand and dust from the air. Soot and unburned fuel in the oil are also considered as the contaminant. Further contamination occurs when water is condensed during the combustion process and due to wear metal particulates that the oil filter cannot trap and hold. It is also the result of corrosion by-products and additive elements that have degraded. These solid contaminants enter continuously the engine and create more wear debris which when combined with other contaminants cause more damage than they would do separately. Table 2-1 shows typical contaminants found in used oils.

Table 2.1 Typical contaminants found in used oil (Mekonnen, 2014)

Metals	**Chlorinated hydrocarbons**	**Other organic compounds**
Cadmium	*Dichlorodifluoromethane*	*Benzene*
Chromium	*Trichlorotrifluoroethane*	*Toluene*
Arsenic	*Tetrachloroethylene*	*Xylene*
Barium	*1,1,1- Trichloroethane*	*Benzo(a)anthracene*
Zinc	*Trichloroethene*	*Benzo(a)pyrene*
Lead	*Total Chlorine*	*Naphthalene*
	Total Chlorine	*PCB's*

2.3.8 Extraneous Contaminants

The additive packages blended into base oils range between 10 to 20 percent, by volume, of the finished lubricants. Performance of the lubricants declines over a period as the additives are altered and the oil becomes contaminated (Yang, 2008; Yang *et al.*, 2018). Contamination sources could be:

1) The breakdown of the additives and their subsequent reaction;

2) Soot and lead from engine blow-by;

3) Dirt and dust; metal particles from engine wear;

4) Residual gasoline or diesel fuels from incomplete combustion;

5) Water from combustion, blow by vapours, and rainwater/salt water ingress;

6) The mixing or dumping of other materials (chemicals or other oil types) into the used oil.

The detergent additives in the auto lube oil can combat the combustion by-products. Burning gasoline or diesel fuel produces acids, moisture, soda, ash and other contaminants. Hence, detergent would fight these by-products and inhibit their build up as sludge or varnishes.

Used oil that is dumped on soil can be washed into surface water by rain or snow, or it can seep through the soil into groundwater to contaminate our water sources. Used lubricant in the soil can also evaporate into the air. The pollutants in used oil that enter the air through evaporation or improper burning can then settle, or be washed by rain or melting snow, into surface water or on the soil. The only way to make sure that used lubricant will not contaminate either water, soil, or air is to not release into the environment at all.

The contaminants in the used lubricants may be toxic to the bacteria strains that are used in the process and may lower product yields.

2.3.9 Tests of Used Lubricating Oil (Awaja & Pavel, 2006).

The physical and chemical standard tests are employed to assess the properties of the lubricant and the amount of the contaminants in the used automotive oils. These tests involve the following measurements:

2.3.9.1 Physicals

(1) Viscosity: viscosity testing is used to confirm the existence of contaminants in the used lubricating oil. The polymerization and oxidation materials that were suspended and dissolved in the oil cause the augmentation of the viscosity of the oil, while a reduction in the viscosity of lubricating oil substantiates the fuel contamination.

(2) Pour point: pour point is the lowest temperature at which the oil flows. Low pour point signifies that the lubricating oil is good.

(3) Flashpoint: the flash point is the minimum temperature at which the vapours in air burn for a moment if catch fire by flame or spark. When the flashpoint decreases, it indicates unburned fuel have contaminated by dilution of lubricating oils. When the flashpoint increases imply that evaporation of the light components from the lubricating oil took place.

2.3.9.2 Chemicals

(1) Acidity or neutralization number: it is a measure of the amount of alkali needed for the neutralization of one gram of the oil. When acid number increases, it is an indication of the degree in the oxidation of the lubricating oil.

(2) Ash content: When the oil is totally burned the remaining solid ash is analysed and it is a measure of oil purity and gives an indication of contamination with metals.

(3) Carbon or coking test: this examines the solid residue got when the oil is heated to total vaporization and it refers to the amount of deposit formed.

(4) Water content: It is determined by fractional distillation and implied the amount of water emulsified in the oil.

(5) Fuel contaminants: It indicates the amount of fuel diluted in the lubricating oil during operation.

Table 2.2 Typical comparison of fresh and used base engine oil (Mekonnen, 2014)

Samples	Base engine oil (Ravenol, VSi SAE 5W-40)	Used engine oil (being in use for 2000–3000 km)
Flash point °C	232	158
Pour point °C	−13	−5
Kinematic viscosity@ (40 °C)	195.62	136.6
Kinematic viscosity@ (100 °C)	18	13.5
Viscosity index	100.27	89.11
Refractive index	1.4886	1.4763
Specific gravity	0.8818	0.9261
Water and Sediment (mL)	-	0.9
Carbon residue (wt %)	0.55	1.82
(TAN) mg KOH/ g(sample)	-	4.5
(TBN) mg KOH/ g(sample)	3.55	-
Metal Contents (ppm)		
• Cu	0	4.6
• Mg	72	81
• Cr	0	1.5
• Sn	0	1.6
• Pb	0	14.6
• Fe	0	72
• Zn	1200	1280

2.4. Importance of used oil recycling

Inappropriate used oil disposal is just a waste of a costly resource. Each gallon of used motor oil which is not recovered gives place to drill for more oil and in some cases causing an increase in oil import. Nevertheless, most of the crude petroleum produced all the way through the world today contains very little of the special hydrocarbon chains essential for motor oil. As a result, refining crude petroleum to make virgin lube oil is a complicated and costly process that necessitates nearly three times energy as much as re-refining used oil. Lube base oil can be improved and ‘regenerated’ to the quality equal to or better than its original virgin form (Merai Yash, 2015; Daham *et al.*, 2017).

A lot of waste oils can be recycled and recovered in a diversity of ways, moreover directly or after a number of forms of separation and refinement. According to the waste management chain of command, the first option is to keep the original properties of the oil allowing for direct reuse. Other options could comprise recovering its heating value and/or using in other lower stage applications. Certain kinds of waste oils, in particular lubricants, can be directly reused after being reprocessed. The use of waste oils, after treatment, can be either as lube base stock comparable to refined virgin base oil or as clean burning fuel (Merai Yash, 2015; Daham *et al.*, 2017).

2.4.1. General Regeneration Scheme

The operational emphases of all technologies include the subsequent four points:

i) Dewater/defuel

In the use of lubricating oil, foreign matters are mixed into it under different conditions. Moisture permeates into the lubricating oil after a long-term service. The basic components of light fuel are fuel and naphtha that are primarily coming from the leakage of fuel from the engine of the motor vehicle to the lubricating oil and the worsening of components of lubricating oil. These strange matters should be isolated with respect to the difference between their physical properties and the lubricating oil (boiling point, specific gravity, being soluble in water or not).

ii) Deasphalting (Desludging)

As stated above, the lubricating oil will be mixed with diverse foreign matters during the process because of the environment. Beside liquid strange matters such as moisture and light fuel, there are solid foreign matters such as metal powder produced from mechanical wear and additive put in the lubricating oil to make deterioration products during process leading to the production of oxidative products such as organic acids, unsaturated, condensed aromatics and mercaptans, asphaltenes and petroleum resins. The elimination of these compounds is known as deasphalting or desludging (Princewill and Sunday, 2010; Abdelwahab Emam, 2018).

When one deals with this kind of foreign matter, one can consider the diverse physical properties (different solubility and different boiling points) or use chemical methods (add in the chemical agent for reaction) to achieve deasphalting.

Before deasphalting was done mostly by the addition of sulphuric acid in the medium or solvent treatment method; at the present moment, people make use of film separation or heat treatment.

Some techniques perform deasphalting throughout the fractionation step where the foreign matters stay on as a residue during the fractional distillation method.

iii) Fractionation

The fractionation categorizes diverse materials according to differences in boiling points of different materials. Frequently, a petroleum product is the combination of diversified organic compounds (including lubricating oil), so to decide or remove a specific kind of material from the mixture, the materials can be found or removed by using fractionation.

iv) Finishing

After the abovementioned techniques, the final treatment is performed to remove some contaminants such as chlorine, nitrogen, oxygen, and sulphur, which cannot be eliminated from the lubricating oil during the above techniques. Clay or hydro treatments are repeatedly employed for the finishing procedure (Chia-Yu, 2008; Jegatheesan *et al.*, 2016).

2.5 Carbon Nanotube

Carbon nanotubes (CNTs) are allotropes of carbon were revealed accidentally by Sumio Iijima in1991, while studying the surfaces of graphite electrodes used in an electric arc discharge. CNTs are defined as hollow manometer sized tubes with up sheets of *sp*2 bonded from graphite (Ajayan et al., 2001; Vardhaman *et al.*, 2018).

The carbon nanotube have been used for water treatments in the process of removing the metal ions.CNTs has an adhesion power and absorption in the challenge of purification and recover certain base metals ions in case of the synthetic solution then applied on ore leachate. Besides that various method such as precipitation (Huisman et al., 2006; Joubert et al., 2015), filtration and reverse osmosis (Kandah and Meunier, 2007; Farghali *et al.*, 2017) have been employed in an attempt to recover some metal from aqueous solutions.

2.5.1 The effect of carbon nanotube on used lubricant oil

Many attempts have been made to make clear the effect of the nanotube on used lubricant oil. Ahmadi, Rashidi, Nouralishahi, and Mohtasebi, (2013) examined the preparation and thermal properties of oil-based nano-fluid from multi-walled carbon nanotubes and engine oil as a nano-lubricant. During their study, they used a nanotube in base engine oil. Amongst the different techniques, that have been applied for dispersing nanotubes inside the base oil, the functionalization method for carbon nanotubes using planetary ball mill was determined to be the best method for stabilization of nanotubes inside the SAE 20 W50 engine oil. According to the obtained results, thermal conductivity and flash point of Nano-lubricants with 0.1 wt% improved by 13.2% and 6.7%, respectively, with respect to the base oil.

Conferring to different investigations, the manner of viscosity change in Nano-fluids is influenced by different factors such as kind of fluid, kind of Nano-additives, the rate of concentration, the method used for dispersion of Nano-additives inside the base fluid. Finally, they concluded that adding up MWCNTs to engine oil SAE 20 W50 has no significant effect on base oil's viscosity at low concentrations.

By paying attention to the higher stability of Nano-lubricants with a lower concentration, the]oil/MWCNTs sample with 0.1 wt.% concentration can be suggested as the most suitable sample for improving the properties of engine oil. It has been established that more specifically, the invention pertains to the use of carbon nanotubes in liquid fuels and lubricants to accelerate the burning rate, dissipate electrostatic changes and/or increase viscosity (Moy et al., 2002; Du *et al.*, 2018). Carbon nanotubes in an amount from about 0.01% to about 5% by weight can also increase the viscosity of lubricants.

A significant concern in using carbon nanotubes in fuels and lubricants, both as single strands and/or as aggregates, is the increased wear of the engine due to abrasion by the fibril growth catalyst support. Carbon nanotubes, even in modest concentrations, can significantly increase the viscosity of liquids (Lubricant and fuel).

2.5.2 The application of carbon nanotube in engine oil

Ajayan and Zhou (2001) have postulated that carbon nanotubes have fascinated many scientists worldwide (Ajay Vardhaman *et al.,* 2018). The small dimensions, strength and remarkable physical properties of these structures make them a unique material with a whole range of promising applications. The following survey describes some applications of carbon nanotubes used in material sciences by stressing on their electronic and electrochemical applications. Nanotubes are also used as mechanical reinforcements in high-performance composites and nanotube-based field emitters, and their use as Nano-probes in metrology and biological and chemical investigations, and as templates for the creation of other nanostructures.

Kałużny et al. (2017) claimed that carbon nanotubes can reduce friction losses and fuel consumption in engine oil resulting in the notable reduction of torque of the engine at low crankshaft gyration of in the motoring speed of 7%. It has been shown that the oil shear during normal operation of the engine can effectively improve the dispersion of nanotubes. At the same time, the oil filtration system removes agglomerates of nanotubes very rapidly. Adding micro- and Nano-particles of substances such as copper, tungsten, molybdenum, and molybdenum disulphide to the lubricating oil is a well-established method of reducing the engine friction. Study of the effect of CNTs on the rheological parameters of the oil was described in the context of an engine the improvement of the thermal conductivity resulting from the addition of CNTs to oil may have a large positive significance.

The results of the tests described by Pottuz et al, (2004) and Yang *et al.*, (2018) clearly show that CNTs added to the oil reduces friction more effectively than graphite and C60 fullerene. The test conditions used by Hwang et al. (2011) and Gawande *et al.*, (2016) lead them to find opposite results; they found that the coefficient of friction of the mixture Nano-oils with the fibrous particle additives (eg. CNT) is higher than the one of Nano-oils with spherical nanoparticle additives. They have debated also the hypothesis proposed by Tao et al. (1996) and Abdullah *et al.*, (2016) regarding the nanoparticles behaviour, which can perform rolling or ball bearing role. The research outcomes of Hwang et al, (2011) and Abdullah *et al.*, (2017) lead to the conclusion that the lubrication performance clearly improved with the decrease in the size of the particles suspended in the mineral oil.

With regards to the effect of CNTs on the rheological parameters of the oil, the improvement of the engine the thermal conductivity resulted from the addition of CNTs to oil (Ahmadi, et al, 2013; Phan et al., 2014; Esfe *et al.*, 2016). Kogovšek et al. (2013), Kalin et al. (2012), Charooa and Wania (2016) and Kogovšek and Kalin, (2019) investigated the concept of adding CNTs or other nanoparticles like molybdenum disulphide to the lubricating oil and their related issues. In their studies of friction components, they have clearly shown that engine oil, in which large agglomerates of CNTs are suspended, has inferior tribological properties in comparison to oil in where CNTs are well dispersed (Chauveau, 2010; Chauveau et al. 2012; Wu *et al.*, 2018).

CHAPTER 3: EXPERIMENTAL METHOD

3.1 Introduction

This section describes the procedure and the nature of the equipment that was used in this investigation. The steps used to re-refining the semi synthetic used engine oil 20W-50 are presented in Figure 3-1, and comprises the following basic phases:

- Filtration of used oil for solid and suspension removal
- Solvent extraction and flocculation (removal of dissolved impurities as sludge)
- Solvent recovery and recycle for process cost reduction
- Characterisation of re-refined oil and sludge (impurities)
- Tribological test of the re-refined oil blended with CNTs

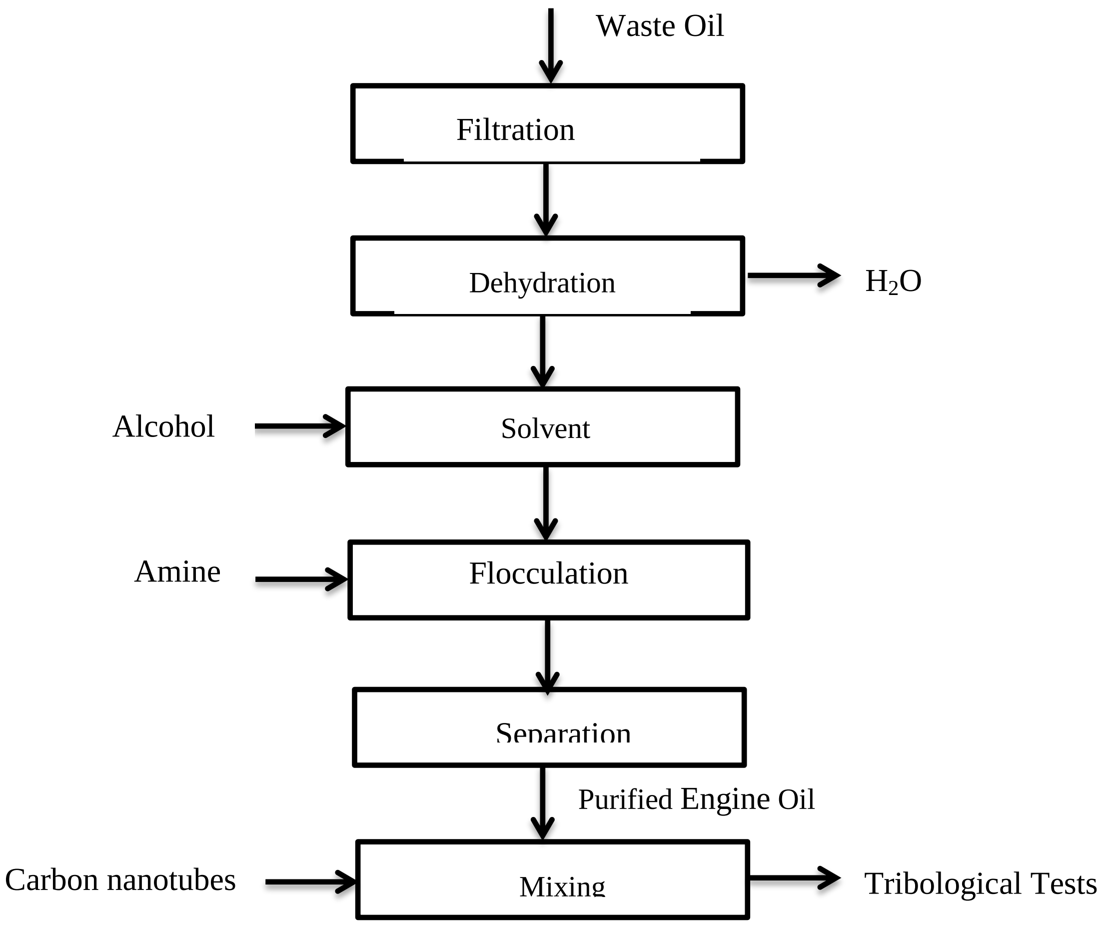

Figure 3.1 Typical process flow sheet for used oil treatment

3.2 Chemical reagents and materials used

The used oil sample, for this project, was be provided by Kappa Engineering Company Otto engine with a mileage between 3000 to 4000 km. The solvents and flocculants were obtained from ACE South Africa. Table 3.1 and 3.2 present the typical characteristics of the used oil as per the supplier record and the list of chemicals used for solvent extraction and flocculation,

Table 3.1 Typical Characteristics of 20W -50 Semi Synthetic

SAE grade	20W-50 Semi-Synthetic
Density @15^{o}C,g/mL	0.871
KinematicViscosity,mm^{2}/s @ 40^{o}C	167.8
KinematicViscosity,mm^{2}/s @ 100^{o}C	19.4
Viscosity Index	132
Pour Point (^{o}C)	-33
Flash point (^{o}C)	236

Table 3.2 List of reagents used in the project

Reagent	**Chemical formula**	**Company**	**Boiling point**
1. n-butan-1-ol	$C_4H_{10}O$	ACE	117,7^{0}C
2. Butan-2-ol	$C_4H_{10}O$	ACE	98-100^{0}C
3. T-butanol	$C_4H_{10}O$	ACE	83^{0}C
4. Ethanolamine	C_2H_7NO	ACE	

Table 3.3 List of major equipment & materials used and their purposes

	Purpose
Equipment	
Viscometer	Viscosity determination
Hot plate	Temperature variation during the process
Vacuum pump	Used in the solvent recovery setup
Condenser	Cooling of valuable materials
Shaker	Gentle mixing process
Centrifuge	Separation of sludge and refined oil
Rotary dryer	Solvent recovery
Distillation set up	Removal of light fuels
Magnetic stirrer	Thoroughly mix acid with sample
Chemicals	
Amine(Ethanolamine (ETA)	Used as a Flocculants for removes the contaminants from waste oil
Alcohol (n butanol, butan-2-ol and t-butanol)	Used for separation of impurities
Carbon nanotube	Tribological behaviour enhancer

3. 2.1 Characterization of used Engine Oil

To oil sample was characterized in order to determine the following:

- Oil density
- Oil viscosity
- Oil flash Point
- Neutralization number
- Coke content
- Ash content
- Water content
- Metal Content

3. 3 Filtration

The sample of semi synthetic engine oil 20W-50 was drained from an Otto cycle with 4 strokes engine in a 5litre container, and stored at room temperature before refining process. The mileage recorded before sample collection was 3000 km. A sample of 5000 ml of used oil (Figure 3.2) was filtered using 200 and 100 mesh filter medium at atmospheric pressure for 200 hours as shown in the Figure 3.3.

Figure 3.2 Typical unfiltered sample for used engine oil

Figure 3.3 Shows typical filtration sample for used engine oil

3.4 Solvent extraction and flocculation

At 50^0C, filtrated used engine oil was added to the alcohol (solvent). Three types of structural isomers alcohol were used in this investigation (Primary alcohol: n-butanol, Secondary alcohol: butan-2-ol and tertiary alcohol: t-butanol). The mixture was cooled to 30^0C, and thereafter ethanolamine was added to flocculate dissolved impurities. Various ratios were used for this investigation, and can be seen in Table 3.5, 3.6 and 3.7.

Table 3.4 Solvent (n-butanol) extraction and flocculation

Primary alcohol	Oil (g)	Solvent (g)	ETA (g)	Total (g)	Ratio Oil - solvent	Ratio solvent - ETA
n-butanol	20	20	0.04	40.04	1:1	500:1
	20	40	0.08	60.08	1:2	500:1
	20	60	0.12	80.12	1:3	500:1
	20	80	0.16	100.16	1:4	500:1
	20	100	0.20	120.20	1:5	500:1
	20	120	0.24	140.24	1:6	500:1
	20	140	0.28	160.28	1:7	500:1
	20	160	0.32	180.32	1:8	500:1
	20	180	0.36	200.36	1:9	500:1
	20	200	0.40	220.4	1:10	500:1

Table 3.5 Solvent (butan-2-ol) extraction and flocculation

Secondary alcohol	Oil (g)	Solvent (g)	ETA (g)	Total (g)	Ratio Oil - solvent	Ratio solvent - ETA
butano-2-ol	20	20	0.04	40.04	1:1	500:1
	20	40	0.08	60.08	1:2	500:1
	20	60	0.12	80.12	1:3	500:1
	20	80	0.16	100.16	1:4	500:1
	20	100	0.20	120.20	1:5	500:1
	20	120	0.24	140.24	1:6	500:1
	20	140	0.28	160.28	1:7	500:1
	20	160	0.32	180.32	1:8	500:1
	20	180	0.36	200.36	1:9	500:1
	20	200	0.40	220.4	1:10	500:1

Table 3.6 Solvent (t-butanol) extraction and flocculation

Tertiary Alcohol	Oil (g)	Solvent (g)	ETA (g)	Total (g)	Ratio Oil - solvent	Ratio solvent - ETA
t-butanol	20	20	0.04	40.04	1:1	500:1
	20	40	0.08	60.08	1:2	500:1
	20	60	0.12	80.12	1:3	500:1
	20	80	0.16	100.16	1:4	500:1
	20	100	0.20	120.20	1:5	500:1
	20	120	0.24	140.24	1:6	500:1
	20	140	0.28	160.28	1:7	500:1
	20	160	0.32	180.32	1:8	500:1
	20	180	0.36	200.36	1:9	500:1
	20	200	0.40	220.4	1:10	500:1

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, results obtained in this investigation are discussed for better understanding of the re-refining process of used lubricant and proposed better operating conditions for the process.

Engine oil has special use in automotive industry. Used oil in Otto, diesel and dual engines can be affected by fuel quality, operating temperature and other engine operating conditions. After certain mileages, the lubricant losses its properties and should be drained out of the engine system. It is not advisable to discharge used oil directly into the environment as this could offend the environmental regulations and standards. Over the years, several researchers have proposed numerous methods of re-refining of used engine oil starting from acid clay treatment to solvent extraction. The use of solvent extraction required an optimum oil - solvent ratio for removal of impurities and flocculates unwanted particles using amine as per work done by Al-Zahrani, Saeed and Putra (2013).

4.2 Product characterisations before and after re-refining of used 20W50 engine oil

Base oil (non-used lubricant) was characterized and compared with the investigated refined oil. The characterized properties are displayed in Table 4.1 and better viewed in Figure 4.1.

Table 4.1 Product characteristics results of 20W50 engine oil

Engine oil	Density @15°C	Kinematic viscosity mm/s@40°C	Kinematic viscosity mm/s@100 °C	Viscosity index	Pour point °C	Flash point °C
Base oil	0.873	162.47	18.78	130	-30	229
Control	0.815	118.3	11.84	86	-19	176
N-butanol	0.826	126.17	14.93	121	-24	196
Butanol-2-ol	0.853	121.06	14.7	124	-27	212
T-butanol	0.31	125.57	14.88	121	-26	203

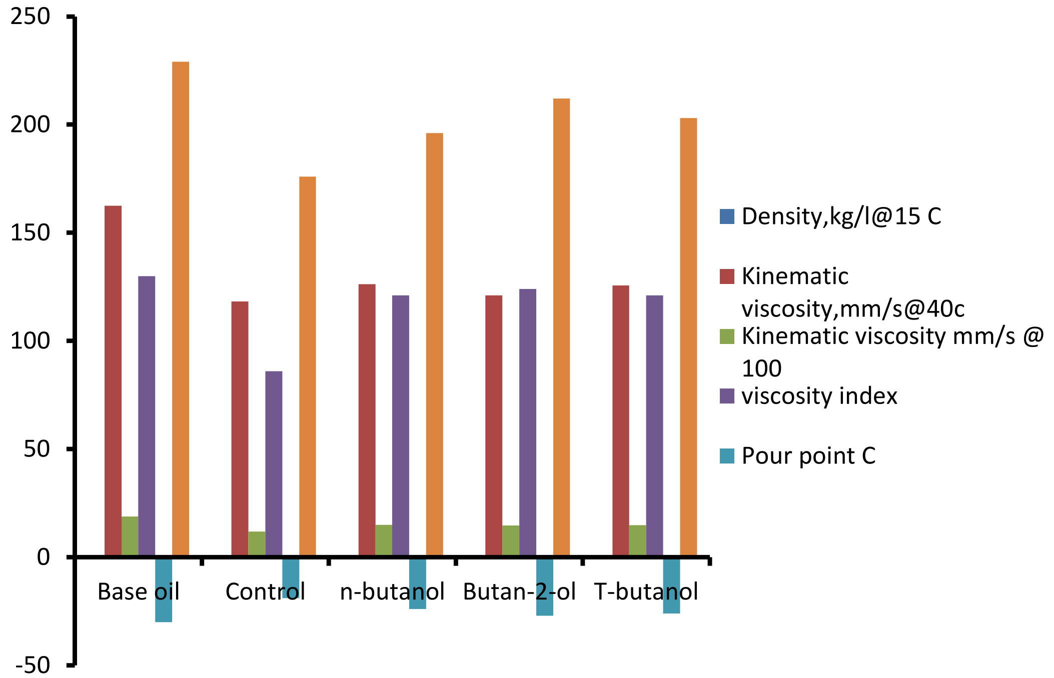

Figure 4.1 Typical Product characteristics results of 20W50 engine oil.

From Figure 4.1, it can be observed that the used of the three-butanol isomers improved the flash point of the purified lubricants compared to the control sample (used lubricant). Butan-2-ol showed a closer flash point to the base oil. Similarly, the density, kinematic viscosity, poor point and viscosity index of the purified oil were improved compared to the controlled oil. The used of butan-2-ol showed a better improved of the physical behaviour of the purified lubricant (density, poor point: -27 ^{0}C and viscosity index: 124). However, the kinematic viscosity was slightly smaller when compared to the two other isomers. The dimensionless number of 124 (viscosity index) indicates better resistance of oil to change at higher temperature.

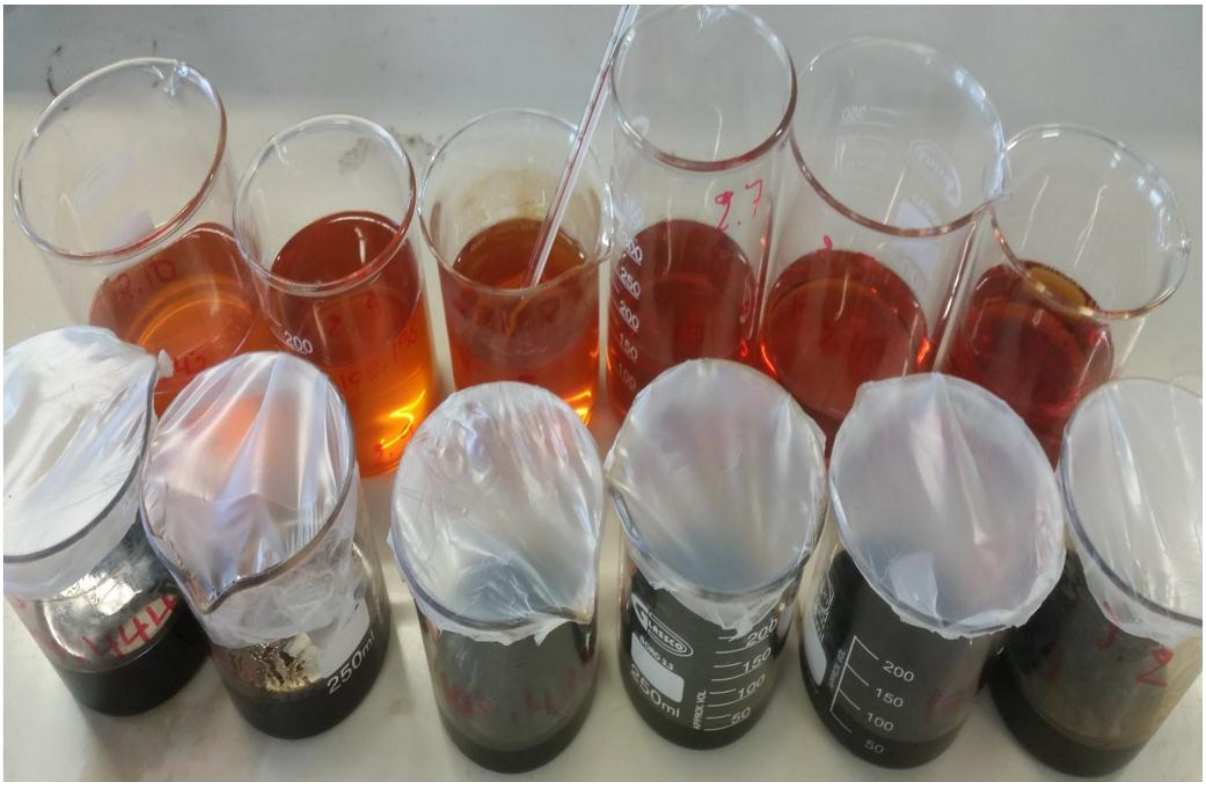

Figure 4.2 Refined oil and sludge produced after flocculation process using butan-2-ol and t-butanol

It can be seen from Figure 4.2 that the impurities (sludge) was sticker and dark in colour. During the lubrication process of the automotive engine process, the engine oil is mixed with various materials such as water and metals. The mixture changed the colour and the use oil become dark in colour.

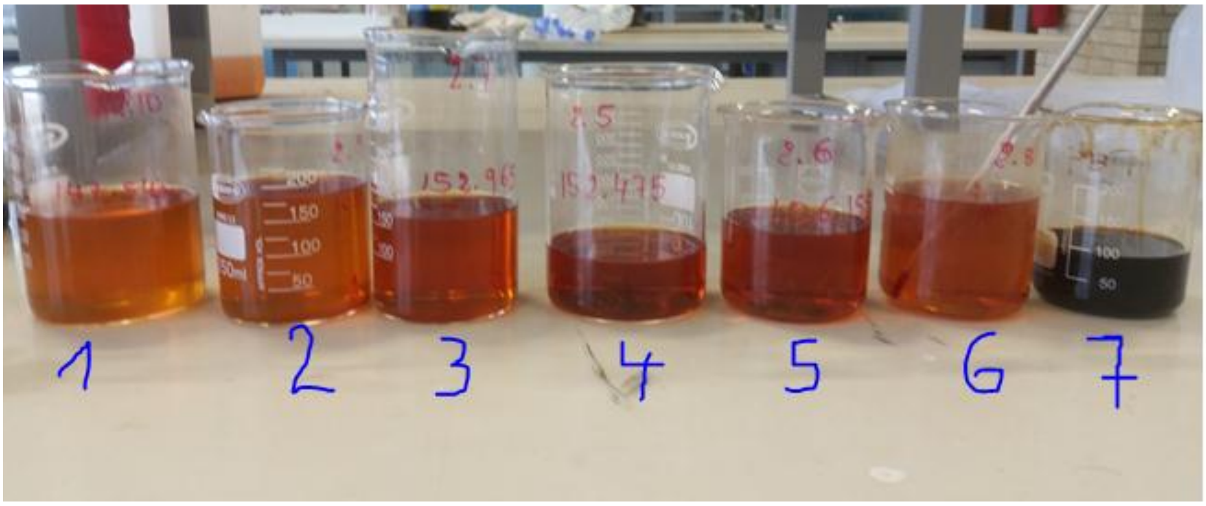

Figure 4.3 Refined oil samples with various oil – solvent ratio using butan-2-ol (1, 2 and 3), t-butanol (4, 5, 6) and used oil sample (7).

Figure 4.3 showed that the refined oil samples using butan-2-ol were more transparent and clear compared to the samples extracted with t-butanol. Tertiary alcohols are more reactive due to the increased in alkyl group number, which increase also the charge density on carbon atom and hence around oxygen atom. This favours the interaction of alcohol and some impurities.

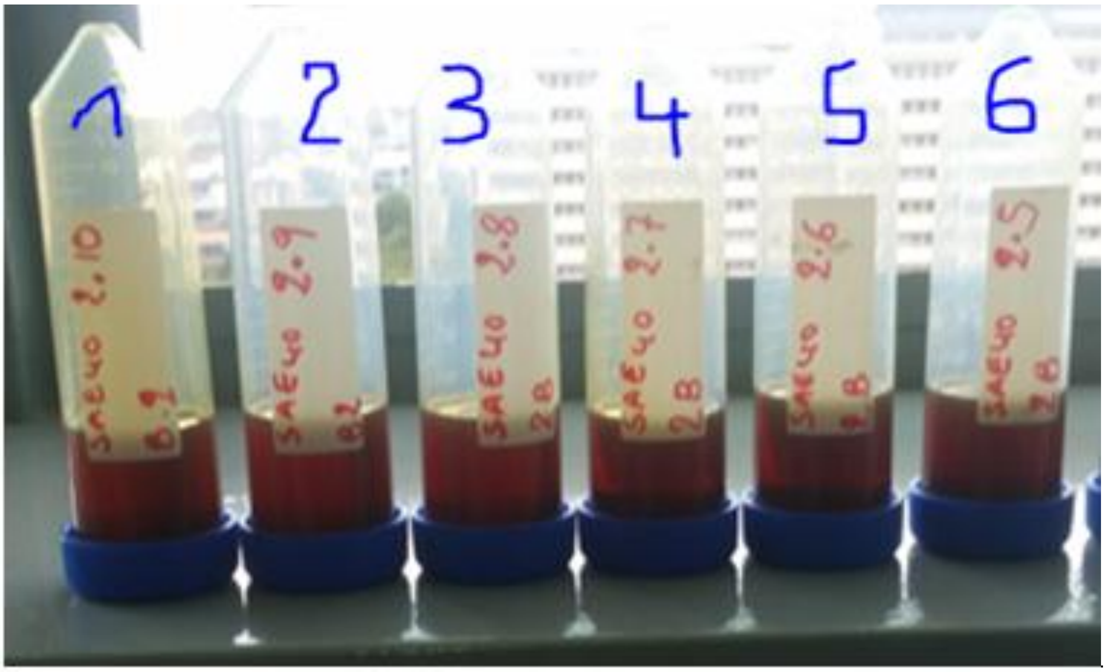

Figure 4.4 Show typical products with butan-2-ol

Figure 4.5 Show typical products with n-butanol

The figure 4.5 show the products with n- butanol that have the number(1,2,3,4and5 in blue) but the colour of n-butanol are the same with t-butanol due to the increased of alkyl group number, which increase also the charge density on carbon atom and hence around oxygen atom. This favours the interaction of alcohol and some impurities.

The Figure 4.6 shows the yield of butan-2-ol that have a number 2 in blue and the number one the yield of t-butanol in blue but the colour of butan-2-ol are better than for t-butanol.

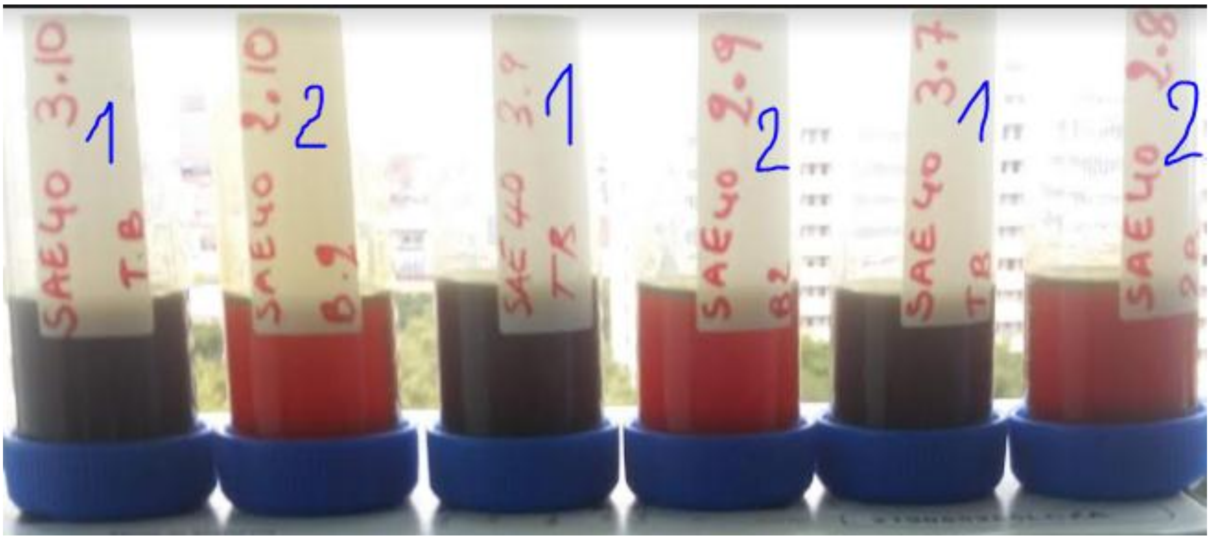

Figure 4.6 show typical yield with butan-2-ol and t-butanol

4.3 Metal content analysis before and after re-refining of used 20W-50 engine oil

The metallic content analyses were performed by atomic absorption spectrometry using a fast sequential atomic absorption spectrometer. Table 4.2 displayed the results of the samples analysis and Figure 4.7 shows better the metal's levels compared to the control lubricant (used oil) as follows:

Table 4.2 Metal contents analysis of 20W-50 engine oil

Properties	Used engine oil	Recovered oil			Base oil
		n-butanol	Butan-2-ol	T-butanol	
Metal content(ppm)					
Mg	7.1	0.53	0.5	0.52	0
Cu	11.2	0.9	0.81	0.86	0
Of Fe	62.75	0.87	0.73	0.82	0
Pb	11.00	1.05	0.94	0.98	0
Ni	10.5	0	0	0	0

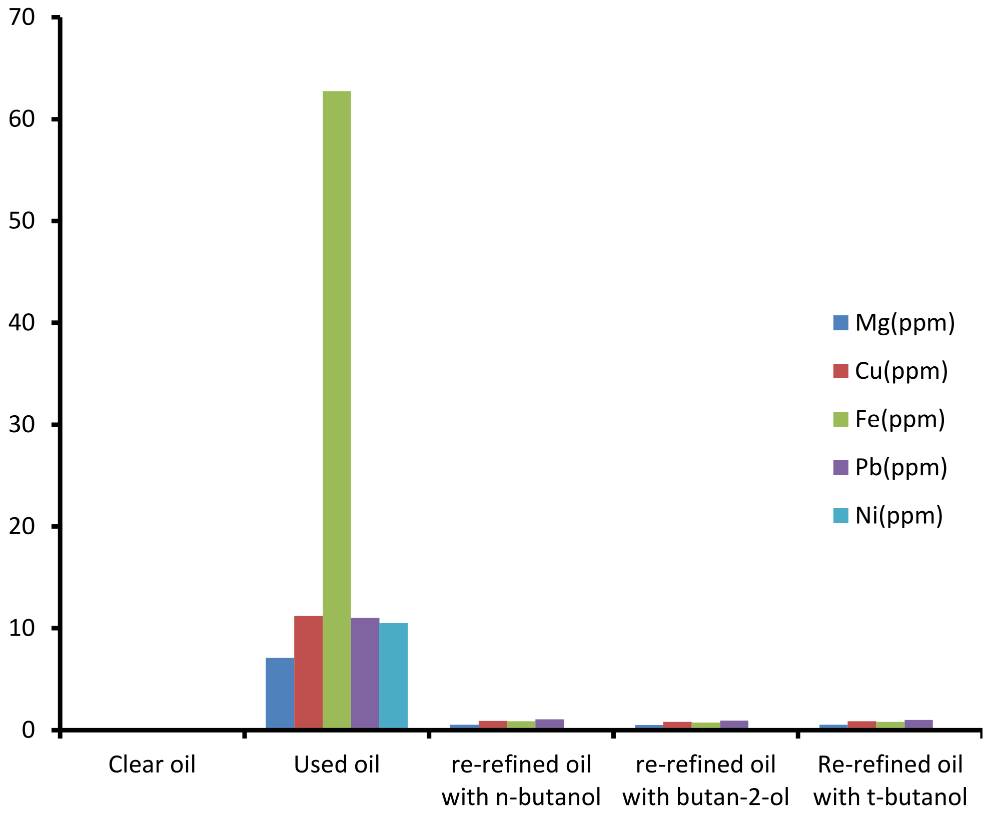

Figure 4.7 Metal contents analysis 20W-50 engine oil

Figure 4.7 showed the metals removal level in ppm compared to the control lubricant (used oil). It can be seen that the refining process removed more than 90 % of metals content. An average of 93, 93, 99, 91 and 100 % of respectively Mg, Cu, Fe, Pb and Ni were observed. Butan-2-ol showed higher percentage of metal removal compared to the other two isomers. It can also be seen that Iron is the most metal impurity in the used oil. This is due to the engine body content and loss of metal particles during the friction. So the refined oil may be proved has less hazardous and good quality during its reuse compared to the used oil.

4.4 Sludge formation during the re-refining process

The amount of sludge removed after the flocculation process was recorded in order to identify the butanol isomer, which removed more impurities. The results can be seen in Table 4.3 and Figure 4.8. Table 4.3 showed that the oil – solvent ratio below 1:4 did not favour the separation of the mixture content. The solvent did not act as major component of the mixture or the solution was saturated. For better result, the solute should be diluted.

Table 4.3 Effect of Sludge as function of ratio (solvent: ETA)

$N^{0:}$ of experiments	Ratio (Used oil:solvent)	Sludge(g)		
		n-butanol	Butan-2-ol	t-butanol
1	1:1	NS	NS	NS
2	1:2	NS	NS	NS
3	1:3	NS	NS	NS
4	1:4	1.503	1.551	1.681
5	1:5	0.993	0.664	0.406
6	1:6	0.912	0.483	1.089
7	1:7	0.566	1.211	1.091
8	1:8	0.387	0.937	1.4
9	1:9	0.329	0.982	0.976
10	1:10	0.285	1.39	1.61

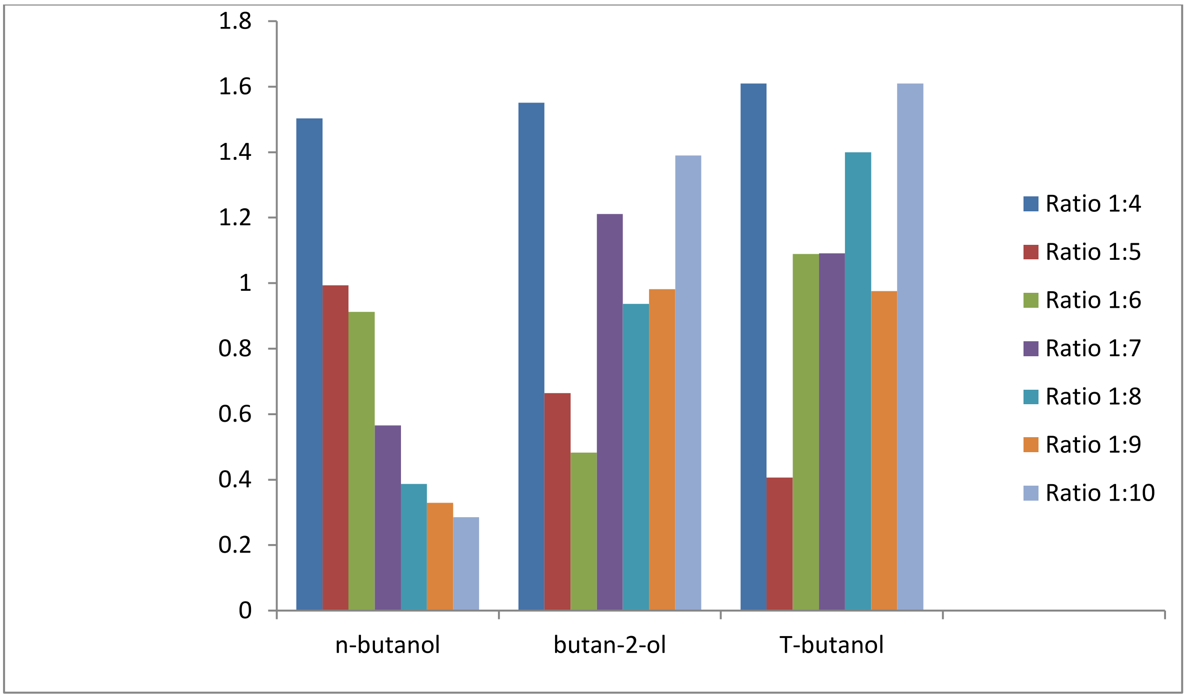

Figure 4.8 Effect of Sludge as function of ratio (solvent: ETA)

Figure 4.8 shows that from the ratio 1:4 and above, there were a clear separation between sludge and oil – solvent after the flocculation process. The ratio of 1:4 flocculated more sludge for all type of alcohol used. It can be seen that the was decrease in sludge amount from 1: to 1:10 using n-butanol. For butan-2-ol and t-butanol, the amount of sludge removed were dumping. However, t-butanol favours the removal of impurities as sludge at 1:4 followed by 1:10. More investigation should be carried out in order to establish a proper trend or explain the dumping behaviour between the two variables (oil – solvent ratio and sludge amount).

4.5 Yield of refined oil produced

As per above discussion and seen in Table 4.4, the yield of refined oil was discussed from the ratio 1:4. There was an increase in refined oil recover from n-butanol as seen in Figure 4.9. More n-butanol was required to reach a comparable yield with other isomers (butan-2-ol and t-butanol). None well trends were observed with butan-2-ol and t-butanol with a maximum variation of yield of 9.7 and 16.3, respectively. Butan-2-ol provided more stable results compared to the other two isomers with higher yield at low ratio.

Table 4.4 Yield as function of solvent: Ethanolamine ratio

N^0 of experiments	Ratio (solvent:ETA)	Yield (%)		
		n-butanol	Butan-2-ol	t-butanol
1	1:1	NS	NS	NS
2	1:2	NS	NS	NS
3	1:3	NS	NS	NS
4	1:4	49.315	77.6	73.08
5	1:5	63.66	83.175	83.45
6	1:6	64.525	87.33	83.97
7	1:7	69.665	80.22	82.615
8	1:8	75.525	84.66	84.395
9	1:9	78.34	86.995	89.565
10	1:10	85.95	84.72	82.76

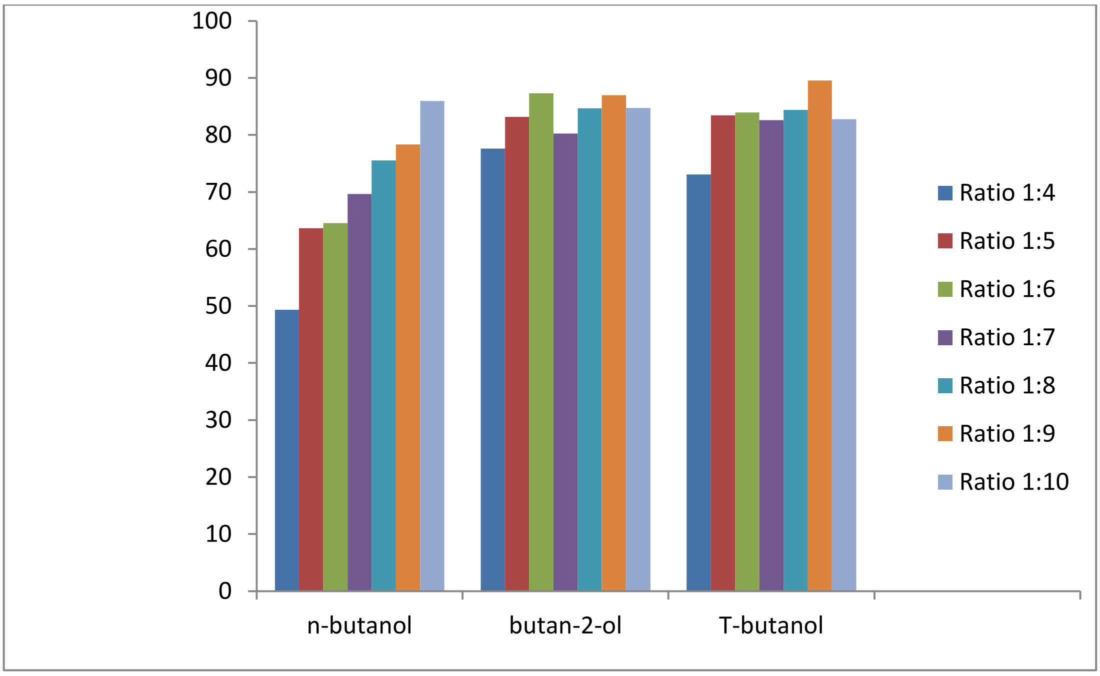

Figure 4.9 Yield as function of (solvent: Ethanolamine) ratio

4.6 Solvent recovery and raffinate after the re-refining process

The amounts of solvent recovered during the oil – solvent separation using the rotary evaporator are presented in Table 4.5. Figure 4.10 a well trend for all alcohol isomers used for this investigation. It can be seen that the boiling point (bp) of the three alcohols used dictates the amount of alcohol lost and recovered during solvent recovery process. Figure 4.11 showed that the percentage recovery for t-butanol is lower due to its boiling point, which is 83 ^{0}C. The amount of butan-2-ol and n-butanol recovered were closed as their boiling points (98 and 117.7^{0}C respectively) were above the solvent recovery temperature (94^{0}C and 40 minutes) using the rotary evaporator. More investigation should be done to understand the drop in recovery amount of butan-2-ol at a ratio of 1:7 (Oil – solvent).

Raffinate (solvent - oil) amounts in percentage collected after sludge removal are presented in Figure 4.11. It can be seen that the amounts of butan-2-ol and t-butanol raffinate are comparable, and higher compared to n-butanol.

Table 4.5 Solvent recovery in the rotary evaporator

N^0 of experiments	Ratio (solvent:ETA)	solvent recovery (distillate) (g)		
		n-butanol	Butan-2-ol	t-butanol
1	1:1	NS	NS	NS
2	1:2	NS	NS	NS
3	1:3	NS	NS	NS
4	1:4	64.936	55.22	34.32
5	1:5	83.01	69.563	53.572
6	1:6	91.745	89.155	60.892
7	1:7	96.831	102.076	68.34
8	1:8	134.87	114.71	81.12
9	1:9	146.48	128.867	94.862
10	1:10	163.768	146.471	109.477

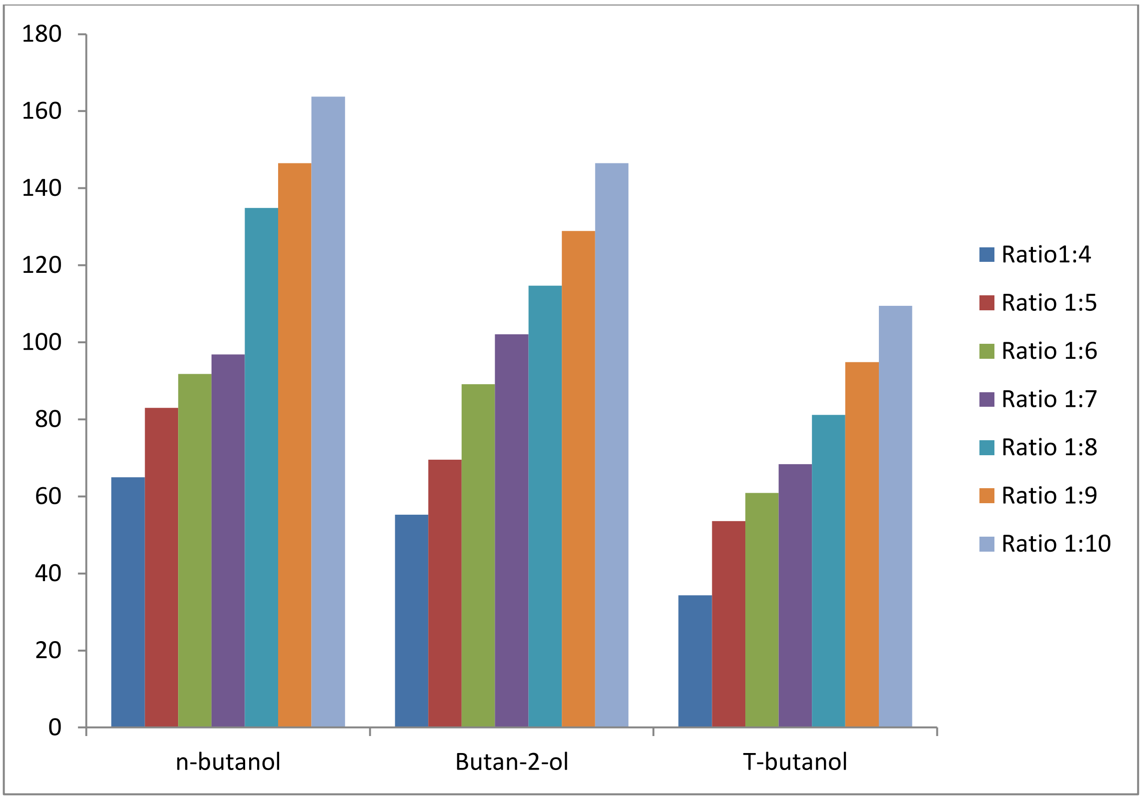

Figure 4.10 Solvent recoveries in the rotary evaporator

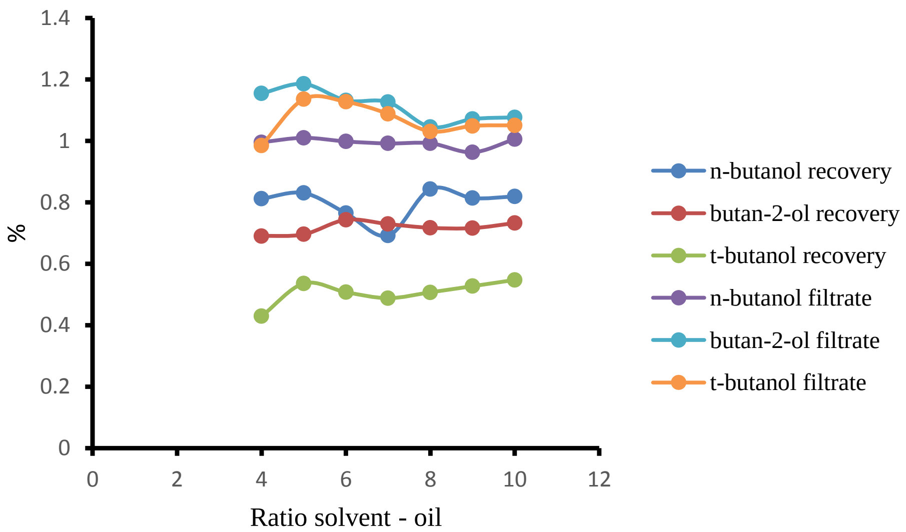

Figure 4. 11 Percentage of solvent recovery and raffinate after the re-refining process

4.7 Sludge removal at various oil: solvent ratio at 50^0C

Figure 4.12 showed that more sludge was removed at a ratio of 1:4, hence more impurities. This was discuss above but this sub-point displayed an exponential decrease in sludge removal using n-butanol as solvent (with R^2 value of 0.97).

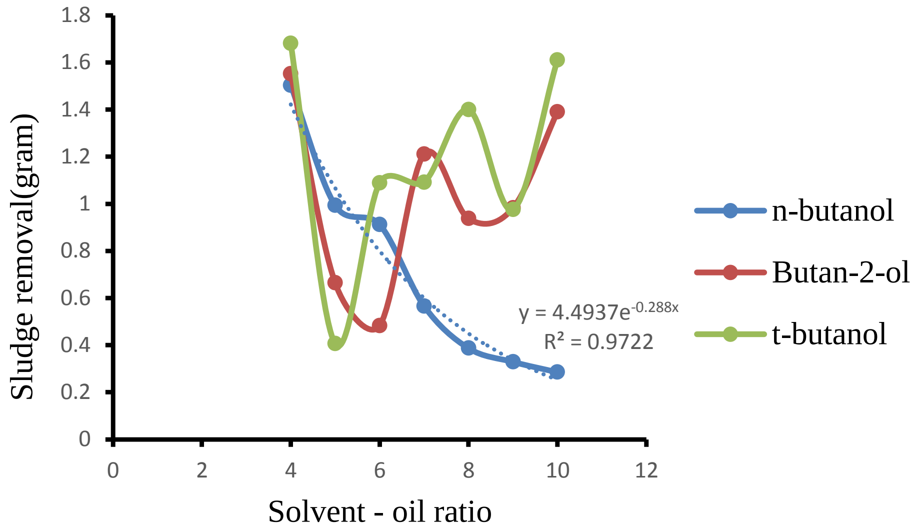

Figure 4.12 Effect of sludge removal as function of solvent - oil ratio

4.8 Sludge removal at various solvent extraction temperature with an oil – solvent ratio of 1:4

Figure 4.13 shows a dumping behaviour of sludge removal as function of temperature. The sludge amount removed using n-butanol is higher due to none clear liquid formed during the process. A long chain hydrocarbon favours the interaction between the solvent and some impurities. It can also be seen that at 50 ^{0}C, more sludges are removed with slightly difference between the three isomers used.

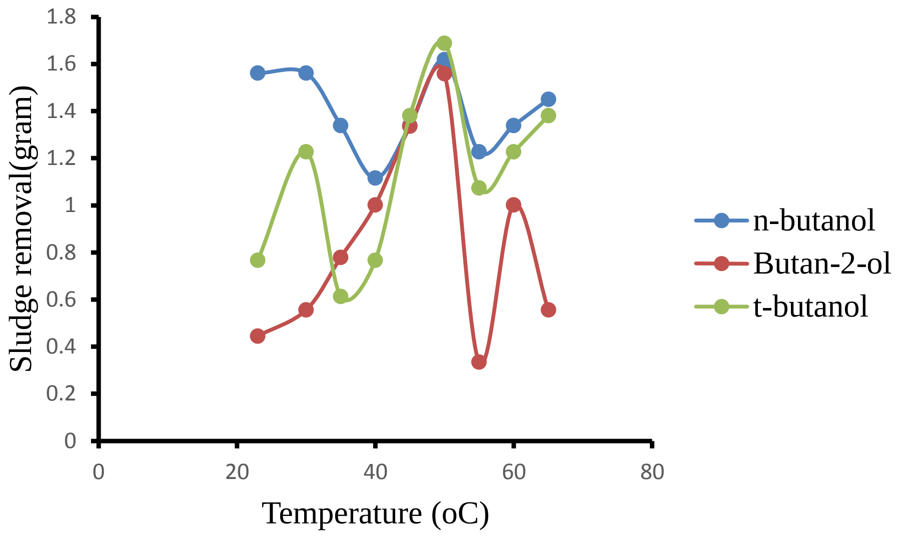

Figure 4.13 Effect of sludge removal as function of solvent extraction temperature

4.9 Sludge removal at various flocculation temperature with an oil – solvent ratio of 1:4

Figure 4.14 showed that n-butanol removed more sludge but its interaction with some impurities did not favour its selection as best solvent for this process. It can be seen that the use of butan-2-ol can remove 1.112 g of sludge at 20 ^{0}C and 1.56 at 50 ^{0}C; and with t-butanol, the sludge removal was 1.23 g of sludge at 30 ^{0}C and 1.68 at 50 ^{0}C.

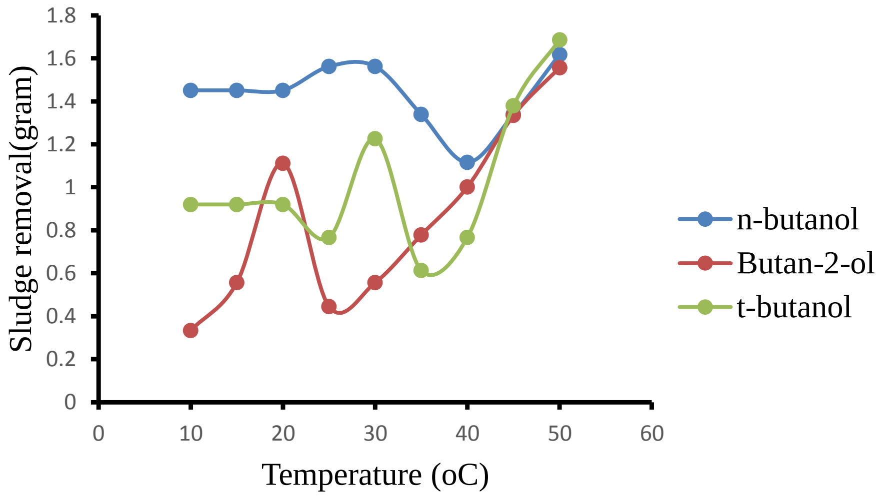

Figure 4.14 Effect of sludge removal as function of flocculation extraction temperature

4.10 Effect of sludge removal as function of ETA amount at a flocculation temperature of 30 ^{0}C and oil - solvent ratio of 1:4

It can be seen from Figure 4.15 that the sludge removal amount did not depend on the excess amount of the flocculent. The solvent – flocculent ratio of 500:1 is an optimum amount as per the work done by Al-Zahrani, Saeed and Putra (2013). Butan-2-ol produced less sludge because of its minimum loss of solvent mixed with the sludge. It can also be seen above that butan-2-ol produced a clear and transparent liquid.

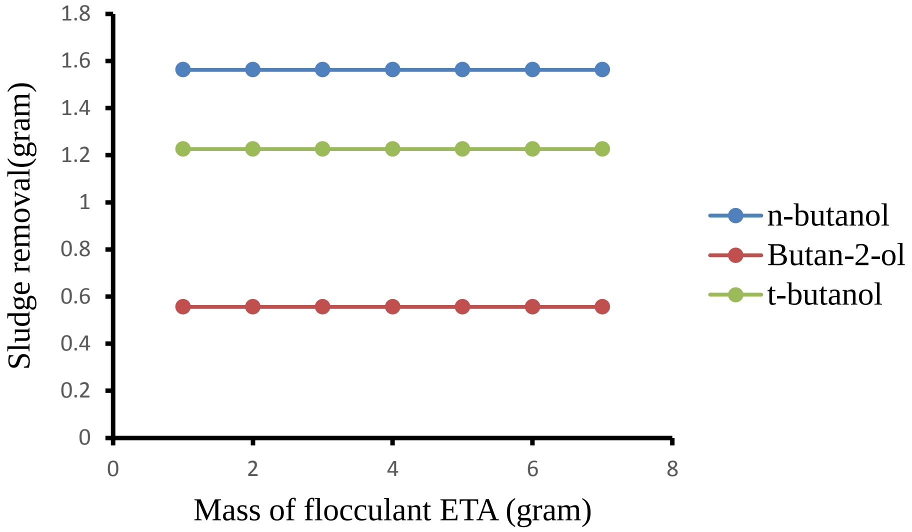

Figure 4.15 Effect of sludge removal as function of flocculation extraction temperature

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Automobiles and machines usage decrease the efficiency of lubricants due to water contamination, variation of heat and damage to solid surfaces. The impurities generated during the degradation are unsaturated, phenolic, aldehyde and acidic compounds; metals, gums and other asphaltic compounds. Poisonous metals waste such as zinc, chromium, copper, Tin, arsenic, lead, barium, cadmium and magnesium are found in some used lubricants and unfortunately disposed into environments and freshwater sources such as rivers, lakes, dams and streams.

Re-refining of used engine oil is crucial prior re-usage and proved as viable method in reducing contaminants in used engine oil. In this project solvent extraction method was employed .The chronological process description was as follows: multi stage filtration, solvent extraction (n-butanol, butan-2-ol and t-butanol), flocculation (ETA), solvent recovery and sludge disposal have been carried out systematically for their effects in used oil re-refining. These concurrent processes were able to enhance sedimentation of sludge therefore removing impurities. The followings are conclusive sentences after the re-refining process of used engine oil:

- Co-current filtration on filter medium of 200 and 100 mesh allows removal of debris and particles. It took 5 minutes to filter 1000ml on 100 mesh and 1200 minutes on 100 mesh. The cake collected was 3 g.
- The high viscosity index of 124 was recorded for sample purified using butan-2-ol .This indicates better resistance for oil to change its behaviour at higher temperature.
- The sludge removal increased with the increasing ratio solvent (n-butano,butan-2-ol,t-butanol) to oil to an optimum ratio of 1:4.The sludge removal decreased with the increase of solvent to oil ratio >1:4.Thefore more impurities could be removed at a ratio of 1:4 and temperature of 50^0C
- A yield greater than 50% was observed at a ratio of 1:5 for sample with n-butanol, butan-2-ol and T-butanol. This was due to evident flocculation at a ratio 1:5

- The lower the boiling point the higher the losses (in evaporation), hence less recovery.

  T-butanol had the lowest boiling of 83^0C, hence maximum evaporation losses and minimum alcohol recovery.
- N-butanol had the highest boiling point of 117.7 ^{0} C, hence minimum evaporation losses and maximum alcohol recovery.
- Butan-2-ol value 98^0C -100^0C lied between minimum and maximum evaporation losses and alcohol recovery, then minimum at 94^0C and 40 minutes.
- From 40 to 50^0C the sludge removal increased with the increase of n-butanol -oil mixture temperature to a maximum sludge removal of 14.5ml corresponding to a mixing temperature of ethanolamine and oil-n-butanol mixture of 50^0C.
- From 40 to 50^0 C, the sludge removal increased with the increase of n-butanol -oil mixture temperature to a maximum sludge removal of 1.618g corresponding to a mixing temperature of ethanolamine and oil-n-butanol mixture of 50 ^{0}C.
- From 50 to 55^0C the sludge removal decreased with the increase of butan-2-ol -oil mixture temperature to a minimum sludge removal of 0.334g corresponding to a mixing temperature of ethanolamine and oil-2-butanol mixture of 55^0C.
- From 55 to 60^0C, the sludge removal increased with the increase of butan-2-ol -oil mixture temperature to a maximum sludge removal of 9 ml corresponding to a mixing temperature of ethanolamine and oil-butan-2-ol mixture of 55^0C.
- From 35 to 50^0C, the sludge removal increased with the increase of t-butanol -oil mixture temperature to a maximum sludge removal of 11ml corresponding to a mixing temperature of ethanolamine and oil-t-butanol mixture of 50^0C.
- From 35 to 50^0C, the sludge removal increased with the increase of t-butanol -oil mixture temperature to a maximum sludge removal of 1,687g corresponding to a mixing temperature of ethanolamine and oil-t-butanol mixture of 50^0C.
- From 10 to 20 ^{0}C, the sludge remained constant with the increase of n-butanol - oil mixture temperature to a sludge removal of 13 ml(1.451g) corresponding to a mixing temperature of ethanolamine and oil-n-butanol mixture of 10, 15 and 20^0 C .At a temperature less than 20 ^{0} C , the mixture n-butanol-oil –ETA became frozen.
- From 35 to 50^0C the sludge removal increased with the increase of t-butanol - oil mixture temperature to a maximum sludge removal of 11 ml(1.686 g) corresponding to a mixing temperature of ethanolamine and oil-t-butanol mixture of 50^0C.

- The metal content (Mg, Cu, Fe, Pb and Ni) of recovered oil were decreased according to the standards after removing contaminants from the used oil. So the refined oil may be proved has less hazardous and good quality during its reuse compared to the used oil
- The sludge was heated for 40 minutes on a hot plate until it became thick and, it was tested for calorific value.

5.2 Recommendations

More investigation should be done in order to understand the dumping behaviour of the sludge removal during the process. An optimization process should also be investigated prior market and economic analysis of the project. It is also recommended to carried out an investigation on the tribological behaviour of re-refined product using carbon nanotube functionalized with anionic surfactant.

REFERENCES

Abdullah, M. F. (2017). The hBN Nanoparticles as an Effective Engine Oil Additive to Enhance the Durability and Performance of a Small Diesel Engine. *The hBN Nanoparticles as an Effective Engine Oil Additive to Enhance the Durability and Performance of a Small Diesel Engine*.

Abdullah, M. I., Abdollah, M. F., Amiruddin, H., Tamaldin, N., & Nuri, N. R. (2016). The potential of hBN nanoparticles as friction modifier and antiwear additive in engine oil. *Mechanics & Industry,* 17(1), p.104.

Abu-Elella, R. O.-E. (2015). Used motor oil treatment: turning waste oil into valuable products. Int. J. Chem. Biochem. Sci,. . *Int. J. Chem. Biochem. Sci,,* 7, pp.57-67.

Afrand, M., Najafabadi, K. N., & Akbari, M. (2016). AEffects of temperature and solid volume fraction on viscosity of SiO2-MWCNTs/SAE40 hybrid nanofluid as a coolant and lubricant in heat engines. *Elsiever,* 45-54.

Ahmadi, H., Rashidi, A., Nouralishahi, A. and Mohtasebi, S.S., . (2013). Preparation and thermal properties of oil-based nanofluid from multi-walled carbon nanotubes and engine oil as nano-lubricant. . *International Communications in Heat and Mass Transfer,,* 142-147.

Ajayan, P.M. and Zhou, O.Z. (2001). Applications of carbon nanotubes. . *Carbon nanotubes,* 391-425.

Algayyim, S. M., Wandel, A. P., Yusaf, T., & Hamawand, I. (2018). Production and application of ABE as a biofuel. Renewable and Sustainable Energy Reviews,. 82, pp.1195-1214.

Al-Zahrani, S. M., & Putra, M. D. (2013). Used lubricating oil regeneration by various solvent extraction techniques. *Journal of Industrial and Engineering Chemistry,* 19(2), 536-539.

Amanam, U. U., & Kovscek, A. R. (2017). Analysis of the effects of copper nanoparticles on in-situ combustion of extra heavy-crude oil. *Journal of Petroleum Science and Engineering,,* 152, pp.406-415.

Araromi, D. O., Aremu, M. O., & Gbolahan, O. O. (2016). Application of solvent extraction process for revivification of used lubricating engine oil. *American Chemical Science Journal,*, 10(4), pp.1-7.

Arumugam, S., Baskar, S., Sankaranarayanan, S., Athreya, S. H., Narayanan, N. L., & Prasad, S. S. (2018, July.). Influence of morphology of anti-wear nano additives on Tribological behavior of Chemically Modified Rapeseed Oil. *In IOP Conference Series: Mate*.

Awaja, F. and Pavel, D.,. (2006.). Design aspects of used lubricating oil re-refining. *Elsevier.*

Bowman, W.F. and Stachowiak, G.W.,. (1996). New criteria to assess the remaining useful life of industrial turbine oils. *Lubrication engineering, 52*(10).

Cai, J., Zheng, P., Qaisar, M., & Zhang, J. (2017). Elemental sulfur recovery of biological sulfide removal process from wastewater: a review. *Critical reviews in environmental science and technology,* ., 47(21), pp.2079-2099.

Cairns, A. and Haycock, R. (1996). *Automotive Lubricants Reference Book.* London, : Mechanical Engineering Publication.

Charoo, M. S., & Wani, M. F. (2016). Tribological properties of IF-MoS 2 nanoparticles as lubricant additive on cylinder liner and piston ring tribo-pair. *Tribology in Industry,* ., 38(2), pp.156-162.

Chauveau, V. (2010). Le pouvoir lubrifiant des nanotubes de carbone. *Doctoral dissertation, Ecole Centrale de Lyon*.

Chauveau, V., Mazuyer, D., Dassenoy, F. and Cayer-Barrioz, J., . (2012). In situ film-forming and friction-reduction mechanisms for carbon-nanotube dispersions in lubrication. *Tribology Letters, 47*(3), 467-480.

Du, H., Zhao, C. X., Lin, J., Guo, J., Wang, B., Hu, Z., et al. (2018). Carbon nanomaterials in direct liquid fuel cells. *The Chemical Record*, 18(9), pp.1365-1372.

Elkhaleefa, A. M. (2016). Waste Engine Oil Characterization and Atmospheric Distillation to Produce Gas Oil. *International Journal of Engineering and Advanced Technology (IJEAT),*, 5.

Emam, E. (2018). Clay Adsorption Perspective on Petroleum Refining Industry. *Industrial Engineering*, pp.19-25.

Epelle, E. I., Otaru, A. J., Zubair, Y. O., & Okolie, J. A. (2017.). Improving the Viscosity Index of Used Lubricating Oil by Solvent Extraction. 04 pp (1581-1585), 12.

Farghali, A. A., Tawab, H. A., Moaty, S. A., & Khaled, R. (2017). Functionalization of acidified multi-walled carbon nanotubes for removal of heavy metals in aqueous solutions. *Journal of Nanostructure in Chemistry*, 7(2), pp.101-111.

Gamlin, C.D., Dutta, N.K., Choudhury, N.R., Kehoe, D. and Matisons, J.,. (2002). Evaluation of kinetic parameters of thermal and oxidative decomposition of base oils by conventional, isothermal and modulated TGA, and pressure DSC. *Thermochimica Acta,*, 392.

Gao, Z., & Bandosz, T. (2009). Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes. *Journal of Hazardous Materials*, 167(1-3), pp.357-365.

Gawande, M. B., Goswami, A., Felpin, F. X., Asefa, T., Huang, X., Silva, R., et al. (2016). Cu and Cu-based nanoparticles: synthesis and applications in catalysis. *Chemical reviews,*, 116(6), pp.3722-3811.

Green, D.A. and Lewis, R. (2008.). The effects of soot-contaminated engine oil on wear and friction: a review.s, Part D: Journal of Automobile Engineering, . *Proceedings of the Institution of Mechanical Engineer, 222*(9), 1669-1689.

Gul, S. I., Gu, S., Irfan, M., Bilal, H., Rehman, A. U., & Khan, S. U. (2014). Recycling of used engine oil using solvent extraction and distillation. Journal of Engineering and Applied Sciences,. . *Journal of Engineering and Applied Sciences,* ., 36-46.

Gul, S., Irfan, M., Bilal, H., Rehman, A. U. and Khan, S.U.,. (2014). Recylcling of used engine oil using solvent extractionand distillation. *Journal of Engineering and Applied Sciences (JEAS) , 33*(2).

Hemmat Esfe, M., Rostamia, H., Afrand, M., & Wongwises, S. (2016.). Examination of effects of multi-walled carbon nanotubes on rheological behavior of engine oil (10W40). *Journal of Nanostructures*,, 6(4), pp.257-263.

Hsu, Y.L. and Liu, C.C. (2011). Evaluation and selection of regeneration of wastelubricatingoil technology. *Environmental monitoring and assessment, 176*(1), 197-212.

Huisman, J., Schultz, C., & Schouten, G. (2006). Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry. *Hydrometallurgy*, 106-113.

Hwang, Y., Lee, C., Choi, Y., Cheong, S., Kim, D., Lee, K., Lee, J. and Kim, S.H.,. (2011). Effect of the size and morphology of particles dispersed in nano-oil on friction performance between rotating discs. *Journal of Mechanical Science and Technology,, 25*(11), 2853-2857.

Idumeh, J. (2000). Lubecon laboritory handbook for engine oil analysis. *Lubecon Blending Company* , 3-11.

Jafari, A. J., & Hassanpour, M. (2015). Analysis and comparison of used lubricants, regenerative technologies in the world. *Resources, Conservation and Recycling*, 103, pp.179-191.

Jegatheesan, V., Pramanik, B. K., Chen, J., Navaratna, D., Chang, C. Y., & Shu, L. (2016). Treatment of textile wastewater with membrane bioreactor: a critical review. *Bioresource technology*, 204, pp.202-212.

Joly-Pottuz, L., Dassenoy, F., Vacher, B., Martin, J.M. and Mieno, T. (2004). Ultralow friction and wear behaviour of Ni/Y-based single wall carbon nanotubes (SWNTs). *Tribology International,, 37*(11), 1013-1018.

Kalin, M., Kogovšek, J. and Remškar, M. (2012.). Mechanisms and improvements in the friction and wear behavior using MoS 2 nanotubes as potential oil additives. . *Wear, 280*, 36-45.

Kałużny, J., Merkisz-Guranowska, A., Giersig, M. and Kempa, K. (2017). Lubricating performance of carbon nanotubes in internal combustion engines–engine test results for cnt enriched oil. . *International Journal of Automotive Technology, , 18*(6), 1047-1059.

Kandah, M., & Meunier, J. L. (2007). Removal of nickel ions from water by multi-walled carbon nanotubes. *Journal of hazardous materials*, 146(1-2), pp.283-288.

Kang, S., Cho, k. k., kIM, K. w., & ChO, G. B. (2008). Kang, S.Catalytic growth of single- and double-walled carbon nanotubes from Fe–Mo nanoparticles supported on MgO. *Journal of Alloys and Compounds*, 269-273.

Kogovšek, J., & Kalin, M. (2019). Lubrication performance of graphene-containing oil on steel and DLC-coated surfaces. *Tribology International,*, 138, pp.59-67.

Kogovšek, J., Remškar, M., Mrzel, A. and Kalin, M. (2013.). Influence of surface roughness and running-in on the lubrication of steel surfaces with oil containing MoS 2 nanotubes in all lubrication regimes. *Tribology international* , 40-47.

Kok, M.V. and Keskin, C., . (n.d.). 2001. Comparative combustion kinetics for in situ combustion process. *Thermochimica acta,, 369*(1), 143-147.

Mariamwit, A. A. (2016). Used automotive lubricant treatment using acid clay method . Addis Ababa: Addis Ababa University.

Mekonnen, H. A. (2014). *Recycling of used lubricationg oilusing acid-clay treatment process.*

Merai Yash, P. (2015). Re-refining of used lubricating oil. 6(3). *International Journal of Scientific & Engineering Research,, 6*(3).

Mohamed, A. (2016). Effect of Engine oil (CF50) on Water Separability of Industrial oil (Gear 320) and Hydraulic oil (Ep150) . *(Doctoral dissertation, Sudan University of Science and Technology).*

Moy, D., Niu, C., Tennent, H. and Hoch, R., . (2002). Inc., Carbon nanotubes in fuels. U.S. Patent 6,419,717. *Hyperion Catalysis International*, .

Nathan, C.C., and Leslie R. Rudnick. (1965.). *Kirk-Othmer Encyclopedia of Chemical Technology.*

Nwachukwu, M.A., Allinor, J., and Feng, H. (2012). Review and assessment of machine village potentials for small scale used engine recycling business. *African Journal of Environmental Science and Technology*, *6*(12), 464-475.

Owolabi, R. U., Akinola, A. A., Oyelana, O. A., & Amosa, M. K. (2017). Some Physico-Chemical and Adsorptive Reclamation Strategies of Spent Automobile Engine Lubricating Oil. *Journal of Engineering Research*, 22(1), pp.98-106.

Phan, N.M., Bui, H.T., Nguyen, M.H. and Phan, H.K. (2014). Carbon-nanotube-based liquids: a new class of nanomaterials and their applications. *Advances in Natural Sciences: Nanoscience and Nanotechnology, 5*(1), 15014.

Roelands, C. J. (1996). *Correlational aspects of the viscosity-tempreture-pressure relationship of lubricating oil.*

Santos, J. C., Santos, I. M., & Souza, A. G. (2017). Thermal degradation of synthetic lubricating oils: Part II–Rheological study. *Petroleum Science and Technology,* 35(6), pp.535-539.

Saunders, J. (1996.). Used oil refining revolution. Lubricants World, . *6*(9), 20-24.

Sudeep, I., Charanpahari, A., Kakade, A., Urame, s. s., & Bhatt, D. V. (2013). TRibological behavior of nano TiO2 as an additive in base oil. *Elsiever*, 776-785.

Tao, X., Jiazheng, Z. and Kang, X. (1996). The ball-bearing effect of diamond nanoparticles as an oil additive. . *Journal of Physics D: Applied Physics, 29*(11), 2932.

Techonology, A. F. (2013, August 14). *Atomic Vacuum*. Retrieved from Acid Free Technology: www.atomicvacuum.com

vardhamna, B. A., Amarnath, M., Ramkumar, J., & Rai, P. K. (2018). Experimental Investigations to Enhance the Tribological Performance of Engine Oil by Using Nano-Boric Acid and Functionalized Multiwalled Carbon Nanotubes: A Comparative Study to Assess Wear.

Westerfield, Z., Tian, T. and Kim, D., . (2017). *An Experimental Study of the Effects of Lubricants on Piston Ring Friction.*

Wu, H., Li, X., He, X., Lu, J., Wang, L., Zhou, B., et al. (2018). An investigation on the lubrication mechanism of MoS2 nanoparticles in unidirectional and reciprocating sliding point contact: the flow pattern effect around contact area. *Tribology In*.

Yang, C. (2008). The feasibility studies on sonochemical processes for treating used oil: Toxin reduction for eliminating recycle interference . *Doctoral dissertation,* . University of Southern California.

Yang, C. (2008). The feasibility studies on sonochemical processes for treating used oil: Toxin reduction for eliminating recycle interference Doctoral dissertation,. University of Southern California.

Yang, Z., Bhowimick, S., Banerji, A., & Alpas, A. T. (2018). Role of carbon nanotube tribolayer formation on low friction and adhesion of aluminum alloys sliding against CrN. *Tribology Letters,* 66(4), p.139.