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Extraction of heavy metals and other pollutant from used oil using reversed micelles

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Dedication

To my faithful husband

To my beautiful and lovely daughters,

Bisan and Maryam,

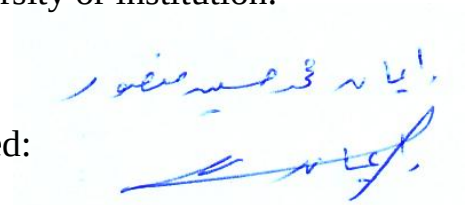
And to my Parents

For their care and support

Iman Mansour

Declaration:

I certify that this thesis submitted for the degree of Master, is the result of my own research, except where otherwise acknowledge, and that this study (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signed: 

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Abstract

Used oils are one of the greatest source of pollution worldwide mainly because of the quantities generated, their high toxicity level and mostly because of their mismanagement.

The conventional processes for recycling of used oil are found to be of low yield, laborious, time consuming and environmentally hazardous, due to the residual acidic sludge. In this sense, new methods of used oil recycling is needed, which lower price, time, reducing environmental pollution, saving foreign exchange for importing virgin lube oils, and conserving of mineral resources.

Reversed micelle extraction method is used in this research by employing nonionic surfactant-alcohol polyethylene glycol ethers (3EO) (alfonic 1412-3) - with used motor oil (SAE 15 W- 40) and buffer solutions. The reversed micelle region was identified using oil-surfactant-water three components phase diagram. It was found that with clean oil, the phase diagram showed the presence of liquid Crystal region which completely disappeared when used oil was used. The region at which the reverse micelle is stable in the presence of used oil is between 0 to 100% oil, 6% to 88% surfactant and from 5% to 25% of buffer solution but the region that which bounded by oil from 40 to 50% display minimum reversed micelle stability.

The extraction process was optimized with respect to oil-surfactant- water ratio within the stable region mentioned above and with respect to pH. The efficiency of the extraction method was judged based on several physical and chemical parameters such as color, density, viscosity, ash content, oleic phase recovered, UV-spectroscopy, IR-spectroscopy and heavy metal content. The density of recovered oil lies between 0.8897 g / cm^3 to 0.9194 g / cm^3, the viscosity range is from 100cp to 690cp, while the ash content have value from 0.0018% by wt to 0.0164% by wt, and the oleic phase recovery is between 84.4% to 96.3%. The peak with λ_{max}= 205 nm which appeared at uv-spectrum was observed for all samples but in used oil the absorbance was higher than that in clean oil. This observation is attributed to the presence of heavy metals and other pollutants like soot, oxidation product …etc.. The IR spectra of recovered oil show that all foreign signals were absent and are identical to that of clean oil without additives. The concentration of heavy metals in the recovered oil is much less than in the used oil with some metals have been completely removed such as Mn, Ni and Cu.

The optimum conditions for the effective removal of soot and heavy metals from used oil occurs at low amount of surfactant and high amount of oil (10g & 85g respectively) at buffer solution having pH=12.

The heavy metals content of used oil as well as recovered oil are analyzed by ICP-MS spectrometer. The used oil is found to contain 0.4152 ppm of Ba , 0.03 ppm of Cd, 9.567 ppm of Fe, 0.0567 ppm of Mn, 3.5744 ppm of Ni, 16.1744 ppm of Zn, 1.1908 ppm of Cu, and 0.2568 ppm of Pb. On the other hand recovered oil is found to contain 0.204ppm to 0.3196 ppm of Ba, 0.0052 to 0.0144 ppm of Cd, 1.1772 ppm to 6.1696 ppm for Fe, 1.6876 ppm to 16.014 ppm for Zn, 0.0444 ppm to 0.1524 ppm for Pb and complete removal (0 ppm) for Mn, Ni and Cu. These results point out to the nobility of the method in complete of removal of heavy metals from use oil that renders this process as a powerful technique for recovering oil for at least as energy source.

This work showed the great efficiency of reversed micelle in recycling used motor oil, especially in removing heavy metals with high efficiency, low cost, and with environmental sustainable fashion.

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List of Abbreviations

ASTM: American Society for Testing and Materials.

WCOs: Waste Crankcase Oils.

ADU: Atmospheric Distillation Unit.

VDU: Vacuum Distillation Unit.

ZDP: Zinc-Diphosphate.

PAHs: Poly-cyclic Aromatic Hydrocarbons.

PCBs: Poly Chlorinated Biphenyls.

OEMs: Original Equipment Manufacturers.

PBCs: Polychlorinated Biphenyls.

WCO: Waste Crankcase Oil.

O/W: Oil-in-Water.

ELM: Emulsion Liquid Membrane.

W/O: Water-in-Oil.

CPE: Cloud Point Extraction.

ULO: Used Lubricant Oil.

ICP: Inductively Coupled Plasma Spectrometry.

UV: Ultraviolet and Visible rays.

FTIR: Fourier Transform Infrared.

$L_{2:}$ Reversed micelle Microemulsion.

$L_{\alpha:}$ Lamellar.

LC: Liquid Crystal.

2Φ: Two Phases.

HLB: Hydrophile-Lipophile Balance.

SAE: Society of Automotive Engineers.

Cp: Centipoises.

λ_{max} :Maximum Wave Length.

IR: Infrared spectroscopy.

EPA: Environmental Protection Agency.

HWMR: Hazardous Waste Management Regulations.

Definitions

Lubricant	Substance introduced between two moving surfaces to reduce the friction and wear between them.
Engine lubricants	A complex mixture of hydrocarbons and other organic compounds, including some organometallic constituents that are used to lubricate parts of an automobile engine, in order to smoothened engine operation.
Used oil	Any semi- solid or liquid used product consisting totally or partially of mineral oil or synthesized hydrocarbons (synthetic oils), and as a result of such use is contaminated by physical or chemical impurities.
Refining of oil	Process of regenerating its used substance so that it can be used again.
Reclaiming	Simple cleaning methods (settling, heating, dehydration, filtration and centrifugation) are used during the recycling process primarily to remove insoluble contaminants and thus making the oil suitable for some sort of further use.
Microemulsion	Low viscosity, clear isotrope and thermodynamically stable mixture which have at least a hydrophilic, a hydrophobic and amphiphilic compound.
Reversed micelle	Nanoscopic water pools in a continuous nonpolar phase stabilized by a surrounding layer of surfactant molecules.

Chapter One

1.1. General Introduction

A huge amount of used lubricating oils are produced worldwide. Waste oils are one of the most abundant pollutant residues that are generated nowadays, reaching the value of 24 million metric tonnes per year [Naima, Liazid, 2013].

The different sources of used lubricating oils are railway workshops, industries, ship garages, defense machinery, automobiles workshops, etc. All types of lubricating oils in service in automobiles and process industries become contaminated and lose their performance due to changes in some of their properties. Therefore, such oils must be removed as used oil from the service as frequently as necessary. How to handle and what to do with the used lubricating oils are serious concerns to environmentalists, governments, industries and research scientists [Shakirullah, *etal.*, 2006]. Worldwide, 45% of waste oil are collected and recycled, while and remaining 55% are either misused or improperly disposed off by the end user severely increase problem of waste discharge into the environment [Durrani, 2013].

The used engine oils can be used in engine as engine oil after purifying it [Sharaf, *et al.*, 2013]. Some reason have necessitated most industries and private users to seek or adopt ways of regenerating the oil like; the rapid depletion of fossil fuel reserve which provide feedstock for the production of lubricating oil, shortage of fresh oil, increasing prices and high demand for lubricating oil [Isah, *et al.*, 2013].

1.1.1. Definition

A lubricant is a substance introduced between two moving surfaces to reduce the friction and wear between them [Thavasigamani, 2008]. Lubricant base oils are mixtures that are essentially formed by the fractions of petroleum which are distilled between 300 °C and 400 °C under atmospheric pressure, containing saturated hydrocarbons and lower amounts of aromatic and naphthenic compounds [Moura, *et al.*, 2010].

Engine lubricants are complex and highly engineered fluids that are designed to allow perfect and proper engine performance over a long service time [Sivarao, *et al.*, 2012].

During lubrication about 20% of the lubricating oil is consumed and the rest 80% are remain as such with some impurities. Thus a huge quantity of used engine oil is left and wastage from different transport sectors every day. Due to scarcity of petroleum products, these used engine oils can be used in engine as engine oil after purifying it [Beg, *et al.*, 2010].

Used oil means any semi- solid or liquid used product consisting totally or partially of mineral oil or synthesized hydrocarbons (synthetic oils), and as a result of such use is contaminated by physical or chemical impurities [Puder, Veil, 2004], such as dirt, very fine metallic scrapings due to engine erosion, water or chemicals, etc., can get mixed in with the oil. Also, due to oxidation or thermal degradation, a lot of impurities are generated in lubricating oil, during its application in internal combustion engines [Bridjanian, Sattarin, 2006].

Alternatively used oil is any oil refined from crude oil or any synthetic oil [Denton, 2004]: including used engine oil, gear oil, hydraulic oil, turbine oil, compressor oil, industrial gear oil, heat transfer oil, transformer oil, spent oil and their tank bottom sludge and suitable for re-refining [Joseph, Jhanani, 2011] that has been used and as a result of use or as a consequence of extended storage or spillage has been contaminated with physical or chemical impurities [EPA, 2005; Denton, 2004] that result in loss of its original properties and become unsuitable for its original purpose [Basel convention group, 1997]. Eventually, this used oil must be replaced with virgin or re-refined oil to do the job correctly [Phakatkar, Ghorpade, 2009].

There are some synonyms for used oil like: used motor oil, used crankcase oil, waste crankcase oils (WCOs), waste oil, lubricating oil (used crankcase oil), used motor oil 10W30, auto lube (used), and mineral-based used crankcase oil [Irwin, *et al.*, 1997].

1.1.2. Composition

Lubricating oils from petroleum [Naima, Liazid, 2013] consists essentially of complex mixtures of C_{16}-C_{36} hydrocarbon contaminants [Delistraty, Stone, 2007; Isah, *et al.*, 2013; Ogunwumi, *et al.*, 2014] (80 to 90% by volume) [Irwin, *et al.*, 1997]; they are mostly composed of isoalkanes having slightly longer branches and the monocycloalkanes and monoaromatics which have several short branches on the ring. These hydrocarbon molecules generally range from low viscosity oils having molecular weights as low as 250g/mol up to very viscous lubricants with molecular weight as high as 1000g/mol. The carbon atoms range from 20 to 34 [Udonne, 2011; Bakare, Udonne, 2013].

Base oils are either derived from crude oil or are synthetic material manufactured by chemical processes [Anwar, *et al.*, 2012]; the first step in the production of mineral base oils is to obtain lubricant feedstock from crude oil. There are two major distillation processes involved in the production of lubricant feedstock; first, crude oil is fractionated under atmospheric pressure by an atmospheric distillation unit (ADU) into various fractions, such as hydrocarbon gases, gasoline, kerosene, diesel fuel, and gas oils, based on the differences in their boiling point as shown in Figure 1.1A. The remaining heavy compounds are continually fractionated by a vacuum distillation unit (VDU) into lubricant feedstock as shown in Figure 1.1B [Fan, 2010]. deasphalting (as required by the nature of the crude oil charge), dewaxing, solvent extraction, filtering and blending including mixing various additives with the final lubricating oil [Udonne, 2011].

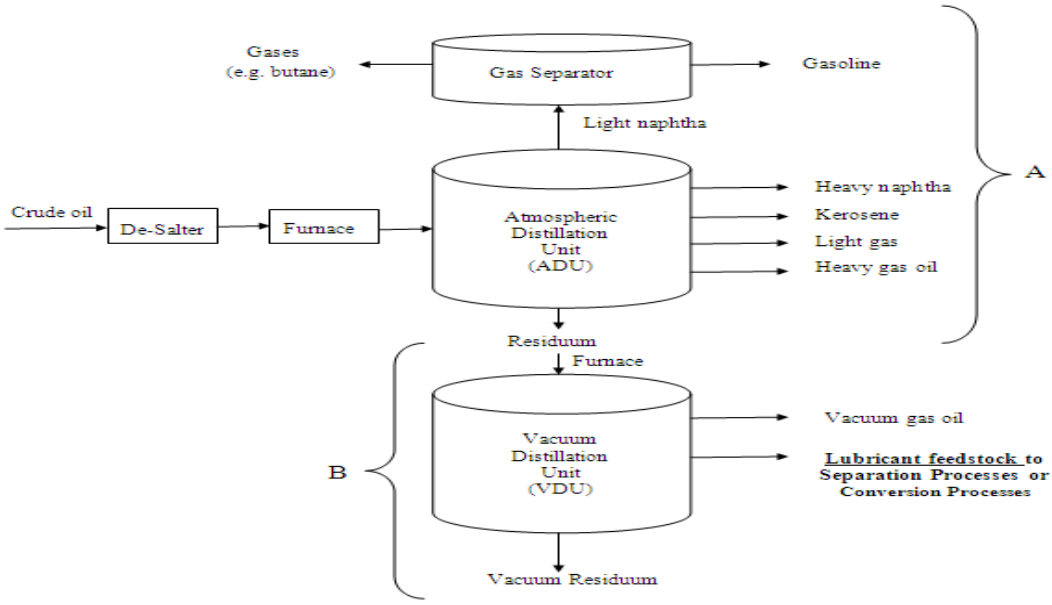

Figure 1.1: Simplified Schematic Diagram of ADU and VDU Processes.

Lubricating oils mainly consists of two materials namely the base oil and the chemical additives. Various types of additives are blended with the base oil according to its grade and specific duty. Used oil is similar to unused oil except that it contains additional chemicals that are produced or introduced when oil is used as an engine lubricant or during engine repair and cleaning operations [Delistraty, 2007]. One of the more important differences between new and used motor oil is the heavy metal content [Duhalt, 1989] such as lead, zinc, barium and magnesium resulting from engine wear, and higher percentages of alkyl benzenes, naphthalene, and methyl naphthalene [Ogunwumi, *et al.*, 2014], which mean used lube oil is organic compound consists of hydrocarbon, solvent, heavy metal, which its components harm the environment and difficult to get rid of or treated (soot, Poly-cyclic aromatic hydrocarbons (PAHs) probably as a result of pyrosynthesis, Chrolinated Paraffins (see Appendix B) and Poly chlorinated biphenyls (PCBs) are big components) [Manasomboonphan, Junyapoon, 2012].

The chemical composition of used mineral- based crankcase oil varies widely and depends on:

1. The various sources (automobile, airplanes, trains, ships, tractors or lawn mowers) of the used oil [Warmate, Ideriah, 2011].
2. The original crude oil.
3. The processes used during refining.
4. The efficiency and type of engine the oil is lubricating.
5. The gasoline combustion products.
6. The additives added to the fuel and to the original oil.
7. And the length of time that the oil remains in the engine [Palus, *et al.*, 2001)].

1.1.3. Additives of Lubricant

During oil fabrication, and in order to improve its physical and chemical properties, several types of additive are employed. The different types of additive are summarized in Table 1 [Duhalt, 1989].

Table1.1: Functional types of lubricating oil additives.

Chemical modifiers	**Physical modifiers**
Boundary lubrication additives: Wear inhibitors	Viscosity modifiers: Viscosity index improvers
Friction modifiers	Thickeners
Lubricity agents	Pour point depressants
Extreme pressure agents	Emulsion modifiers
Corrosion inhibitors	Foam decomposers
Oxidation inhibitors	Tackiness agents
Detergents and dispersants	Dyes

Three major roles of additives were to impart new, useful and specific properties to lubricant oil, to enhance present properties, and to reduce the rate of undesirable change that takes place during its service life. A typical composition of lubricating oil is shown in Table 2 [Durrani, 2010].

Table 1.2: Typical composition of lubricating oil.

Ingredients	Weight %
Society of Automobile Engineers (SAE) 30 or base oil stock	71.5 - 96.2
Metallic detergent	2.0 - 10.0
Ashless dispersant	1.0 – 9.0
Oxidation inhibitor	0.5 – 3.0
Antioxidant / antiwear	0.1 – 2.0
Friction modifier	0.1 – 3.0
Pour point depressant	0.1 – 1.5
Antifoaming agent	2 – 15 ppm

Major additive classes (10–20% by volume) include corrosion and rust inhibitors, antioxidants, emulsifiers detergents and dispersants, viscosity and color stabilizers, and anti-wear additives [Durrani, 2013; McCoy, 2007]. Degraded additives, metallic debris, oxidation products and carbon soot. , metal deactivators, corrosion inhibitors, rust inhibitors, friction modifiers, extreme pressure withstanding elements, antifoaming agents, demulsifying or emulsifying agents and stickiness improver [Diphare, *et al.*, 2013][a].

Metallic detergent is added at 2.0-10.0 % to neutralize the deposits formation from combustion of high sulfur fuel or acidic combustion material, which also help to prevent the deposition of lacquered resulting from oxidation. An example of metallic detergent that usually added is magnesium sulfonates. Dispersant (1.0-9.0 %), is blended with base stock to disperse or suspend sludge formation during usage, such as polymeric succinimides and polyester. Zinc dithiophosphate is introduced into the base oil as 0.5- 3.0% of weight as the oxidation inhibitor, where it helped the base oil to form a film layer to prevent acid from reaching the metal surfaces [Yaaccob, 2010]. Easters or acids (0.1-2.0 %) perform as the antiwear to reduce the effect of wear and friction. Friction modifier and antifoaming agent are added at 0.1- 3.0% and 2- 15 ppm, respectively. Antifoam collapses the small bubbles into big bubbles, which tend to rise and collapse at the surface. Pour point depressant (e.g. methacrylates polymers) is mixed into the oil as 0.1- 1.5%. It helps to inhabit the formation of wax crystal structure, which prevents the oil flow, during usage at low temperature. The summery of additive's functions is listed in Appendix A [Durrani, 2010].

1.2. Type of Lubricant oil

There are four major types of lubricants, namely-liquid, solid, gaseous and plastics lubricants. Examples of lubricants include oil, grease, air and graphite. Liquid and plastics lubricant are the most commonly used lubricant in industries because they are inexpensive, easily applied and good coolants while Gaseous and Solid lubricant are recommended only in some special application [Ogbeide, 2010].

1.3. Functions of Lubricant oil

Motor oils have been used since the development of steam engines as a buffer between moving and static engine components [Warmate, Ideriah, 2011]. Lubricating oil creates a separating film between surfaces of adjacent moving parts to minimize direct contact between them, decreasing heat caused by friction and reducing wear, thus protecting the engine [Sharaf, *et al.*, 2013; Rahman, *et al.*, 2008]. A fundamental requirement of engine lubrication is that when the engine starts, the lubricating oil must be able to flow to all the critical parts of the engine within a short period of time [Goldmints, Goberdhan, 2010] and reduce abrasions between machine parts. It can reduce noise and be used for cooling [Hsu, Liu, 2011].

Lubricants are essential elements used to improve the operating efficiency and reduce loss in energy and materials almost for all modern industries from manufacturing to space program [Fan, 2010], it is designed to impact varieties of properties and to protect engine in so many ways. Lubricating oil is highly specialized product carefully developed to perform many essential functions among which permit easy starting of engine, protecting machine against rust and corrosion, lubricating of engine parts [Ogbeide, 2010], prevent metal-to-metal contact and to transfer heat from friction away from the contact points, help to protect rubbing surfaces and promote easier motion of connected parts. In the process, they serve as a medium to remove high build up of temperature on the moving surfaces [Udonne, 2011, Isah, *et al.*, 2013]. Provide hydrodynamic film between moving components, including heat dispensing, suspending contaminants, acid neutralization, and preventing corrosion [Sivarao, *et al.*, 2012], and inhibits corrosion and improves sealing [Tippayawong, Sooksarn, 2010].

1.4. Deterioration of lubricant oil

Lubricating oils undergo various environmental stresses and leads to thermo-oxidative degradation of its base stock. This waste lubricating oil has higher values of ash, carbon residue, asphaltenic materials, metals, water, and other dirty materials; which are built during the course of lubrication inside the engine [Abdel-Jabbar, *et al.*, 2010]. If these materials deposit on the surface and in the flow passage, it is likely to cause malfunctions of the machine and reduce the overall productive efficiency [Hsu, Liu, 2011].

Initially the degradation rate is slow due to protective action of additives; however, the rate dramatically increases as soon as the additive package gets depleted [Sagi, *et al.*, 2008].

This is normally reflected in abrupt changes in the oils various physical and chemical properties, and also in the system performance indicating the end of useful life oil and may lead to failure of the mechanical components [Kaleli, Yildirim, 2008]. So they must be replaced on a regular basis in all operating equipment due to the contamination [Al-Ghouti, Al-Atoum, 2009].

Oil deterioration is subdivided into two main categories:

- Ageing which causes physical and chemical changes to occur in the oil as a result of oxidation.
- Ageing related to adverse external conditions such as sand dust, dirt, fuel, water, blow-by gases and metallic particles being introduced into the oil [Tippayawong, Sooksarn, 2010].

1.5. Contaminants in Lubricant oil

Used engine oil itself contains a number of additives and is contaminated by impurities and residues resulting from the combustion process [Vest, 2000]. The amount of contaminants in waste oil depends on several factors such as the original detergents and diluents added to the virgin oil, storage location, and management practices. For example as leaded gasoline is gradually being phased out, lead concentrations in waste oil will decrease significantly, and consequently, the quantities of bromine and chlorine additives will also be lower, further reducing the presence of halogenated hydrocarbons in waste oil [Diphare, *et al.*, 2013][a].

These impurities contain: unsaturated, polar, asphalt-like, acidic compounds, aldehydes, phenolic compounds, alcohols, non-stable products of hydrocarbons poly-condensation (gums, poly-nuclear aromatics, etc.). Besides, it absorbs NOx and the acidic fuel combustion exhaust gas, these compounds besides dust, fuel additives, soot [Bridjanian, Sattarin, 2006; Rahman, *et al.*, 2008], water, salt, broken down additive components, varnish, gum and other materials [Durrani et al., 2011; Kamal, Khan, 2009; Ogbeide, 2010]. It should be noted that heavy metals, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) are main contaminants in used lubricant oil [Kanokkantapong, *et al.*, 2009].

Moreover, the metallic scrapings act as catalysts at the high combustion temperature and oxygen vicinity, and produce an asphalt-like sludge [Bridjanian, Sattarin, 2006]. Furthermore, the engine wear introduced other metals to the used oil such as copper, aluminum, chromium, iron, manganese, nickel, silicon and tin [Warmate, 2011]. In addition, used oil contains small amounts of water, gasoline, antifreeze, and chemicals that come from gasoline when it burns inside the engine [Agency of toxic substances, 1997]. Chlorinated solvents may also be present in significant quantities as a result of the breakdown of additive packages and the addition of chlorine and bromine that act as lead scavengers in leaded gasoline [Al-Ghouti, Al-Atoum, 2009].

1.6. When oil must be changed

Through their use of oil, they lose their properties, become contaminated and at some point they cease to be fit for the use they were originally intended to. These used oils are then replaced by fresh lubricating oils and we are left with some waste oils. Some 50% of what is purchased will become waste oils (the rest is lost during use, or through leakages [Sharaf, *et al.*, 2013]. In order to avoid an engine failure, the oil must be changed before it loses its protective properties. At the same time, an unnecessary oil change should be avoided for environmental and economical reasons [Agoston, *et al.*, 2005].

In common practice, people change their engine oil at a constant time or mileage interval according to the recommendation of the lubricant oil manufacturers or vehicle original equipment manufacturers (OEMs). However, since this oil changing system is not based on the real oil condition of the specific engine, it can be replace before reaching the end of its useful life or after its useful life is exceeded. This is uneconomical as it will be a waste, and also to deteriorate the engine performance as time passes. The typical lubricant oil can sustain between 5,000 km to 10,000 km mileage depending on the type used. The oil replacement is necessary upon reaching its useful life to maintain maximum engine protection [Sivarao, *et al.*, 2012]. Crankcase oils are altered during use because of the breakdown of additives, contamination with the products of combustion, and the addition of metals from the wear and tear of the engine [Irwin, *et al.*, 1997]. This used oil needs proper management to make it a valuable product by minimizing the quality of oil being improperly disposed off and reducing the waste oils environmental burden [Emam, Shoaib, 2012].

1.7. Effect on Environment

Waste oil has some negative features to environmental protection, such as uneasy removal, treatment, and containing compositions hard to degenerate, and it will cause severe environmental pollution if discarded randomly [Hsu, Liu, 2011].nMillions of tons of used oils are disposed through dumping on the ground or in water, land filling [Joseph, Jhanani, 2011], forming films of oils on the surface of water prevent the replenishment of dissolved oxygen thereby hamper aquatic life, impair photosynthetic processes and block sunlight [Rahman, *et al.*, 2008].The used or waste oils can be refined and treated to produce fuels or lubricating oil base stock. On the other hand, the waste oils pose an environmental hazard due to both their metal content and other contaminants [Naima, Liazid, 2013].

Waste lubricant oil creates environmental pollution if not disposed off properly, there is a possibility that other substance that it may contain, enter natural cycles through the food chain via water, soil and air. In this way waste lubricant oil pose risk to human health and impede the growth of plants and their ability to take up water as some times waste lubricant oil contained hydrocarbons, heavy metals polychlorinated biphenyls (PCBs) and other halogen compounds. To convert the harmful wastes into harmless substance, it is necessary to make it beneficial for reuse, recycling keeps oil out of our groundwater supplies, thus protecting drinking water resources [Durrani, 2013]. Little waste engine oil

is enough to ruin millions of gallons of fresh water [Hidayah, *et al.*, 2013; Isah, *et al.*, 2013].

Several components of the oil, e.g. solvents and detergents added during the blending process, aliphatic hydrocarbon and PAHs distilled from crude oil, and metals from engine wear are either toxic in themselves or can combine with products of combustion to generate car cinogens and endocrine disrupters [Adelowo, *et al.*, 2006] contamination of water bodies leading to impairment of aquatic life, impairment of plants metabolism through plant root toxicity, and adverse effect on soil organisms such as bacteria, fungi, and other multicellular organisms. Moreover, research findings have shown statistically significant impact of such reckless disposal on plants, including height reduction, chlorophyll loss and protein level reduction [Ogunwumi, *et al.*, 2014].

Furthermore, severe soil contamination can result from waste oils being left on the ground [Sharaf, *et al.*, 2013]; it adsorbs to the soil particles, reduces porosity and therefore reduces aeration of soil [Warmate, Ideriah, 2011].

1.8. Economic Impact

When lubricants are disposed in the water system, the layer of grease becomes thicker, and the flow of wastewater in the sewer pipes becomes restricted. Blockages in the wastewater collection system are serious, causing sewage spills, manhole overflows, or sewage backups in homes and businesses. These overflows can result in costly clean-up and repairs as well as attracting severe fines from the regulatory agencies. Countries spend billions of rands every year unplugging or replacing grease-blocked pipes, repairing pump stations, and cleaning up costly and illegal wastewater spills. These repairs cost money and may lead to higher local wastewater rates, thereby affecting the business and citizens as well. These extra charges are brought to recover cost of the extra techniques employed to remove these hazardous material from the waste water stream prior to purification process. On the other hand, waste minimization and recycling has resulted in a number of businesses and employment opportunities being created. Further motivates that 1 liter of waste-oil reprocessed as fuel contains about 8000 kJ of energy, which is enough to light a 100 W bulb for 24 hours [Diphare, *et al.*, 2013] or to operate a 1000 W electric heater for 2 h. Also, while 67 liters of crude oil are needed to obtain 1 liter of motor oil, only 1.6 liter of waste oil are required to produce the same amount of motor oil [Durrani, 2013]. The efficient recycling of waste lubricant could help reduce both the environmental pollution and gas emission from greenhouses, thus creating an environmental and economic benefit [Diphare, *et al.*, 2013].

The cost of recycling is relatively low compared from its production from crude oil as the numbers of purification stages are reduced. From the research carried out it was discovered that when 25 liters of spent oil was recycled appropriately, 10 liters of lubricating oil was obtained from the process whereas 220 liters of crude oil would be required to produce the same 10 liters of oil [Ogbeide, 2010]. During times when the price for crude oil was high or in isolated economies the refining of used oil made economic sense. One gallon (3.8 kg)

of used oil can be re-refined into 2.3 kg of lubricating oil. For comparison, a 42-gallon (150 kg) barrel of crude oil typically contains only 1/2 gallon (1.9 kg) of lubricant quality base oil [Durrani, 2013]. Re-refining of waste oil is energy efficient; less energy (about one third) is used to produce a gallon of base stock from waste oil than to produce the same gallon from crude oil. It is also environment friendly [Rahman, *et al.*, 2008].

1.9. Dealing with waste oil

Used oil is a valuable resource because of its lubrication and heat value [Denton, 2004] but the lifetime of the motor oil is limited and has to be changed periodically. In the West Bank, there are no regulations to organize the disposal of the used motor oil [Qumsieh, *et al.*, 2001].

There are basically three options to deal with the regarding waste oil in world:

- Dumping the waste oil on land, garbage heap and sewerage system.
- Regeneration of base-oil from waste oil.
- Extracting of heat value of waste oil through combustion process [Rahman, *et al.*, 2008].

Used oil re-refining is not a new process, but some of its applied old versions produce pollutants which are not less environmentally harmful than the used oil itself. Generally speaking, there are three categories for waste oil disposal:

1. Reuse, including re-refining.
2. Thermal cracking.
3. Incineration / Use as a fuel.

The first one is the best one, the second one – although produces acceptable (cracked) products, but is not as good as re-refining and the third one produces a lot of ash, which contains heavy metals and pollutes the environment [Bridjanian, Sattarin, 2006]. The common disposal technique of used lubricating oil is burning for generation of energy. Burning and all other routes of disposals of used lubricating oils are uneconomical and result in the wastage of resources [Shakirullah, *et al.*, 2006]. Therefore, recycling and re-refining of waste into virgin lubricating oil may be a suitable option for protecting the environment from hazardous waste. Another benefit associated with waste lubricating oils recycling could be the economic gain due to the high price of mineral oils [Al-Ghouti, Al-Atoum, 2009].

1.10. Heavy metals removing

The pollution of the environment with toxic metals is a result of many human activities, such as mining and metallurgy, and the effects of these metals on the ecosystems are of large economic and public-health significance [Gavrilescu, 2004]. Distribution and availability of heavy metals to plants is important when assessing the environmental quality of an area [Aydinalp, Marinova, 2003]. Extraction of heavy metals by organic acids

is likely to be representative of an available fraction to plants [Oustan, *et al.*, 2011]. The process extracts heavy metal contaminants from matrices such as low grade ore, soil, sediment, used catalysts, or industrial wastes, by using a volatile organic reagent was achieved [Lecourt, *et al.*, 1999].

Environmental exposure to chemical mixtures may adversely affect health. Many such mixtures of a hazardous nature when released into the environment can impact human and/or wildlife via air, soil or water contamination. One of the sources of pollution from the transport sector is waste crankcase oil (WCO). The WCO is removed from the crankcase (engine sump) when the engine is drained during an oil-changing procedure [Ssempebwa, Carpenter, 2009].

The most conventional method of heavy metals extraction from industrial effluents is their precipitation as metallic bases under appropriate pH conditions. Other methods for reducing the concentration of heavy metals in influents also include ion exchange, reverse osmosis, adsorption and liquid–liquid extraction for effluents treatment, including metallic cations extraction [Dantas, *et al.*, 2003], an unconventional process of liquid–liquid extraction using a microemulsion as solvent [Dantas, *et al.*, 2001].

Extraction of heavy metals by microemulsions (oil-in-water (o/w)), using vegetable oils as surfactants was achieved. This method has two stages. The first one, the heavy metal ion present in the aqueous phase is extracted by the microemulsion. In a second step, the re-extraction process occurs: the microemulsion phase, rich in metal, is acidified and the metal is recovered in a new aqueous phase, with higher concentration [Dantas, *et al.*, 2003].

Extraction processes using emulsion liquid membrane (ELM) have received significant attention due to their potential as an effective technique for the separation of metals. ELM process generally consists of three steps. The first step is emulsion preparation in which emulsion is prepared as water-in-oil (W/O). The second step is permeation of solute through membrane phase from a feed phase to a receiving phase through interfacial contact between emulsion and continuous phase consisting metal waste. The third step is settling of the emulsion and external phases followed by demulsification to recover the membrane phase [Ahmed, *et al.*, 2011].

1.11. Refinery of used oil

The idea of recycling used lubricating oil was presented in the year of 1930 [Nagy, *et al.*, 2010]. Initially the used lubricating oils were burnt to produce energy, and later these oils were blended to engine oils after treatment [Diphare, *et al.*, 2013][b]. The waste lubricating oils can be recycled as lubricating oil, and re-used as fuel or made into diesel-like fuel. Industrial and engine waste oils, wood pyrolysis oils, fresh and waste fats and vegetable oils have been proposed as pyrolysis raw material to produce gasoline and diesel-like fuels. A large range of waste oils can be recycled and recovered in a variety of ways, either directly or after some form of separation and refinement [Anand, Hussain, 2013].

Re-fining is the use of distilling or refining processes on used lubrication oil to produce high quality base stock for lubricants or other petroleum products [Diphare, *et al.*, 2013][a]. Used oil is re-refined to yield base oils that are blended into lubricating products, thus reducing the consumption of virgin oils [Basel Convention Group, 1997]. Re-refining restores the physical and chemical properties of lubricating oil so that it can go back to its original and intended use. Used oil contains 70 to 75 percent lubricant base oil and less energy is required to produce the same amount of base stock from used oil than from crude oil [Denton, 2004].

Refining of spent engine oil is the process of regenerating its used substance so that it can be used again. It is the process involving the removal of the impurities in the spent oil and bringing it back to the initial state [Rahman, *et al.*, 2008].

The processes of re-refining of used lubricating oils depend greatly on the nature of the oil base stock and on the nature and amount of contaminants in the lubricant resulting from operations [Aziz, *et al.*, 2011; Rahman, *et al.*, 2008].

Different techniques have been developed for reclaiming and re-refining waste lubricants oils to either restore the original usefulness of the oil or clean the contaminated oils to a point that they can become suitable for subsequent use. Among these methods, reclaiming by heating and filtration, re-refining by introducing waste oil into crude oil refining streams, recycling by acid/clay treatment, thin film evaporation/clay contact finishing, thin film evaporation/hydrotreats finishing, etc, are now employed in different countries worldwide [Shakirullah, *et al.*, 2006].

Consistent with earlier agency review and investigation, two distinct used oil recycling entities exist within the used oil management system:

1. Reclaiming, wherein relatively simple cleaning methods (settling, heating, dehydration, filtration and centrifugation) are used during the recycling process primarily to remove insoluble contaminants and thus making the oil suitable for some sort of further use.
2. Re-refining, where refining processes during recycling are used in order to produce high quality base stock for lubricants or other petroleum products. Refining may include distillation, hydrotreating, and/or treatments employing acid, caustic, solvent, clay [Office of water United States environmental protection agency and/or chemicals Office of water regulations and standards, 1989].

Other methods for reducing the concentration of heavy metals in influents also include ion exchange, reverse osmosis and adsorption. Studies have also been carried out in order to use liquid–liquid extraction for effluents treatment, including metallic cations extraction. The utilization of microemulsified systems in metallic cations extraction has been a good alternative, since they have some characteristics, which can make them profitable when compared to the conventional solvent extraction [Dantas, *et al.*, 2003].

Some major recycling processes in use include; setting centrifuge system, acid-clay process, Philips refined oil process, fixed bed sand filtration process to produce relatively clean oil. Limitations of the activated sand filtration processes arises from the fact that the process incorporates only physical separation of contaminants by filtration, as such there is usually no appreciable change in the color of the used oil. This should be expected because most of the chemical properties remain relatively unaltered by physical separation. This necessitates adopt of a different process route to improve and also enhance the chemical properties of the recycled oil. In the recycling process, a number of stages are possible depending on the original source of the used oil, the level of contamination, and the sophistication of the technology utilized.

In Europe, three groups of technologies can be considered as representatives of existing regeneration methods:

I. Vacuum distillation plus clay treatment.
II. Vacuum distillation plus chemical treatment.
III. Hydrogen pre-treatment plus vacuum distillation [Bridjanian, Sattarin, 2006]

It has been reported that some conventional methods especially evaporation, membrane or chemical separation generate a concentrated stream which is more harmful than the original waste. Accordingly, no ideal solution was reported in the literature to resolve such problem; where the combination of two or more treatment processes was the sole issue to increase the purification efficiency. Since conventional treatment methods (evaporation, phase separation, filtration) are often inefficient or environmentally unacceptable, the development and application of new method is highly necessary. Recently, new interest on micellar extraction based on the phase separation at cloud point temperature in the non ionic surfactant solutions was developed. The cloud point extraction method (CPE) was firstly adopted by Watanabe et al. for the extraction of metal ions. CPE is considered to be convenient and environmentally safe alternative to extraction with organic solvents. Many advantages were claimed to CPE compared to conventional liquid–liquid extraction, including high extraction efficiency, ease of waste disposal and the use of non-toxic and less dangerous reagents.

During re-refining the mechanical, physical and chemical contaminations are removed with the following processes:

- Distillation,
- Acidic refining,
- Solvent refining,
- Clay treatment,
- Hydrogenation,
- Combinations of the formers [Nagy, *et al.*, 2010].

Solvent extraction followed by adsorption has been found to be one of the competitive processes for recycling of used lubricating oil. Solvent chosen should have maximum

solubility for base oil and minimum for additives and carbonaceous matter. Sulfuric acid has been used to remove asphaltenic material. The product is then clay treated. This solvent extraction treatment has received considerable attention in recent years; because it overcomes the problems associated with acid sludge produced from chemical treatment and its cost is one third of the cost of physical re-refinery [Durrani, *et al.*, 2011]. Recently, used oil has been re-refined by thin film distillation under high vacuum followed by clay treatment or hydro-treatment [Olugboji, Ogunwole, 2008; Emam, Shoaib, 2012].

Vacuum distillation recovers lubricating oil hydrocarbons, while removing light-end fuels from the base oil. The light-end fuels can be burned onsite for energy or sold to industrial furnaces and boilers. The subsequent hydrotreatment step is a hydrogenation process that removes about 90 percent of contaminants such as nitrogen, sulfur, oxygen and metals from liquid petroleum fractions. This step also reduces polynuclear aromatic components and higher-boiling halogenates and polar compounds. Other re-refining processes include chemical pretreatment, solvent extraction, wiped-film (or thin-film) evaporation, and clay polishing [Denton, 2004]. Among all the various techniques, refining with acid clay is a traditional method to treat and recycle used lubricant oil (ULO). However, this technique is, at present, only allowed in some developing countries such as Thailand, and not in developed countries. This could be because this particular acid clay process is quite toxic to the environment due to the containing of heavy metals in acid sludge [Kanokkantapong, *et al.*, 2009].

1.12. Objectives

The scope of this work is to recover and recycle used oil in reference to International quality standards so that it can be employed as lubricant and substitute of base oil. To achieve the objectives of this experiment, the following aspects have been identified:

1. To characterize heavy metal contents and other pollutants of used oil in Palestine generated from different resources.
2. To investigate the efficiency of purifying used oil containing heavy metal by reverse micelles formed by non-ionic surfactant.
3. To compare the rheology and other properties of the purified oil with that of clean oil. These parameters include density, viscosity, ash content, heavy metals content, UV-visible spectra as well as IR spectra.

Chapter Two

2. Materials and Methods

2.1. Materials

Alcohol polyethylene glycol ethers (3EO) (alfonic 1412-3) (M wt. ~ 341) was obtained from Sasol North America Inc. (Westlake, Louisiana, USA). Used motor oil (SAE 15 W-40) was obtained from local garage in Ramallah. Clean motor oil (SAE 15 W- 40) was obtained from Castrol Tection, Turkey. All other chemicals were pure and of analytical grades and used without further purification. All solutions were prepared using Milli-Q water with electrical conductivity less than 3μs/cm (Milli pore system, Daihan Labtech Co. LTD, WD-1004, Gagok-ki, Hwado-Eup, Namyangju-City, Kyonggi- Do, Korea).

2.2. Instruments and Equipment

The UV-visible spectra were recorded on AQuanal™-professional spectro1000 rectangular Cell 10 mm Quartz-UV Glas for Spectro 1000, UV-1601, Shimadzu Corporation, Japan. Infrared spectra were recorded on Bruker FTIR Tensor, 27 Spectrometer, Japan. Heavy metals were determined using ICP spectrometer Elan 9000, Perkin Elemer with autosampler. The samples were centrifuged using (Sigma 3k30 centrifuge Newtown, Wem, Shropshire .Viscosity was measured in a DV-1 P R digital viscometer (Anton Paar GmbH, Graz, Austria). Thermolyne Furnace 4800, United Kingdom, European was used to measured the ash content on the refined oil. Density was recorded on Pycnometer 25 ml, acc. to ISO 3507; cap ST 5/13, precisely adjusted to the third place of decimal, Germany. pH meter with spectral 1-14 from Hydrian product™. The sample anisotropy was determined using polarized microscope (Olympus BX41, BX41TF, Tokyo, Japan).

2.3. Methods

2.3.1. Construction of Three Components Phase Diagrams

The behavior of a three- components system is described on ternary phase diagram in which the weight ratio of two components was fixed. The construction of the phase diagram was conducted in a thermo-stated bath (25.0 ± 0.5^{o}C). Ten weighted samples composed of mixtures of surfactant and oleic phase (clean or used motor oil) were prepared in culture tubes sealed with viton-lined screw caps at predetermined weight ratios of surfactant to oleic phase [Fanun, 2008]. The two components homogeneous samples were then titrated with MQ water until its solublization limit was reached. The solution was vigorously stirred after each added aliquot of the aqueous phase additions using vortex mixer and left to equilibrate. The time for equilibrium between each addition was typically from few minutes up to 24 hours [Mohammad, 2010]. Phase separation was detected by naked eye. The Anisotropy phase (Lamellar liquid crystal, hexagonal liquid crystal) was detected by polarizer microscope with their brightening or isotropic which contain micelle

and cubic appeared dark under the polarizer. Finally the boundary detected and the phase diagram drawn by using OriginPro8 [Al-Jabarei, 2010].

2.3.2. Preparation of Buffers Solutions

Universal buffer system was used to prepare all buffer solutions employed in this study. The buffer system was prepared by mixing different proportions of two solutions. The first solution was prepared by dissolving 12.37g of anhydrous boric acid (H_3BO_3) and 10.51g of citric acid ($H_3C_6H_5O_7.H_2O$) in distilled water and dilute to 1L in a volumetric flask. The second solution (solution 2) was prepared by dissolve 38.01g of $Na_3PO_4.12H_2O$ in distilled water and dilute to 1L in volumetric flask. Table 2.1 display the different volumes that were mixed to obtained the desired pH and checked experimentally by means of pH meter [Shugar, *etal.*, 1981].

Table 2.1: Volumes of solution 1 and solution 2 that were mixed to obtain the indicated pH at 25.0^{o}C.

Desired pH	Solution 1 (ml)	Solution 2 (ml)
8	425	575
9	345	655
10	270	730
11	220	780
12	85	915

2.3.3. Extraction of heavy metals and soot from used motor oil

The extraction of heavy metals and soot from used oil was carried by titrating the oleic-surfactant binary mixture, having reversed micelle composition as identified by the phase diagram, with buffer solutions having different pH instead of pure water as outlined in section 2.3.1The samples were then centrifuged at 20000 rpm at 25.0^{o}C. This procedure practically resulted in full separation of suspended particulate matter from used oil (soot, heavy metals….Etc.) and settled at the bottom of flask. The clear oil was obtained by decantation and stored for further analytical tests.

2.3.4. Effect of pH on the efficiency of removal of soot and heavy metals from used motor oil in the reversed micelle range

The efficiency of removal of heavy metals and soot from used motor oil was studied at different pH. The range of buffer solutions having different pH was chosen depending on the mathematical calculation according to the solubility of the heavy metals in the aqueous solutions [Zumdahl, 2010]. The range that was selected is between 7 to 12 pH units.

2.3.5. Determining the core radius

The core radius of the reversed micelle within the stable boundary region in the phase diagram was determined as outlined in the literature [Fanun, 2008]. This will help in determining the relationship between the core radius and the efficiency of soot and heavy metal removal.

2.4. physical and chemical analyses

2.4.1. Viscosity

Digital viscometer was used to measure the viscosity of the oil in centipoises (cp) at 25.0^{o}C by dipping the spindle into the sample and then report the reading.

2.4.2. Density

Pycnometer was used in measuring the density of the oil as follows. At beginning the volume of pycnometrer was determined by filling it with distilled water at 24.0^{o}C and close the cap. The excess water from the overflow orifice was removed. From the known density of water and its weight, the volume of the pycnometer was readily obtained. The same pycnometer was filled with oil sample and weighed. The density of each oil sample was then calculated. [William, *etal.*, 1972].

2.4.3. Ash content

To determine the ash content of oil 1.0 g sample was weighed into a previously dried and weighed porcelain crucible (W1). The crucible with its content was placed in a furnace preheated to 600°C for 1 h. The sample was allowed to cool in the furnace to 250^{o}C and then was cooled further to room temperature in desiccators. The crucible with its content was weighed (W2). The weight of the ash was expressed as a percentage of the initial weight of the sample [Eshun, *etal.*, 2013].

2.4.4. Percent oleic phase recovery

The percent oil recovery was obtained by centrifuging pre-weighed used oil-surfactant-buffer emulsion. The clean oil obtained after centrifugation was weighed and the percent recovery was calculated.

2.4.5. UV- Visible spectra

The UV-visible spectra of the lubricating oil samples were recorded in the range of 200-400 nm. The samples were diluted with n-hexane in the ration of 1: 100 (oil/solvent) by volume [Shakirullah, *etal.*, 2006].

2.4.6. FTIR spectra

To determine the presence of different functional groups and hence different substances in the sample, FTIR spectroscopy was used. The source setting of FTIR was middle-infrared light. KBr pellet holder disc used for FTIR analysis was cleaned using dichloromethane and a few drops of sample to be analyzed was placed in between the discs. The data was scanned from 4000 to around 400 cm^{-1} **[**Babu, *etal.*, 2011].

2.4.7. Metal content

In order to determine the concentration of heavy metals in used and clean motor oil samples, digestion must do. A small amount of oil (0.5g) was introduced into the digestion flask, mixed with 4 ml of conc. H_2SO_4 and refluxed for 5 min. at 440^oC. Then 10 ml of (percent) H_2O_2 were added and the mixture was refluxed for additional 2 min. The solution was then cooled to room temperature and diluted to 100.0 ml in a volumetric flask.

A portion of the solution was then filtered using 0.45 μm filter and then the introduced to the ICP spectrometer. The concentrations of heavy metals in these samples were calculated using calibration curves with external standards. [Rosad, Pichtel, 2003].

Chapter Three

3. Result and Discussions

3.1. Ternary Phase diagram of water/Alfonic 1412-3 ethoxylate/ fresh clean motor oil system

Figure (3.1) displays the ternary phase diagram for water, surfactant ($C_{12}E_3$) and fresh clean oil at 25.0^{o}C (appendix C1). Inspection of this figure reveals that the binary phase $C_{12}E_3/H_2O$ (at the baseline of the triangle opposite to oil) shows the formation of three regions. The first region between the boundary of 0 to 10% water, exhibits low viscosity, clear isotrope and thermodynamically stable which is denoted by (L_2) and represents microemulsion. The second region located between 12% to 30% water in the phase diagram is identified by polarizer microscope as anisotropy Lamellar (L_α) liquid Crystal (LC) phase. The third region which occupied the rest of the binary line represents surfactant monomer in water (gel phase). This result was found to be in full agreement with the binary phase diagram that was published elsewhere [Patrick, H., *et al*., 1997].

Figure 3.1 also reveals the phase diagram for the ternary phase diagram between water/Alfonic 1412-3 ethoxylate/fresh clean motor oil. It is clear that the phase diagram is made from three regions. The boundary that is labeled L_2 represents the reverse micelle phase. While the region labeled LC, represents the lamellar liquid crystal phase. Moreover, the region labeled 2Φ identifies the separation into two phases. This general behavior of the ternary systems, that consists of water, surfactant and oil, display similar phase regions [Kanan, *et al.*, 2012]. Reversed micelle phase is known to be formed when water is solubilized in oil by the help of surfactant [Feader, et al., 2003]. The core of reversed micelles exhibits unique properties where hydrophilic, ionic or polar substances can be transferred from the oil phase to this region, thus providing a thermodynamically stable environment for such substances. Altering the physical conditions of this core such as changing pH, ionic strength or dielectric constant will result in changing the state of the reversed micelle and presumably break it to two phases. However, the presence of impurities in oil might result in changing the phase behavior of this system.

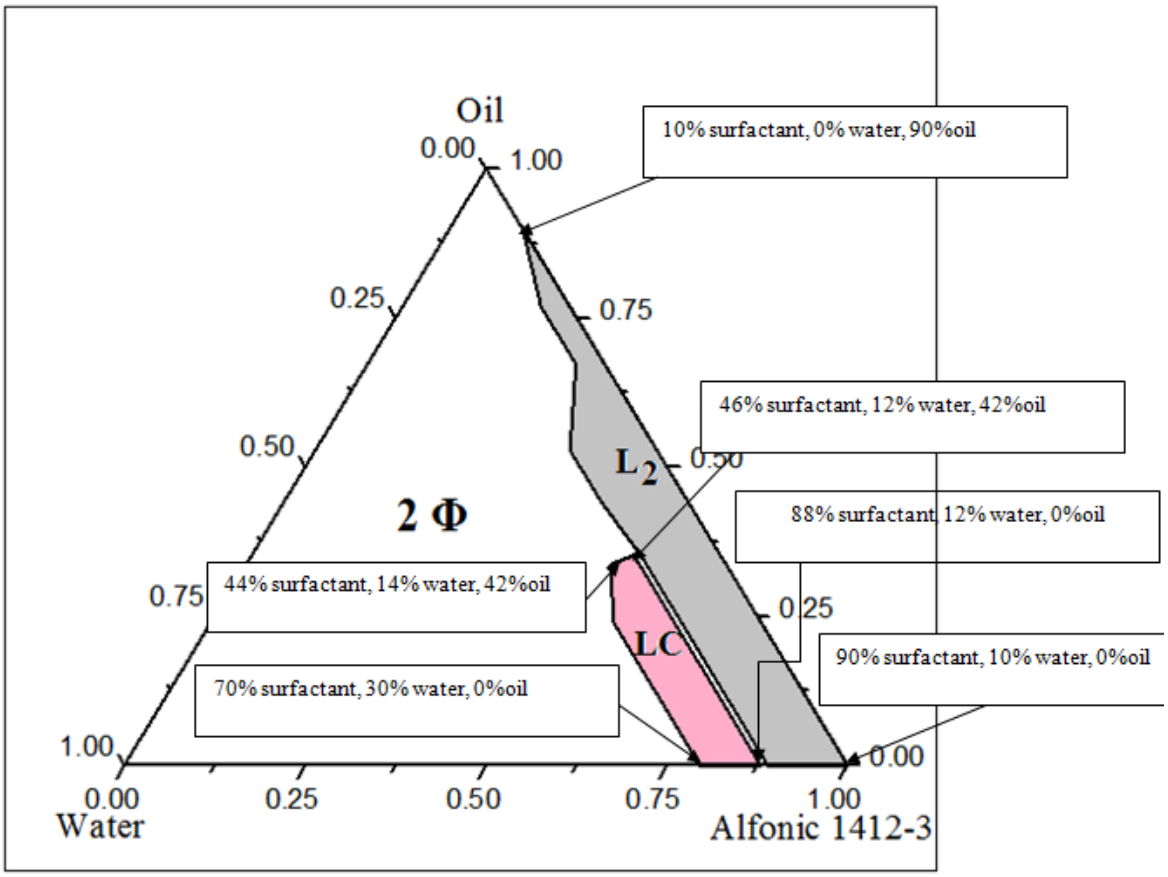

Figure 3.1: Ternary phase diagram of $H_2O/C_{12}E_3$/ fresh clean motor oil system at 25.0^oC.

3.2. Ternary Phase diagram of water/Alfonic 1412-3 ethoxylate/ used motor oil system

Figure 3.2 displays the ternary phase diagram for $H_2O/C_{12}E_3$/used motor oil system at 25.0^oC (appendix C2). Upon comparison of the phase behavior in this Figure with that in Figure 3.1, the liquid crystal region was completely disappeared. This can be attributed to the presence of impurities in the oil which breaks the long range intermolecular forces that leads to the formation of the highly ordered LC phase. However, Figure 3.2 reveals that the reversed micelle phase (L_2) which is characterized by an isotropic, low viscosity and phase microemulsion region persists in the used motor oil system with larger boundary than that of clean oil [Feitosa, *etal.*, 2008]. This behavior could be attributed to the presence of impurities in the used oil which enhanced the stability of the core with larger water percentage. Additionally, The region that is bounded by oil from 40% to 50 % display minimum reversed micelle stability as shown by the decrease in water percentage. This region is vulnerable to any external perturbation and can lead easily to the break of the reversed micelle phase. Hence, in the formulation of systems that exhibit reverse micelle phase, this range of oil percentages should be avoided so that better stability could be achieved. It is worth mentioning that this phase behavior for used oil is reported for the first time and no similar studies were performed in the literature. This outstanding finding

of the formation of reversed micelle phase in used oil system, can lead to breakthrough methods for its recycling and removal of oil pollutants.

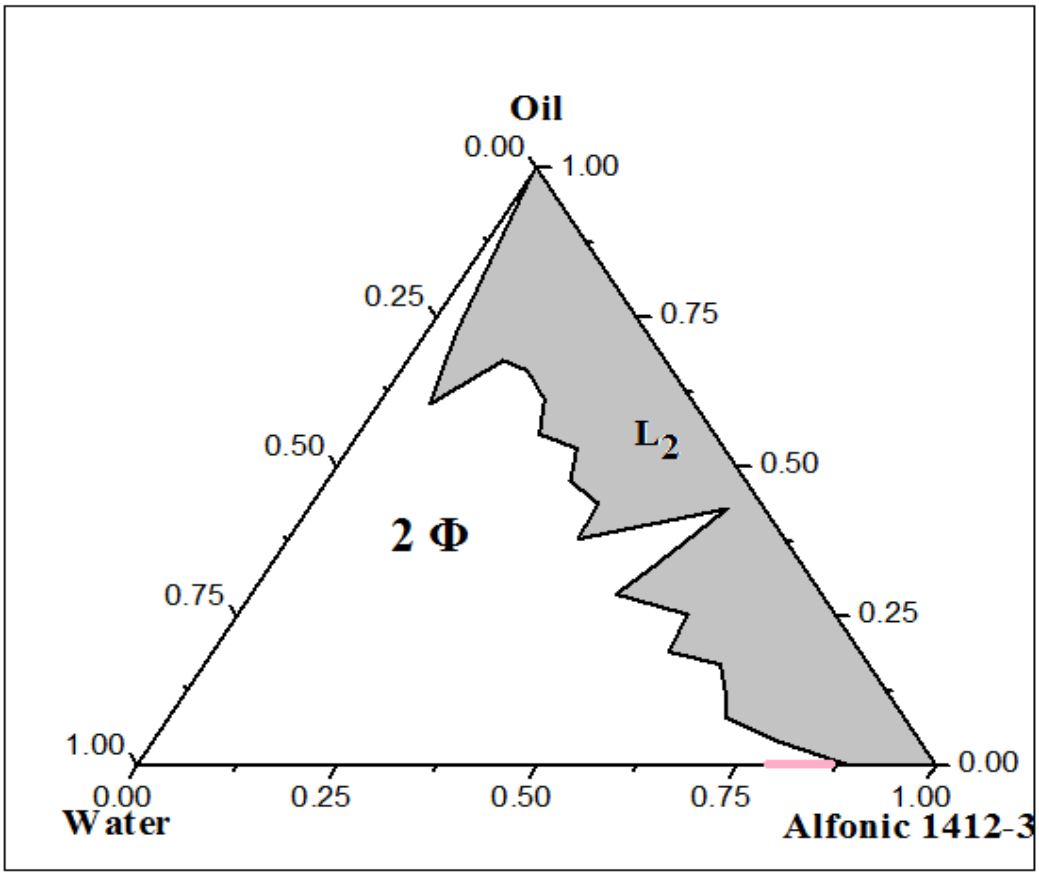

Figure 3.2: Ternary phase diagram of $H_2O/C_{12}E_3$/ used motor oil system at 25.0^oC.

3.3. Core radius

In order to quantify the effect of water percentage on the core radius of the reversed micelles in the L_2 phase, the core radius was calculated in this region using the method that was described in section 2.3.5 [Fanun, 2008]. Figure 3.3 shows that variation of core radius as function of water volume added at different initial composition of used oil-surfactant system. Inspection of this Figure reveals that a linear relation is obtained between the volume of water added and the core radius. The observed general trend for each composition is that increasing water volume results in obtaining larger core radius. This behavior is similar to what was obtained in the literature using similar systems [Natarajan, *etal.*, 1996]. The largest core radius that was obtained in this work is 55.6 ^oA and occurs only in the oil/surfactant system with 90% oil and 10% surfactant. On the other hand, Figure 3.3 reveals that as the amount of surfactant increases the core radius decrease for the same volume of water. This result could be explained on the bases that the HLB (Hydrophile-Lipophile Balance) of the used surfactant is 7.8. This number signifies that the surfactant is more soluble in the oil phase as compared to water phase. Hence increasing the amount of surfactant will result in narrowing the reversed micelle core with reduced volume.

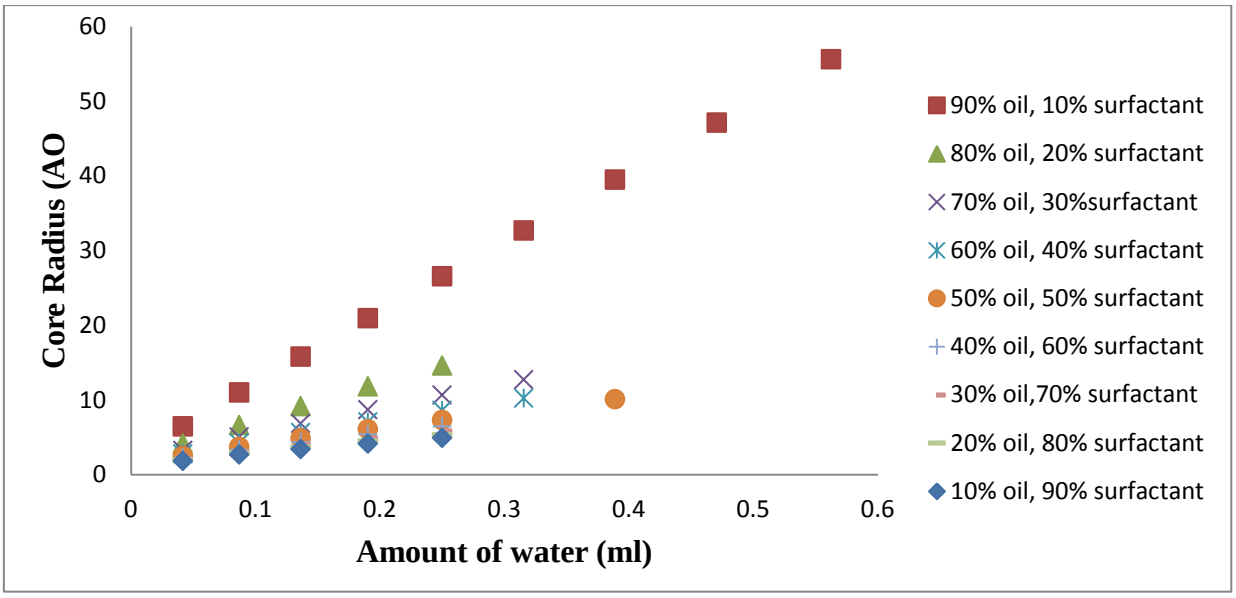

Figure 3.3: Core radius of reversed micelle as function of added volume of water in different initial percentage of used oil-surfactant system.

3.4. Used oil treatment in the reversed micelles phase

One of the major objectives of used oil treatment are to make the oil free from polar pollutants such oxidation by-products, organic acids, residual additives, suspended soot, and trace heavy metals [Rahman, etal., 2008]. Several factors can affect directly the efficiency of this process. These factors are; pH, surfactant- oil percentage, temperature and ionic strength. In this study, the effect of pH and percentage of oil-surfactant on the treatment efficiencies were deeply investigated.

3.4.1. Effect of pH

The effect of pH on the efficiency of used oil treatment was studies at constant surfactant-oil composition of 50% by weight at 25.0^{o}C. The system was titrated with aqueous buffer solutions having a pH in the range of 7.0- 12.4 so that revered micelle phase is obtained. The choice of this pH range was selected based on the solubility of different hydroxide of heavy metals in solution (see section 2.3.4). Figure 3.4 displays the photos of different test tubes prepared at different pH. Inspection of this Figure reveals that the reversed micelle phase was destabilized and converted to two phases: water rich phase at the bottom and oil rich phase at the top for all systems. However, the amount of water rich phase that contains soot and other pollutants is visually varies as function of pH. Furthermore, the mixture with pH 12.4 exhibits the larger water phase by volume as compared to other mixtures. Hence, we can conclude that the optimum pH for maximum separation of pollutants for oil is at pH 12.4.

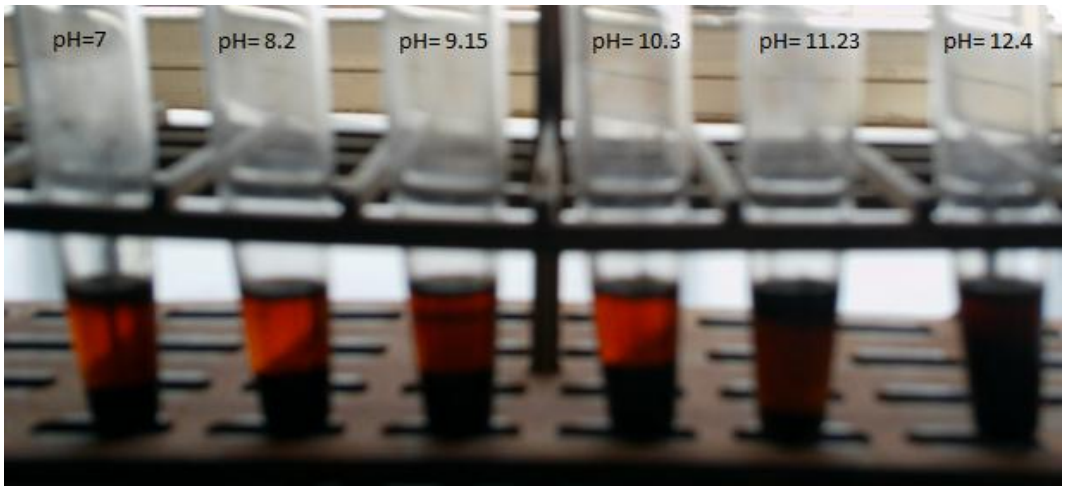

Figure 3.4: Effect of pH of the efficiency of used oil treatment at constant used oil-surfactant composition of 50% by weight at 25.0^{o}C.

3.4.2. Effect of surfactant- oil percentage

The effect of oil-surfactant composition on the efficiency of used oil treatment and phase separation at constant pH of 12.4 was studies. Figure 3.5 displays the photos for the test tubes at different composition after centrifugation. Table 3.1 display the detailed composition of each test tube. Inspection of Figure 3.5 and Table 3.1 reveals that the composition of binary surfactant-oil system of 90% to 10%, respectively, has the larger oil phase. However, this oil phase contains large amount of surfactant. To eliminate this complexity, the mass of water rich phase which contains soot and other pollutants, was calculated as function of surfactant and pH (Figure 3.6). Inspection of this Figure 3.6 reveals that the maximum water rich phase removed and hence maximum pollutants removal is obtained at minimum amount of surfactant (4g or 10%). The oleic phase recovered from each system was stored for further physical and chemical tests.

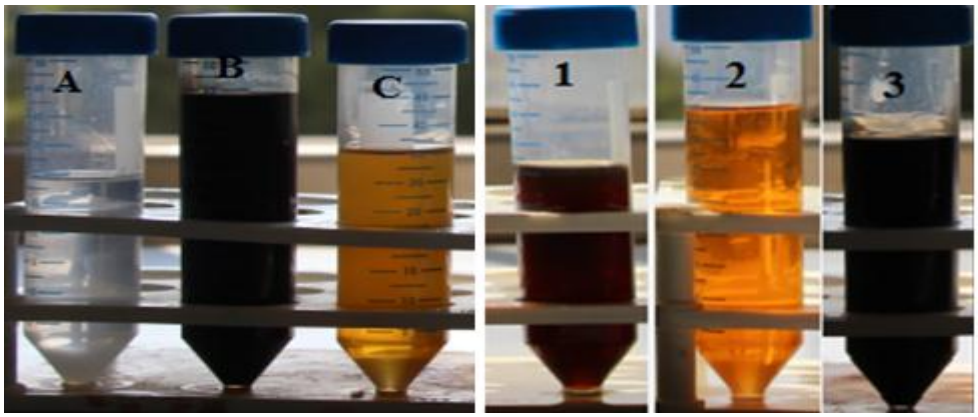

Figure 3.5: Effect of oil-surfactant composition on the efficiency of used oil treatment and phase separation at constant pH of 12.4 at 25.0^{o}C as described in Table 3.1.

Table 3.1: Amount of surfactant-oil at pH=12. The mass of water added to each test tube is 5.0 g.

No. of test tube	Description of Component
A	Surfactant
B	Used engine oil
C	Clean engine oil
1	47.5 g surfactant, 47.5 g used engine oil.
2	85.0 g surfactant, 10.0 g used engine oil.
3	10.0 g surfactant, 85.0 g used engine oil.

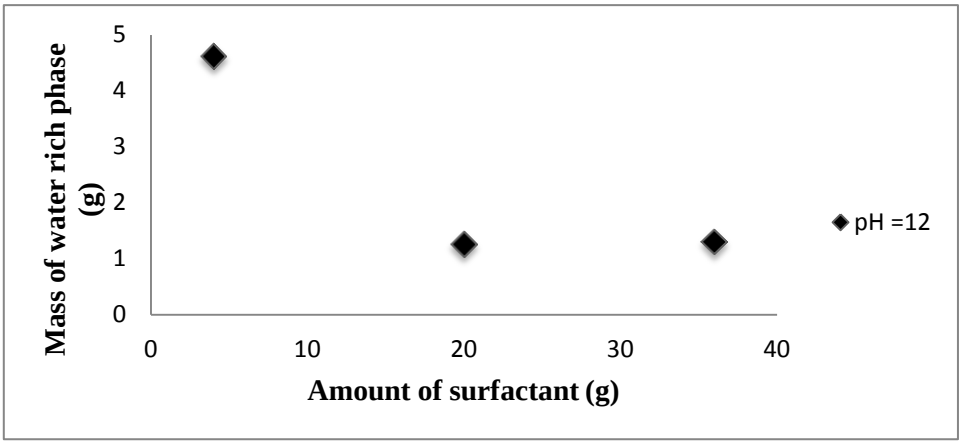

Figure 3.6: The mass of water rich phase which contains soot and other pollutants, as function of surfactant amount. The pH = 12 and T= 25^{o}C.

3.5. Physical and Chemical Properties

The chemical contents of various types of motor oils significantly differ both qualitatively and quantitatively, However, upon applying oil to engines, the chemical and physical characteristics of the used oil is hard to identify since it contains complex mixture which is highly dependence on the time of used, efficiency and types of engines [Palus, etal., 2001]. Moreover, the physical and chemical properties of clean oil are very important is ranking the oil for different applications. The most important properties that control the performance of oil are viscosity, density, UV-visible spectra, IR spectra, heavy metals and ash content. Hence, in determining the efficiency of used oil treatment, these parameters should be determined for the recovered oil and compared with those of clean oil for quality assurance [Diphare, Muzenda, 2013]. Table 3.2 summarizes the results of these parameters for clean oil and recovered oil at various conditions.

Table 3.2: Density, viscosity, ash content for the recovered used oil together with the percent removal of impurities as function of surfactant-oil percentages and pH. The mass of water added to each test tube is 5.0 g. All experiments were performed at 25.0^{o}C.

pH ±0.1	Amount of surfactant (g)	Amount of oil (g)	Test tube #	Density (g/cm^3) ± 0.0030	Viscosity (cp) ± 20.0	Ash content % by wt ± 0.0007	Oleic phase recovery % ±0.1
			Used oil	0.8807		0.0202	---------
			Clean oil	0.8455	130	0.0074	---------
			Surfactant	0.9166		---------	----------
7.0	47.5	47.5	1	0.9027	140	0.0049	91.3
10.0	47.5	47.5	2	0.9018	220	0.0041	84.4
12.0	47.5	47.5	3	0.9035	210	0.0035	85.5
7.0	85.0	10.0	4	0.9194	120	0.0018	96.3
10.0	85.0	10.0	5	0.9171	120	0.0018	95.4
12.0	85.0	10.0	6	0.9197	100	0.0028	95.9
7.0	10.0	85.0	7	0.8922	410	0.0164	94.3
10.0	10.0	85.0	8	0.8897	360	0.0161	92.6
12.0	10.0	85.0	9	0.8921	690	0.0156	88.6

3.5.1. Density

Table 3.2 lists the density of clean oil, used oil and recovered oil at different pH. Inspection of this Table reveals that the density of used motor oil is higher than that of clean oil. This increase in density could be attributed to the presence of impurities such as oxidation by products, soot, and heavy metals [Udonne, 2011]. Furthermore, the presence of suspended solid will also result in this observed increase in density [Forsthoffer, 2011].

Table 3.2 also reveals that for all pH's and surfactant-used oil ratio, the density of recovered oil is high than that of clean oil. This result could be attributed to the ability of the surfactant to partition between the water phase and the oil phase. Hence, the presence of surfactant in the recovered oil could explain the observed increase in density. This explanation is gaining support from the experimental data since increasing the amount of surfactant in the ternary mixture, resulted in an increase in oil density (Table 3.2). Our results demonstrate that the optimum density (which in the vicinity of clean oil) is obtained

when the percent of surfactant is minimum (Tubes 7, 8 and 9). Figure 3.7 shows the density of recovered oil as function of surfactant mass and pH. Inspection of this Figure reveals that a mixture of 10.0 g of surfactant, 85 g of used oil and 5.0 g of water at pH 12 gives the optimum density.

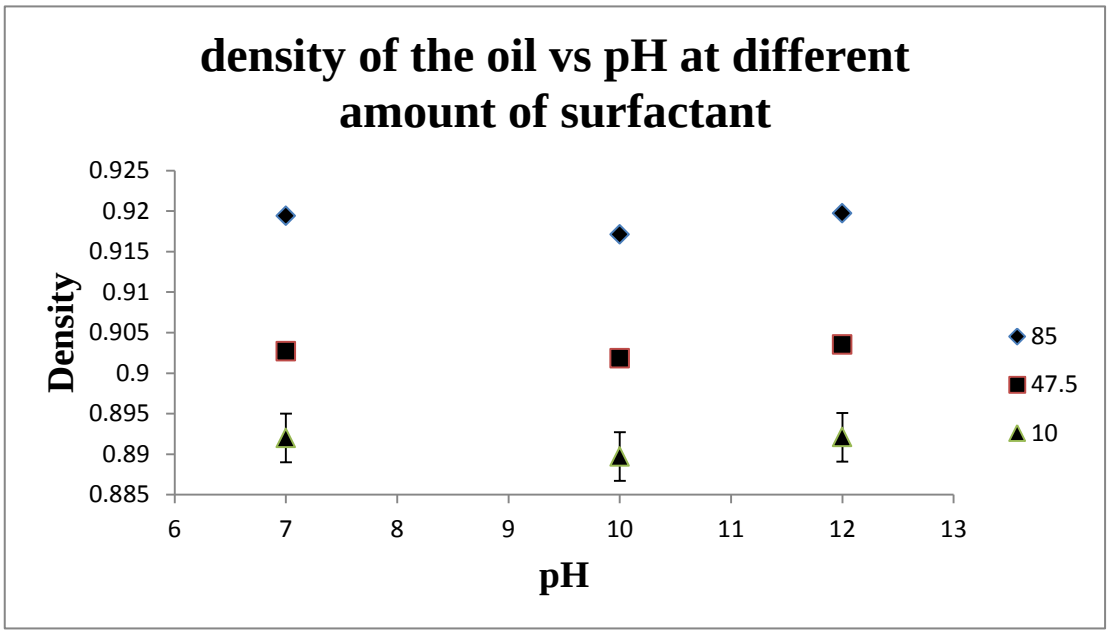

Figure 3.7: Density of recovered oil as function of mass of surfactant, mass of oil and pH. The amount of used oil in each case is given Table 3.2.

3.5.2. Viscosity

Viscosity is the most important physical property by which lubricant oil is specified [Kaleli, Yildirim, 2008]. Motor oil is usually classified using two viscosity values: the first one is at low temperature and the second one at high temperature. This classification was introduced by Society of Automotive Engineers (SAE) and used worldwide [Safieva, Balabin, 2008]. Lubricating oils have viscosities ranging from 10 to 1000 centipoise (cp) [Isah, etal., 2013].

Inspection of Table 3.2 reveals that the viscosity of recovered oil obtained from all ternary mixtures prepared at different pH's and surfactant-used oil ratio are higher than that of clean oil. This signifies that the presence of surfactant in oil will increase intermolecular forces, thus giving rise to the observed increase in viscosity [Isah, etal., 2013]. The observed increase in viscosity of used oil as compared to clean oil can be attributed to the presence asphalt-like sludge (soot) in the used oil since it was reported that soot increases the viscosity of oil [Bridjanian, Sattarin, 2006; Rahman, etal., 2008].

As shown at Figure 3.8 the nearest viscosity to the clean oil occur at high amount of surfactant (85.0g), on the otherwise the stronger oil film formed at high viscosity [Emam, Shoaib, 2012] and give the best performance to the viscosity this achieved at minimum amount of surfactant (10.0 g at pH 12).

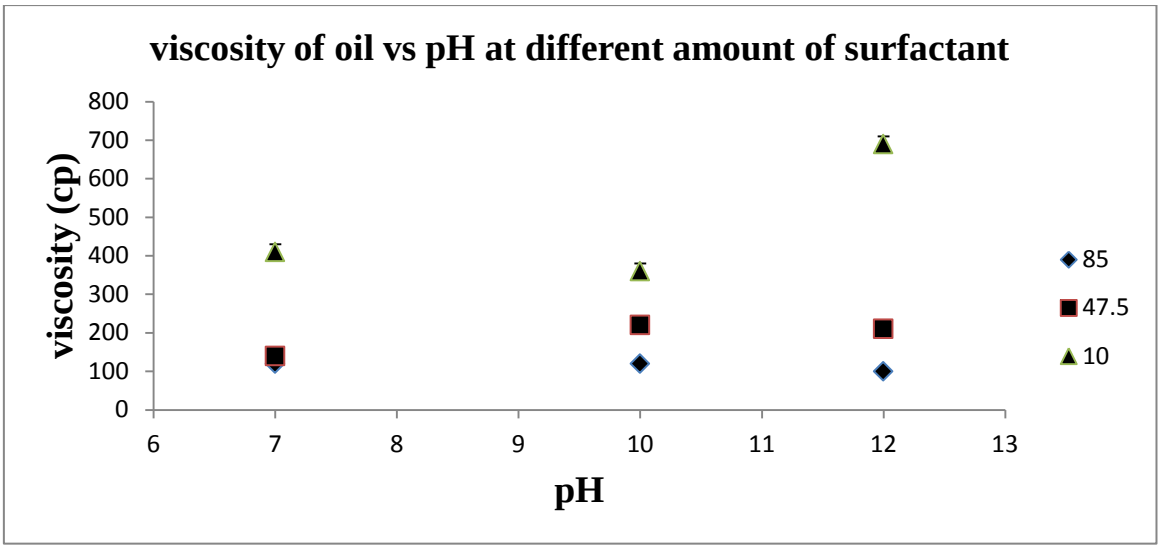

Figure 3.8: Effect of pH and amount of surfactant on the viscosity of recovered oil. Masses of used oil and water at each point are given in Table 3.2.

3.5.3. Ash content

When the lubricating oil is completely burned, the remaining solid is called ash and it is a measure of oil purity [Abro, etal., 2013], so ash is the inorganic residue that remains after the combustion of oil in air at a specified, high temperature [Speight, Exall, 2014]. Soot is enveloped by the surfactant, which forms micelle in the oil Figure 3.9. The nonpolar tails on the outside of the micelles prevent adhesion of the particles on metal surfaces as well as agglomeration into larger particles [Watson, 2010].

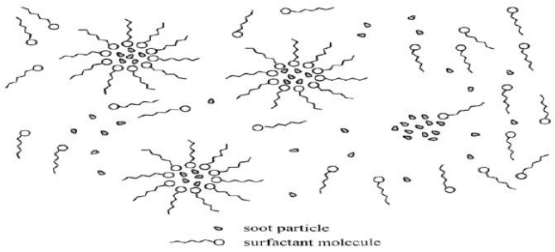

Figure 3.9: Solubilization of a soot contaminant by surfactant molecules in oil.

Table 3.2 list the ash content of used oil, clean and recovered oil at different conditions. Inspection of this table reveals that the percentages of ash in clean and used oil are 0.0074% and 0.0202%, respectively. It is evident that the ash content of used oil is higher than that in clean oil. This can be attributed to the presence of impurities that will result during the course of lubrication inside the engine [Katiyar, Hussain, 2010]. Table 3.2 indicates that the ash content in recovered oil is between 0.0018% to 0.0164% by weight which significantly lower than that of used oil. This indicates that most of the impurities are removed during our proposed method.

Figure 3.9 shows the plot of % ash content as function of pH at different surfactant amount. Inspection of this figure and Table 3.2 reveals that the lowest optimum ash content is obtained in a mixture containing 47.5 g surfactant, 47.5 g used and 5.0 g of water at pH=12.

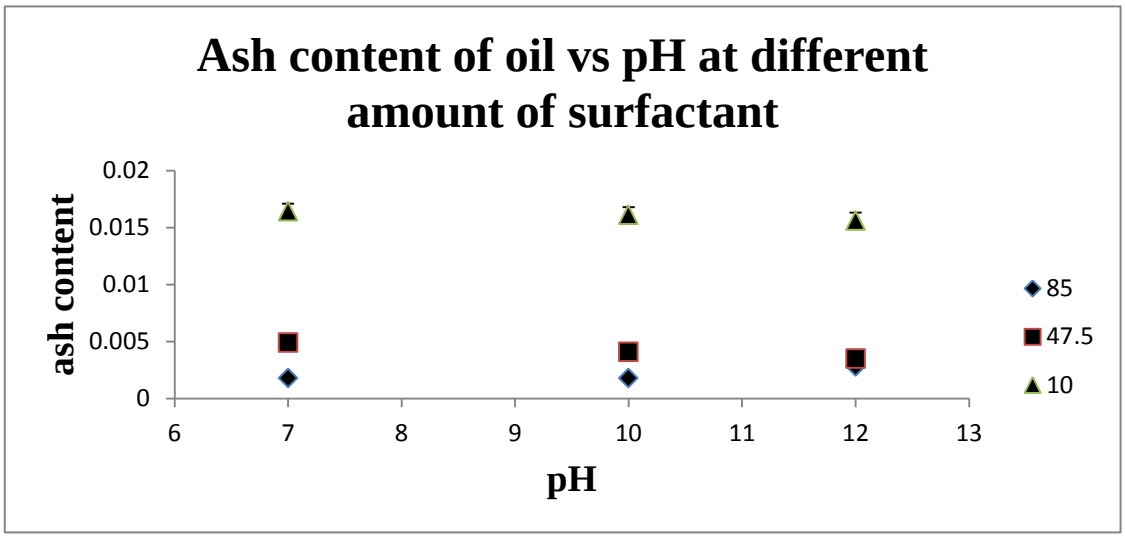

Figure 3.10: percent ash content of recovered oil at different pH and amount of surfactants. Masses of used oil and water at each point are given in Table 3.2.

3.5.4. Oleic phase recovery

Figure 3.10 reveals that the maximum amount of oleic phase recovered happen at using high amount of surfactant and reach 96.3% and it is because the sample contain high amount of surfactant and less amount of oil which cause in less precipitate of impurities that result from the centrifuge, so a best oleic phase recovered must occur at high amount of oil used and minimum amount of surfactant, in this method it is reached from 88.6 to 94.3% at 85.0g of oil and 10.0g of surfactant and it is a very good percent and it is reflect the effectiveness of the process [Emam, Shoaib, 2012].

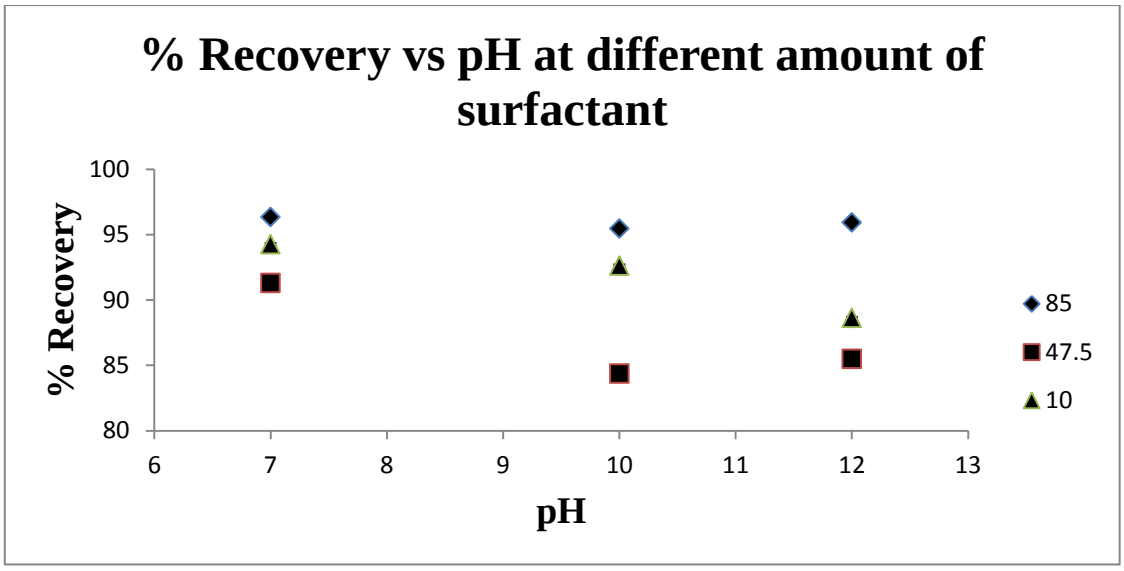

Figure 3.11: Show the oleic percent recovery in each sample versus pH at different amount of surfactant.

3.5.5. UV-Visible Spectroscopy

The UV-Visible spectra of clean, used, and recovered lubricants are shown in Figure 3.11. A peak with λ_{max} = 205 nm was observed in all the spectra. The absorbance at this wavelength of used oils was higher than of the clean oils, but the recovered oils have values of absorbance nearly the same as those of the clean oils.

It may be observed from Figure 3.11 that the spectra of clean, used, and recovered oils are similar to each other in all respects which may suggest that significant change has not occurred in the composition and nature of the base oil during use in an engine and by the methods developed for recovery [Shakirullah, *etal.*, 2006].

The high absorbance of used oil may be retraining to the presence of impurities due to its usage and storage (heavy metals and soot) but tube 9 has a minimum absorbance which is a sign there is no particle or soot in it, also tube 3 which contain equal amount of oil and surfactant had the behavior of absorbance the same as clean oil.

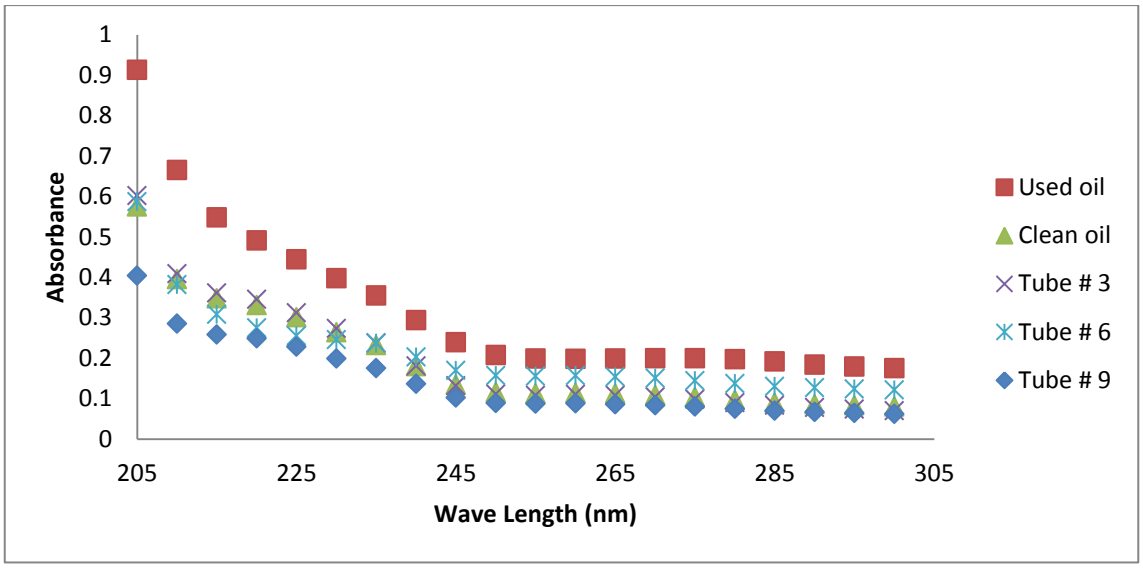

Figure 3.12: UV- Visible spectra of clean, used and recovered lubricants at different component of oil-surfactant (Table 3.2) at pH=12, T =25.0^{o}C.

3.5.6. IR Spectroscopy

Infrared (IR) spectroscopy has always played an important role in lubricant formulation and evaluation because of the detailed information on chemical composition provided by this technique [Sedman, etal., 2006].

A spectral band at 1700-1750 cm^{-1} indicated the presence of oxidation compound, because of the fact that (C=O) bond strongly absorbs at this frequency region. Figures 3.13, 3.14 and 3.15 display the IR spectra of clean, used and refined oil. Inspection of Figure 3.13 reveals that no peaks appear in the above mentioned frequency region indicating the absence of any oxidation products. On the other hand, the IR spectrum of used oil (Figure 3.14) shows a sharp peak at this region which indicates strongly the presences of oxidation products. This result is in full agreement with similar IR studies on used oil [Hamawand, 2013]. The IR spectra of refined oil by the method presented in this work (Figure 3.15) with reverse micelle composition of 85 g oil, 10 g surfactant and 5 g of buffer of pH 12, show the absence of this oxidation peak. This result indicates that the proposed method removes the oxidation products from used oil, thus restoring back its original properties.

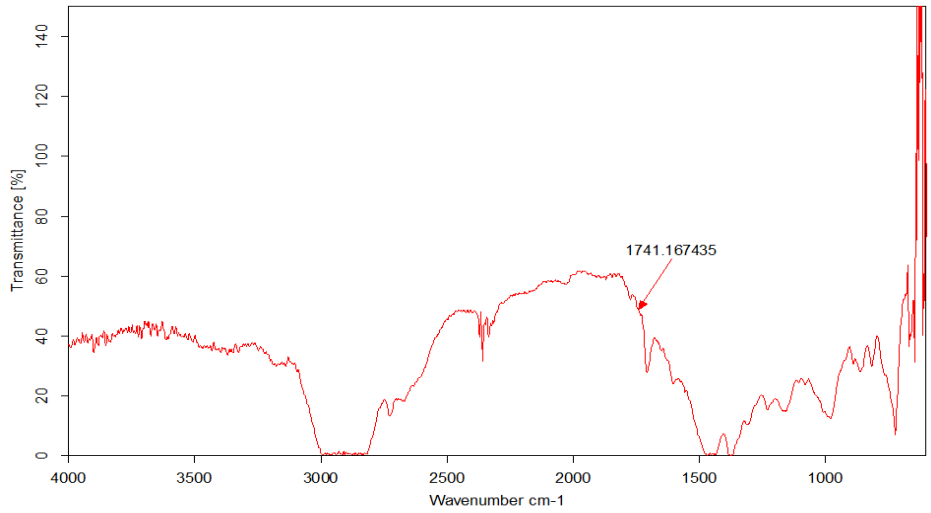

Figure 3.13: IR spectra of clean oil.

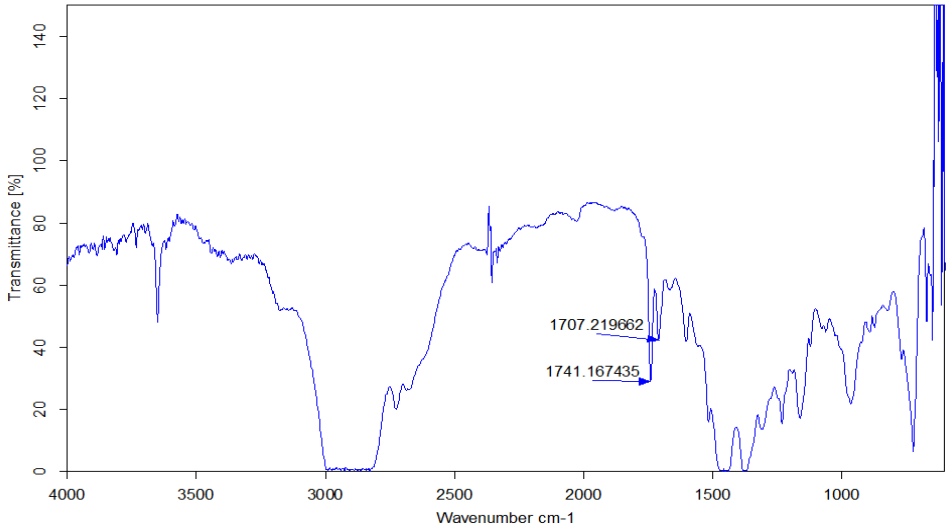

Figure 3.14: IR spectra of used oil.

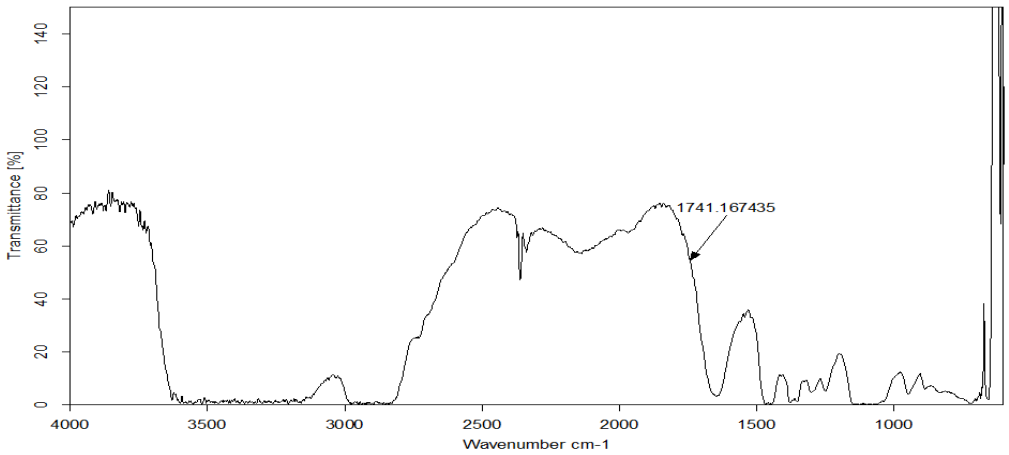

Figure 3.15: IR spectra of refined oil (sample 9) using reverse micelles composition of 85g oil, 10g surfactant, 5g buffer of pH=12, T =25.0^{o}C.

Furthermore, comparing Figure 3.13 with Figure 3.15 reveals that refining used engine oil by the reverse micelles method yield base oil spectra with no oxidation products, . The obtained IR spectra for refined oil are similar to the recorded spectra by other studies [Olugboji, 2008].

3.5.7. Metal analysis

Heavy metals are natural constituent of the earth crust having density generally larger than 5g/ cm^3 [Abed Al-Obaidi, 2011]. These heavy metals can be released to the environment from different sources including transportation. The source of heavy metals from transportation can be attributed to car exhaust, worn tires, worn engine parts, brake pads, rust, used oil or used anti-freeze. Table 3.3 lists the types of heavy metals released by each source of transportation [Nixon, 2007]. Furthermore, heavy metals concentrations due to transportation are normally low, but their level increases slowly with longer operation periods [Kaleli, Yildirim, 2008].

Table 3.3: Sources of heavy metals as a result of transportation

Source	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Gasoline	X			X				X	X
Exhaust							X	X	
Motor oil and grease		X			X		X	X	X
Antifreeze	X		X	X	X			X	X
Undercoating								X	X
Brake linings				X	X		X	X	X
Rubber	X			X				X	X
Asphalt				X			X		X
Concrete				X			X		X
Diesel oil	X								
Engine wear					X	X	X	X	X

In this section, we will focus on the hazards of used oil due to its heavy metals content and other pollutants, According to EPA standards [Denton, 2004] and Hazardous Waste Management Regulations (HWMR) [Vermont agency, 1996] (Table 3.4), used oil exceeding the limits indicated in the Table is labeled as hazardous waste and should be

treated and disposed off as such. Hence, used oil generators, collection centers, transporters, transfer facilities and recycling facilities are required to determine the concentration of each quality parameter in listed in Table 3.4 in each used oil shipment before any recyclic protocol is accepted.

Table 3.4: Specification for constituents in recycled oil.

	U.S. EPA limits (ppm)	HWMR limits (ppm)
Lead	100	----
Arsenic	5	5
Cadmium	2	2
Chromium	10	10
Halogen	4000	4000

In this study, the heavy metals content of used, clean and refined oil by the reverse micelles method was analyzed by ICP-MS and presented in Table 3.5. Inspection of this table reveals that the heavy metals content of used oil are higher than that of clean oil. This is not a surprising result, since it is expected that engine wear will release heavy metals, thus contaminating the oil. However, in all samples listed in Table 3.5, the concentration of heavy metals is less than the regulatory limits listed in table 3.4. This is not surprising for clean and refined oil; however, for used oil this result could be attributed to shorter period of operation of the engine and frequent oil change. The following discussion addresses the source of each detected heavy metal with its environmental implication.

The high concentration of zinc (12.8 ppm) in clean oil can be attributed to its introduction in the form of additives package which include anti-oxidant, corrosion inhibitor and detergents [EPA, 2005; Durrani, 2010]. The concentration of zinc in used oil is increased to 16.2 ppm. This increase can be attributed to the motor wear as indicated in Table 3.3.

The most common wear metal in a car's engine is iron. Iron comes from many places in the engine such as liners camshaft and crank shaft, piston, gears, rings, and oil pump [Hamawand, etal., 2013]. Iron concentration in engine oil depends on the bearing conditions inside the engine [Mckenzie, 1981]. If a bearing fails, iron concentrations in used engine oil increases. Table 3.5 reveals that the concentration of iron in clean engine oil is 1.48 ppm and increased to 9.75 ppm in used oil.

Lead concentration in used oil (Table 3.5) is less than the regulatory limit (Table 3.4). This finding could be attributed to the change to unleaded gasoline standard in 1996. Furthermore, the concentrations of lead in Table 3.5 are much lower than those reported in earlier studies performed before invoking the new standard [Vermont Agency, 1996].

Table 3.5 and Figure 3.16 indicate that the refining procedure by reverse micelles method is very effective in the removal of heavy metals from used oil. The method yielded complete removal (within the instrument detection limit) of manganese, nickel and copper while lowering significantly the concentration of other metals to those found in clean oil. This variation in heavy metals removal by the new method could be attributed to the nature of the metal, its oxidation state, and its hydroxide solubility product constant. For iron removal, it is found that sample number 1 gave the best results. For Ba, all samples gave similar results with 50 % removal efficiency. For Cd, samples 3, 4, 5, 6 and 8 yielded complete removal. For Mn, Ni and Cu, all samples yielded similar results with complete removal of these metals from used oil. For Zn, sample 4 gave the best removal efficiency. Finally, for lead, sample number 8 gave the optimum removal efficiency result.

Table 3.5: Concentration of detected heavy metals in clean, used and refined oil at different oil-surfactant composition. The samples composition of the reversed micelles for each treatment is the same as in Table 3.2.

Samples /Elements	Ba	Cd	Fe	Mn	Ni	Zn	Cu	Pb
Used oil	0.415 ± 0.04	0.030 ± 0.01	9.567 ± 2.41	0.0564 ± 0.02	3.5744 ± 0.06	16.1744 ± 0.32	1.1908 ± 0.01	0.2568 ± 0.02
Clean oil	0.141 ± 0.01	0.011 ± 0.01	1.482 ± 2.30	ND	0.0284 ± 0.05	12.7684 ± 0.43	ND	0.0588 ± 0.02
1	0.204 ± 0.02	0.012 ± 0.02	1.1772 ± 0.37	ND	ND	3.3372 ± 0.10	ND	0.0584 ± 0.03
2	0.244 ± 0.01	0.012 ± 0.01	1.4832 ± 1.15	ND	ND	2.0072 ± 0.05	ND	0.0732 ± 0.01
3	0.209 ± 0.02	ND	1.7492 ± 0.40	ND	ND	2.488 ± 0.38	ND	0.1048 ± 0.01
4	0.222 ± 0.03	ND	2.8152 ± 0.69	ND	ND	1.6876 ± 0.05	ND	0.0744 ± 0.01
5	0.228 ± 0.01	ND	3.9728 ± 1.50	ND	ND	5.5764 ± 0.15	ND	0.0636 ± 0.01
6	0.319 ± 0.02	ND	5.3396 ± 1.37	0.034 ± 0.01	ND	3.0004 ± 0.10	ND	0.0444 ± 0.00
7	0.230 ± 0.02	0.014 ± 0.03	6.1696 ± 1.53	0.04 ± 0.01	0.0608 ± 0.11	16.0144 ± 0.14	ND	0.1524 ± 0.01
8	0.219 ± 0.01	ND	2.1928 ± 2.18	ND	ND	10.438 ± 0.38	ND	0.0456 ± 0.01
9	0.319 ± 0.01	0.014 ± 0.01	2.9084 ± 1.13	ND	ND	10.6988 ± 0.73	ND	0.0852 ± 0.01

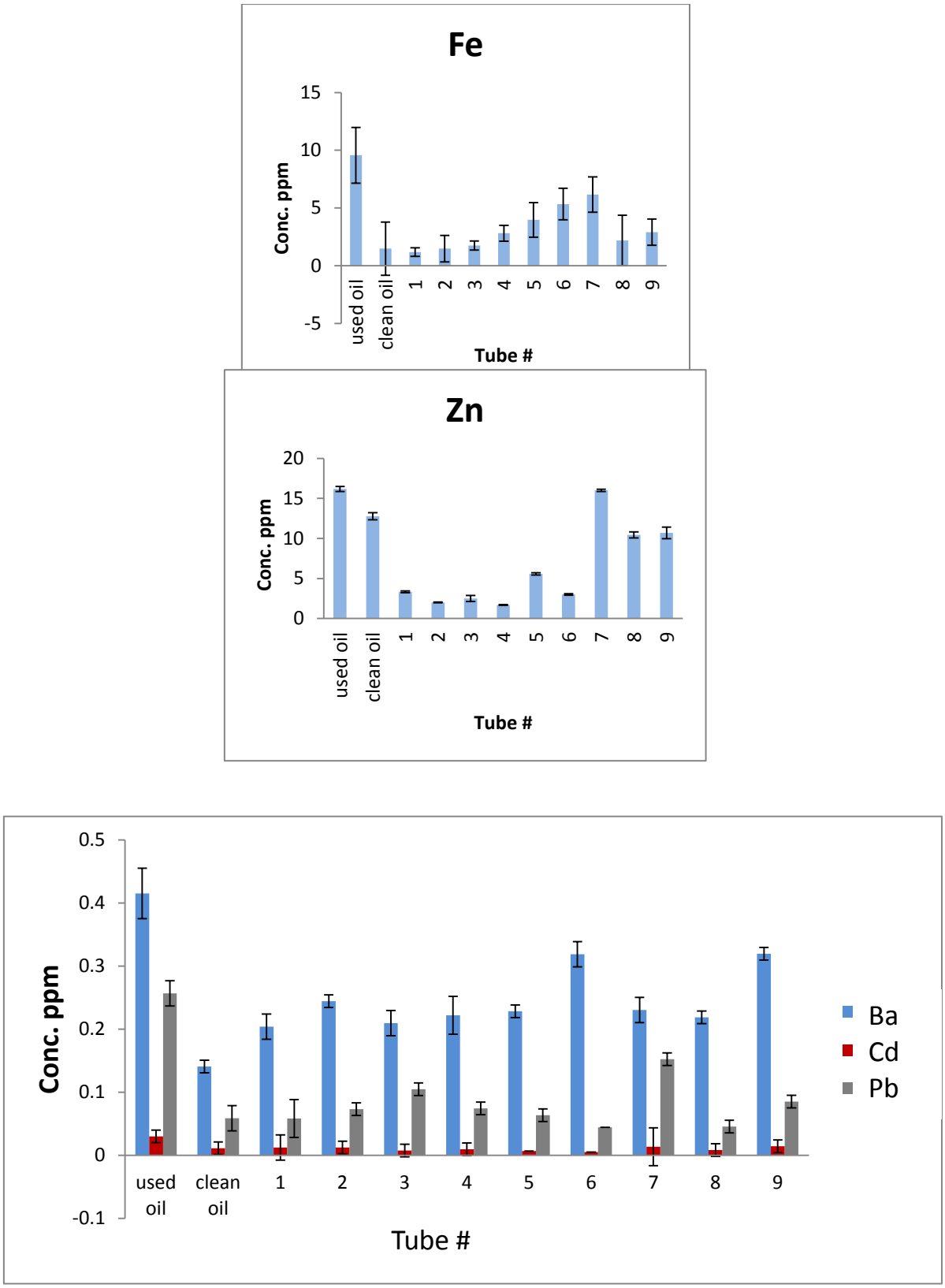

Figure 3.16: Concentration of heavy metals (Fe, Zn, Ba, Cd, Pb) for clean, used and recovered lubricants at different components of oil-surfactant and 5g of buffer at different pH (Table 3.2), T =25.0^{o}C.

In conclusion, the results of removal of heavy metals in this work are comparable with the results reported elsewhere [Hamawand, *et al.*, 2013]. This finding renders our new method to be powerful, cost effective and environmentally friendly for heavy metals removal from used oil.

4. Conclusion

The efficiency of re-refining used oil by using reversed micelle process was studied. The physical and chemical characteristics of refined used oil are compared with those of virgin base oil for quality assurance. The processes of re-refining of used oil are performed using environmentally friendly surfactant. Ternary phase diagrams are prepared for water, C_{12} E_3 and either clean or used oil at room temperature. The results point out that the phase diagram for water, C_{12} E_3 and clean oil is composed of three regions. The first region is the reverse micelle phase which starts from the surfactant corner and extends up to 10 % wt. surfactant and 90% wt. oil. This phase, and towards its middle, solubilizes up to 11% wt. water. The second region is a viscous and anisotropic as evident by the cross polarizers and optical microscopy representing the lamellar liquid crystal region. It appears on the binary line of surfactant and water between ratios of 88% - 70% wt. surfactant and extends towards the oil corner solubilizing up to 42% wt. oil. The third region is two-phase in which oil and water form heterogeneous solution. On the other hand, the phase diagram for water, C_{12} E_3 and used oil displays similar features of that displayed by clean oil, however, with absence of the liquid crystal region. For used oil recovery, different percentages of oil, water, and surfactants are prepared in the reverse micelle region with varying pH. The result of recovered oil as function of surfactant mass and pH; that a mixture of 10.0 g of surfactant, 85 g of used oil and 5.0 g of water at pH 12 gives the optimum density, and best performance of viscosity. The ash content in recovered oil is between 0.0018% to 0.0164% by weight which significantly lower than that of used oil. Good oleic phase recovery was achieved (from 88.6 to 94.3%) at 85.0g of oil and 10.0g of surfactant. IR- spectra of the refined oil showed that the oxidation products and additives were removed. The concentration of heavy metals for refined oil is much less than the used oil and show a complete removal of some heavy metals like Mn, Ni and Cu.

The UV-spectrum of all sample shows a peak at λ_{max} = 205 nm. The absorbance at this wavelength of clean oil, surfactant and recovered oil are much lower than that of used oil due to the absence of pollutant. Furthermore, some of samples of recovered oil displayed even lower absorbance than clean oil which could be attributed to the removal of additives from the oil during the recycling process. The IR-spectrum for used oil shows the

appearance of a spectral band at 1700-1750 cm^{-1} indicating the presence of oxidation compound. On the other hand, the IR spectrum of all samples of recovered oil shows that the spectral band at 1700-1750 cm^{-1} is absent, hence, the success of the our method in removing these oxidation by products.

Heavy metal concentrations are obtained using ICP-MS. The results show that using reversed micelle at the optimum conditions, resulted in effective extraction and removal of heavy metals from used oil. Furthermore, the removal efficiencies of heavy metals from used oil are found to be highly dependent on oil-surfactant-water percentage and pH and vary from one metal to another. Whereas some metals concentrations are highly decreased, other metals are completely removed within the detection limit of the instrument.

In conclusion, our novel method for refining used oil is found to be very efficient in removing heavy metal, soot and other pollutants from used oil to a level compared with virgin base oil with sustainable, environmentally friendly and cost effective fashion.

5. Future Works

1. To scale-up the process to include larger amount of used oil for refining and show if this method still effective at these large scale operation. Furthermore, the cost and economy of the recycling process will be assessed as another tool for optimizing the process for different re-use of the refined oil.

2. Extent the study to involve more points in reversed micelle region and determine the optimum conditions for the extraction of heavy metals and other pollutants from used oil more effectively.

3. To perform the extraction process at different temperature. This might enhance the reverse micelle region and hence enhance the oil recovery effectiveness.

4. To optimize the method with respect to other related surfactants. This might lead to more extended reverse micelle region which will lead to more freedom in optimizing the process.

5. Check the heat content of the refined oil and determine its effectiveness as energy source in industry.

6. To test the performance of refined oil as lubricant for engines and compare its effectiveness with clean as well as refined oil using other processes.

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Appendix A

Types and function of lubricating oil additives.

Type	Function	Example
Detergent	Neutralise the deposits formation from combustion of high sulfur fuel or acidic combustion material, helps to prevent the deposition of lacquer resulting from oxidation.	Metallo-orgnic compounds, calcium, zinc magnesium sulphonates.
Dispersant	Disperses or suspends any potential sludge forming material in oil.	Ash less dispersants and polymeric succinimides.
Viscosity index improver	Increases the relative viscosity of oil at high temperature.	Methacrylates polymers and acrylates polymers.
Oxidation inhibitor	Forms protective film on metal to prevent acid from reaching its surface.	Zinc dithiophosphate.
Rust inhibitor	Forms tenacious film by high polar attraction towards the metal surface.	Neutral material; ethioxylated alkyl phenils.
Antifoam	Attachs to air bubbles in foam, which coalesce into larger bubbles and rise to the foam surface and collapse.	Silicon type chemicals; polymethyl siloxanes.
Pour point depressant	Inhibits formation of wax crystal structure that prevent oil flow at low temperature.	Alkylaromatic polymers, methacrylates polymers.
Antiwear	Reduces friction, wear scuffing/ scoring under boundary lubrication conditions.	Esters, acids.

Source: [Durrani, 2010]

Appendix B

Risk Factors of PAHs

PAH	Route of Exposure	Health Hazards
Acenaphthene	Drinking contaminated water; eating food s grown in contaminated soil; skin contacts with contaminated water and foods	Reproduction and fertility problem; gastrointestinal (including liver) problem
Acenaphthylene	Drinking contaminated water; eating foods grown in contaminated soil; Skin contacts with contaminated water and foods	Reproduction and fertility problem, accumulation in wildlife and people
Anthracene	Drinking contaminated water; eating foods grown in contaminated soil; skin contacts with contaminated water and foods	Respiratory and skin toxicant, gastrointestinal toxicant, and endocrine toxicant
Benzo(a)an thracene	Drinking contaminated water; skin contacts with contaminated water	Probable carcinogen
Benzo(a)pyrene	Breathing air containing it; skin contacts with contaminated air, water, soil, or food; drinking contaminated water or cow's milk; eating grilled or charred meats	Probable carcinogen (skin, lung, and bladder cancer in humans and animals)
Benzo(b)fluoranthene	Drinking contaminated water; skin contacts with contaminated water and soil	Probable carcinogen, very harmful to aquatic organisms, long term damage to the environment
Benzo(f)fluoranthene	Skin contacts with contaminated aerosol	Probable carcinogen, genetic damage to humans
Benzo(g,h,i)perylene	Breathing contaminated air; eating or drinking contaminated food or	Effects found in laboratory animals only. Reproductive problems, birth

	water; skin contacts with contaminated soil or products	defects, and skin problems
Chrysene	Drinking contaminated water; skin contacts with contaminated water or soil	Probable carcinogen to human and animals
Dibenzo(a,h)anthracene	Breathing contaminated air; skin contacts with contaminated products; ingesting contaminated fluids	Probable carcinogen to human and animals
Fluoranthene	Drinking contaminated water; eating food s grown in contaminated soil; Skin contacts with contaminated water and foods	Respiratory and skin toxicant, gastrointestinal (including liver) toxicant, endocrine toxicant, and carcinogen
Fluorene	Drinking contaminated water; eating foods grown in contaminated soil; Skin contacts with contaminated water and foods	Gastrointestinal (including liver) toxicant
Indeno(I,2,3-cd)pyrene	Breathing contaminated aerosol; skin contacts with contaminated products	Possibly carcinogenic to humans
Naphthalene	Drinking contaminated water	Hemolytic anemia, cancer, vomiting, nausea, diarrhea, blood in the urine, and yellow skin
Phenanthrene	Drinking contaminated water; eating food s grown in contaminated soil; Skin contacts with contaminated water and foods	Respiratory and skin toxicant

Source: [Fan, 2010]

Appendix C1

Result of ternary phase diagram of water/Alfonic 1412-3 ethoxylate/ fresh clean motor oil system for each addition of water.

Test tube #	Phase number (Φ)									
Amount of water	91	82	73	64	55	46	37	28	19	101
0 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ
4 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	2 Φ	1 Φ
8 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	2 Φ	2 Φ	2 Φ	1 Φ
12 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	2 Φ	2 Φ	2 Φ	1 Φ
16 %	1 Φ	1 Φ	1 Φ	1 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	1 Φ
20 %	1 Φ	1 Φ	1 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	1 Φ
24 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
28 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
32 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
36 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
40 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
44 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
48 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
52 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
56 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
60 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
64 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
68 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
72 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
76 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
80 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
84 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
88 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
92 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
96 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ

Appendix C2

Result of ternary phase diagram of water/Alfonic 1412-3 ethoxylate/ used motor oil system for each addition of water.

Test tube #	Phase number (Φ)									
Amount of water	91	82	73	64	55	46	37	28	19	101
0 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ
4 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ
8 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ
12 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ
16 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	2 Φ
20 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	2 Φ
24 %	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	2 Φ
28 %	2 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	1 Φ	2 Φ
32 %	2 Φ	2 Φ	1 Φ	1 Φ	1 Φ	1 Φ	2 Φ	2 Φ	1 Φ	2 Φ
36 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	1 Φ	2 Φ
40 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
44 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
48 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
52 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
56 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
60 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
64 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
68 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
72 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
76 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
80 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
84 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
88 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
92 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ
96 %	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ	2 Φ

الظروف المثلى لإزالة فعالة للسخام والعناصر الثقيلة تحدث عند استخدام كمية قليلة من السطحي وكمية عالية من الزيت المستخدم (10 غم، 85 غم على التوالي) في محلول منظم درجة حموضته 12.

تم تحليل محتوى المعادن الثقيلة من الزيوت المستعملة وكذلك الزيت المعاد تكريره من خلال استخدام مطياف الكتلة الحثي البلازمي(ICP-MS).

وجد أن الزيت المستعمل يحتوي على 0.4152 جزء من مليون من الباريوم, و 0.03 جزء من مليون من الكادميوم, و 9.567 جزء من مليون من الحديد, و 0.0567 جزء من مليون من المنغنيز, 3.5744 جزء من مليون من النيكل, 16.1744 جزء من مليون من الخارصين, و1.1908 جزء من مليون من النحاس وكذلك 0.2568 جزء من مليون من الرصاص. ومن ناحية أخرى وجد أن الزيت المعاد تكريره يتراوح تركيزالمعادن الثقلية فيه حسب التالي: 0.204 جزء من مليون إلى 0.3196 جزء من مليون من الباريوم, و 0.0052 جزء من مليون إلى 0.0144 جزء من مليون من الكادميوم, و 1.1772 جزء من مليون إلى 6.1696 جزء من مليون من الحديد, و 1.6876 جزء من مليون إلى 16.0144 جزء من مليون من الخارصين, و 0.0444 جزء من مليون إلى 0.1524 جزء من مليون من الرصاص أما المنغنيز والنيكل والنحاس فوجد خلو الزيت المعاد تكريره منها. وهذه النتائج تشير إلى نبل وكفاءة الطريقة المستخدمه في إزالة المعادن الثقيلة من الزيت المستعمل مما يجعل هذه الطريقة بمثابة تقنيه قوية لاستعادة الزيت المستخدم على الأقل كمصدر للطاقة.

أظهر هذا العمل كفاءة كبيرة من المذيلات العكسية في إعادة تدوير زيت المحركات المستخدم, خصوصاً في إزالة المعادن الثقيلة بكفاءة عالية وتكلفة منخفضة وبطريقة مستدامه بيئياً.

وقد وجد أن الزيت النظيف قد أظهر من خلال الرسم البياني السلوكي وجود منطقة LC والتي اختفت تماماً عندما تم استخدام الزيوت المستعمله. وقد كانت المنطقة المستقرة للمذيلات العكسية بوجود الزيوت المستخدمه ما بين 0–100% من الزيت و 6% –88% من السطوح و 5% –25% من المحلول المنظم ولكن المنطقة التي حدودها ما بين 40% –50% من الزيت فهي أقل استقراراً للمذيلات العكسية.

عملية الاستخراج الأمثل للمعادن الثقيلة والملوثات الأخرى تتمثل في نسبة الزيت– السطوح – الماء في داخل المنطقة المستقرة للمذيلات العكسية وكذلك درجة الحموضة. وتم الحكم على كفاءة عملية الاستخراج هذه بناءً على عدة معايير فيزيائية وكيميائية مثل: اللون والكثافة واللزوجة، محتوى الرماد، كمية الزيت المستخرج، التحليل الطيفي للأشعة الفوق بنفسجية والتحت الحمراء ومحتوى المعادن الثقيلة.

وجد أن كثافة الزيت المعاد تكريره تمتد ما بين 0.8897 غم/سم^3 الى 0.9194 غم/سم^3، واللزوجة بمعدل ما بين 100 سنتيستوك الى 690 سنتيستوك, بينما محتوى الرماد فأخذ قيم تتراوح من 0.0018% الى 0.0164% من الكتلة, أما كمية الزيت المستخرج فتمتد من 84.4% الى 96.3%.

ظهور الموجه لجميع العينات على الطول الموجي 205 نانوميتر ولكن الامتصاص في حالة الزيت المستخدم كان أعلى من باقي العينات هذا في حالة استخدام التحليل الطيفي للأشعة الفوق بنفسجية أما في حالة استخدام التحليل الطيفي للأشعة التحت حمراء فأظهرت أن الزيت المعاد تكريره قد عاد في تركيبه للزيت البكر ولكنه خالٍ من المواد المضافة (المحسنات) مما وسع وزاد من الطرق الممكن الاستفاده منه في استخدامه. أما بالنسبة لتركيز العناصر الثقيلة فجميع العينات أظهرت انخفاضاً واضحاً فيها وبعض العناصر الثقيلة قد تم ازالتها بالكامل وهي النحاس والنيكل والمنغنيز.

استخراج المعادن الثقيلة والملوثات الأخرى من الزيوت المستعمله باستخدام عكس الذيلات.

إعداد:ايمان محمد حسين منصور

اشراف: د. مصطفى خميس د.ابراهيم الكيالي

ملخص:

تعتبر الزيوت المستعمله من أكبر مصادر التلوت في العالم، وذلك بسبب الكميات الهائلة الناتجة عنها، وسميتها العالية وسوء ادارتها.

وجد أن العمليات التقليدية لإعادة تدوير الزيوت المستعمله تكون ذات عائد منخفض، وعملية شاقة وتستغرق وقتاً طويلاً، وتعتبر عملية خطرة بيئياً، وذلك بسبب الحامض الناتج عنها.

وفي هذه الحاله كان لا بد من البحث عن اساليب جديده لإعادة تدوير الزيوت المستعمله والتي تعمل على الحفاظ على السعر والوقت والحد من التلوث البيئي والتقليل من الزيوت البكر المستوردة للتشحيم والحفاظ على الموارد المعدنية.

الاستخراج بالمذيلات العكسية هي الطريقة التي استخدمت في هذا البحث من خلال توظيف السطوح الغير أيونية – الكحول البولي ايثيلين جلايكول ايثر (3–Alfonic 1412)(3EO) مع زيت المحرك المستخدم (SAE 15W– 40) والمحلول المنظم. وقد تم تحديد منطقة المذيلات العكسية باستخدام الرسم البياني السلوكي لنظام مكون من ثلاث عناصر هي: الزيت – السطوح – الماء.