The Effect of Degrading Agents and Diluents on Oil Recovery from Lithium Based Waste Lubricating Grease

Motshumi J. Diphare, Jefrey Pilusa, and Edison Muzenda

Abstract—In this study, the recovery of base oils from waste lithium based lubricating grease was investigated using a novel combination of thermal degradation in an aqueous caustic solution and solvent extraction. Lubricating grease is an important resource that cannot be disposed of randomly due to the presence of pollutants. In response to economic challenges and environmental protection, there is a growing trend to regenerate and reuse waste lubricant. Waste grease was initially dissolved in a 20 w/w% KOH solution at 80°C while being agitated for a period of 15 min. Two distinct layers were observed after 10 min of settling time. The top layer being of dark brown oil and the bottom layer was a heterogeneous mixture. The two layers were separated by decantation. The bottom layer was cooled to 45°C followed by slow addition of n-hexane while agitating to prevent the settling of solids. Two distinct layers were also formed, the top homogeneous mixture of light brown oil–toluene mixture and the bottom sludge layer. This research has further optimized the process by studying the effect of KOH concentration to enhance flocculation and recovery of oil. Oil recovery increased from 5% to 30%. The recovery also increased with an increase of solvent-to-grease ratio up to 1:6. A solvent recovery of 82.6% to 88% by mass was obtained through fractional distillation. The overall oil recovery from waste grease using the combined extraction processes was 75 w/w% .

Keywords—Degrading agent, lubricating grease, oil recovery, solvent extraction, sludge

I. INTRODUCTION

LUBRICATING greases are usually made from petroleum oils thickened with metal soaps. Lithium 12-hydroxystearate soap is the most widely used thickening agent. The thickener is added to prevent loss of lubricant under operating conditions. In addition, lubricating greases usually contain performance additives [1]. They are used in various mechanical applications to reduce the wear and friction between mechanical moving parts such as metal joints, shafts and bearings.

Due to its semisolid characteristics, lubricating grease remains in place and act as a seal, thus preventing both solid and liquid contaminants from entering the system [2]. Generally, lubrication is achieved by oil, which after use is deemed as a valuable renewable resource. Oil viscosity decreases with increasing temperature hence the requirement for additives to support its functioning at higher temperatures [3].
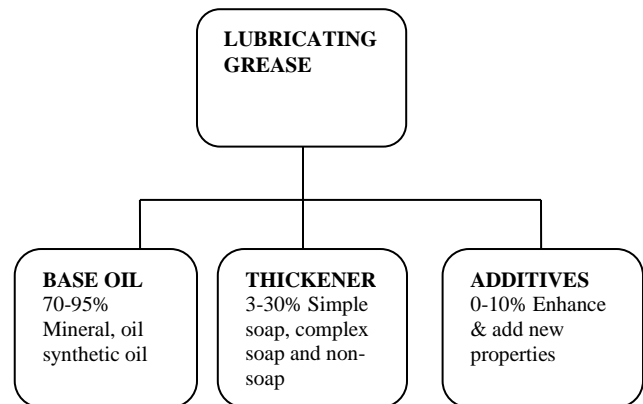

Fig. 1 Grease anatomy [3]

When additives and foreign substances, such as metal powder, chips, moist, dirt and dust, are mixed with the lubricant, aging, degrading and failure will likely occur, leading to mechanical fault and degraded performance. In such cases, the lubricant is replaced to improve the working efficiency [4]. During usage, lubricating greases undergo changes such as degradation and contamination, which render them ineffective for further application. Lubricants go through normal degradation and about 50% is lost through this process, and the remainder picks up a number of contaminants from the working environment [5]. Degradation involves changes in the desired viscometric properties due to the alteration in lubricant molecular structure caused by cracking, isomerization and polymerization reactions prompted by high temperatures in the running machinery. The overall effect of this degradation is the formation of low molecular weight

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compounds and oxidation products which include polymerized or condensed molecules such as gum and sludge [6]. Waste lubricating grease is an abundant and valuable waste that requires treatment. There are basically three options to deal with the waste lubricants in the world: (a) dumping them on land, garbage heap and sewerage system, (b) regeneration of base-oil from waste lubricants, (c) extracting the heat value of waste oil through combustion processes [7].

The contaminants in waste lubricants have adverse environmental and health impacts. Reference [8] reported that the presence of degraded additives, contaminants, and by-products of degradation render waste lubricants more toxic and harmful to health and environment than virgin base oils. When deposited into water drains or sewers, they can affect waterways and coastal waters [9]. When dumped in soil or sent to landfills, they can migrate into ground and surface waters though numerous land treatment processes. When burnt, harmful metals and other pollutants may be released into the atmosphere. Therefore, it is essential that waste grease is reduced in volume, by extracting and recycling of the oil component.

Various techniques have been practiced for recycling used lubricating oils and grease. Among the alternative processes proposed during recent years, solvent extraction has received considerable attention. Solvent extraction is a simple process; used grease is first degraded with a caustic solution and followed by addition of solvent in appropriate proportions to assure complete miscibility of the base oil in the solvent. The extracting solvent should also reject the additives and carbonaceous impurities normally found in used oils and greases. These impurities flocculate and settle by gravity. The solvent is then recovered by distillation for reuse [10]. Solvent extraction is capable of removing about 10-14% of the used oil as contaminants, which corresponds roughly to the amount of additives and impurities normally found in used oil [11]. The efficient recycling of waste lubricants could help reduce both the environmental pollution and gas emission.

The objective of this study was to evaluate the oil recovery efficiency by degradation-flocculation and solvent extraction processes. The influence of various degrading agent concentrations, solvent to grease sludge ratio parameters were investigated and optimized. Oil recovery, sludge removal and other properties were used to obtain optimum experimental conditions and as well as improving the treatment process. The results provide a sound basis for developing an environmentally friendly and economically competitive method for waste lubricating grease treatment.

## II. MATERIALS AND METHODS

A. Materials

Technical grade n-hexane (95%) and analytical grade potassium hydroxide (KOH) pellets (99.9%) were supplied by Laboratory Equipment Supplies (Pty) Ltd. (Germiston, South Africa). The contaminated high temperature metal bearing grease was supplied by the Engine Petroleum (Pty) Ltd. Samples of waste grease were collected from various drums to prepare a representative sample.

B. Methods

Degrading and Flocculation – Addition of a base for example KOH promotes fast flocculation of the impurities, which are segregated from the base oil by the solvent. The flocculation is enhanced by the presence of OH groups that neutralize the electrostatic repulsion. This electrostatic repulsion exists since alcohol groups are linked with the ions from the additive. Addition of a solution containing ions that neutralize these charges, break this stability. Participation of OH groups in ion exchange reactions with the electrolyte ions helps to neutralize the electrostatic repulsion. The stoichiometric equation is illustrated as in (1):

$$C_x\text{-OH} + K^+ \longrightarrow C_x\text{-OK} + H^+ \qquad (1)$$
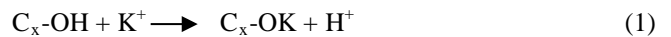
In (1), C_x-OH is the type of alcohol, K+ is the ion of potassium, and H+ is the ion of Hydrogen. Metal complexes are classified as colloidal particles that are destabilized by the addition of coagulant, such as potassium hydroxide (KOH) [6].

Fig. 2 Laboratory extraction system setup

Solvent Extraction – Many processes for the recycling of used lubricants involve the use of vacuum distillation followed by a polishing or decolorizing treatment. However, this present serious problems related to coking and column fouling during distillation. Therefore, some form of pre-treatment to remove additives and contaminants from the oil is preferred [1]. In principle, extraction with solvents can be used to this end. Oil extraction is favoured by the application of pre-treatments that break and/or degrade the cell wall structures, facilitating not only the oil release from the oil bodies, but also solvent access [13]. The basics of this pre-treatment is the use of a solvent to selectively extract the base oil components from the waste lubricant in a process that would be quite similar to that commonly used in crude oil refining to separate out asphaltenes for producing heavy neutral base oil.

A good solvent should be miscible with waste grease and

not additives and reject other impurities. There are several solvents with these properties and their behaviour with waste oil should be well understood. Contact time is important in two ways, it should be long enough to dissolve the base oil from waste grease and promote the rejection of additives and impurities by permitting their aggregation to large particles that can separate from solution through sedimentation.

Solvent Recovery – After extraction, the solvent can be recovered and reused. The solvent is recovered by vacuum distillation utilizing volatility difference. For example, to recover hexane, the mixture needs to be heated to just above $60^{o}C$. The solvent can further be reused for the extraction process. Reference [14] reported a solvent recovery of up to 88%.
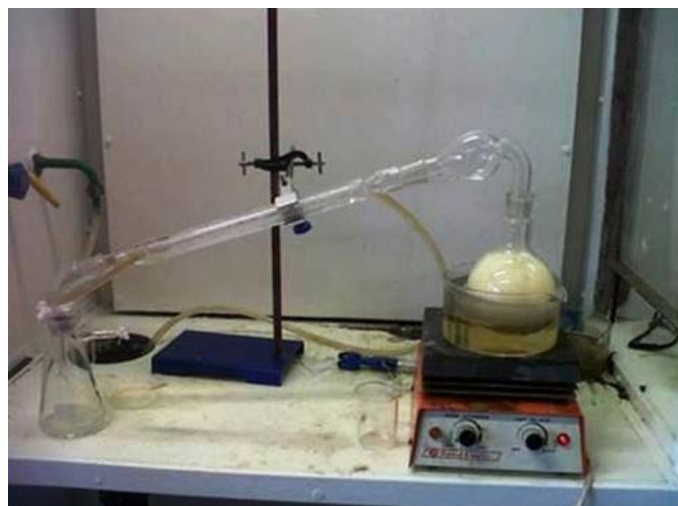

Fig. 3 Laboratory distillation apparatus

C. Experimental Procedure

Fig. 4 shows the schematic diagram for the extraction system used in this study. The process consists of three stages: the decomposition of grease into the thickener and oil, solvent extraction and distillation for solvent–water recovery. When hot KOH solution is introduced into used grease, it breaks the polar bonds that hold together the constituents of grease and free the base oil from thickeners, soaps and other additives [6,14].

During the second stage an organic solvent is added for polar–polar dissociation, to dissolve the remaining base oil trapped in the pores of the additive–soap sludge and form two distinct layers, an organic layer and an aqueous layer. The organic layer contains the solvent and a dissolved fraction of extracted oil, this is further separated by fractional distillation.

Aqueous KOH solutions ranging from 5 to 40 w/w% were prepared and heated to 80 ^{o}C. This temperature was selected to increase the decomposition of grease without boiling the water. A batch of 100g grease sample was slowly added into the solution at a mass ratio of 1:3. Reference [14] reported that KOH is a suitable degrading agent based on its optimal strength, decomposition rate, cost and density. An aqueous solution of 20% by mass of the degrading agent (potassium hydroxide) was prepared in a 1000 ml flask. 300g of solution was transferred into a beaker (thermal reactor) and heated up

to 80 ^{o}C as represented by stream (2) in Fig. 1. 100 g of waste grease (1) was slowly dissolved in the hot solution while agitated at 700 rpm using high shear impeller blades.

The resulting mixture (3) is then cooled forming about 48.7g of a floating dark brown oil layer (4) which was decanted from the beaker and the remaining bottom layer (5) was further treated using solvent extraction (stage 2). n-Hexane (6) was slowly added into the mixture, and then agitated until a uniform homogeneous mixture was formed. 702.2 g of n-Hexane was added to the mixture, which was calculated on a basis of 2:1 mass ratio of feed to solvent.

The mixture (8) was transferred into a round bottom flasks were it was distilled at 110 ^{o}C using a hot plate and glycerol as a heating medium. The vapour was collected and condensed in a glass condenser into a collecting funnel (10). 923.2g of the condensate, a mixture of water and n-hexane was collected.

The condensate was further distilled at the boiling temperature of n-hexane, 69 ^{o}C and 617.9 g of the vapour were condensed (11). A clear liquid remained at the bottom of the distilling flask (12) which mainly consisted of water. 23g of oil was recovered at the bottom after distilling at 110 ^{o}C. The same procedure was followed using n-hexane as an extracting agent with various solvent-to-sludge ratio ranging from 1:1 to 1:7.
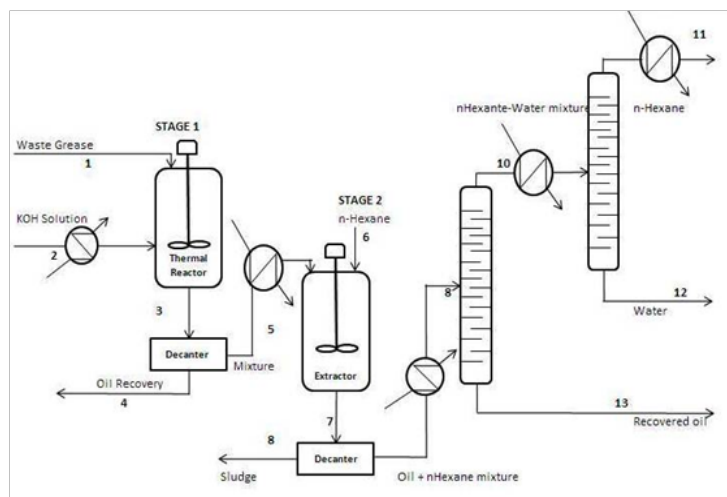

Fig. 4 Process flow diagram for two stage thermo-chemical oil extraction from waste grease.

III. Results and Discussions

The parameters investigated in this study were the concentration of degrading agent (KOH) and solvent to grease sludge ratio. The concentration of KOH was varied from 5% to 40%. Solvent to grease ratio was varied from 1:1 to 7:1. Used lubricating grease is a complex mixture of base oil, polymeric additives, water, light hydrocarbons, metals and carbonaceous particles. Addition of KOH promotes a fast flocculation of the impurities, which are segregated from the base oil by the solvent. The flocculation is enhanced in the presence of OH groups that neutralize the electrostatic repulsion. This electrostatic repulsion exists since alcohol groups are linked with the ions from the additive. Addition of

a solution containing ions that neutralize those charges, break this stability. Participation of alcohol OH groups in ion exchange reactions with the electrolyte ions helps to neutralize the electrostatic repulsion [6, 14, 15]. Fig. 5 shows the influence of KOH concentration on oil recovery. The optimum KOH concentration was found to be 30%, this is in with the findings of Ping *et al*, 2000 [16].
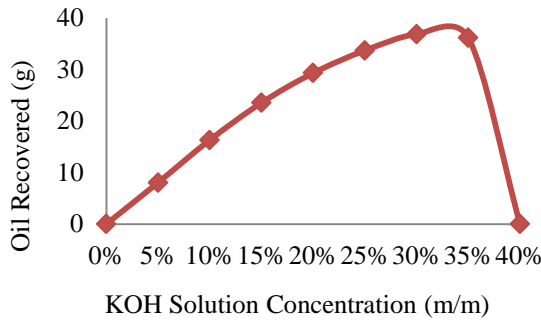

Fig. 5 Effect of degrading agent concentrations on oil recovery.

A good extraction–flocculation solvent should dissolve base oil and precipitate other substances to form sludge [6]. n-Hexane was found to be an efficient extraction–flocculation solvent for used grease due to its good solubility parameters for base oil and anti-solvent effect for non-polar or slightly polar polymeric additives, metals and carbonaceous particles. Reference [14] explained in his findings that effective solvent extraction is mainly influenced by polar–polar bond interaction between the solvent and the oil. Active surface area of oil is also critical in ensuring efficient dissolution of oil from the thickener surface into solvent liquid stream which in this instance is n-hexane.

The role of high speed shear agitation at 1000 rpm in this process was to break down the grease molecules in order liberate oil molecules thereby increasing its active surface area to interact with n-hexane. 80 ^{o}C was found to be the optimum temperature for caustic KOH solution which acts as a catalyst to degrade the grease into its constituent thickener and base oil. Once the bonds holding the thickener and oil are broken down with the aid of high speed shear agitation and a catalyst at optimal temperature, stage 1 oil floated in the mixture since it is less dense than both the thickener and KOH solution. This was followed by stage 2 where n-Hexane was introduce to further extract the remaining oil in the mixture.

Fig. 6 shows the influence of solvent to grease sludge ratio on oil recovery. This phenomenon can be attributed to the fact that increasing the solvent to grease ratio, increases the medium mutual solubility of oil in the solvent, resulting in reduction of oil losses in the sludge phase [10].

The test results in Fig. 6 show that base oil recovery increase with increase in extraction phase ratio due to the higher affinity of the oil for the solvent [17].
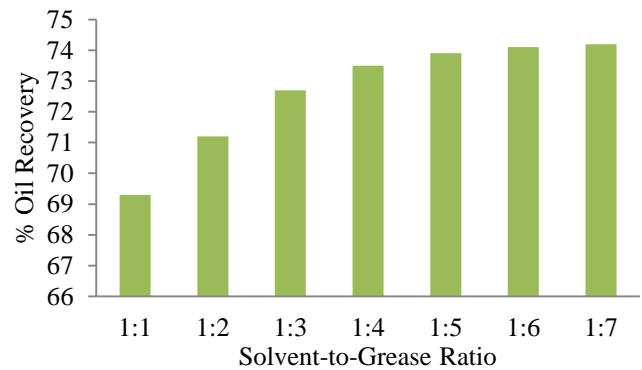

Fig. 6 Effect of solvent-to-grease ratio on oil recovery.

The data for ratios from 1:1 to 1:4 are described by a linear relation ($R^2 = 0.97$), this is in agreement with the findings of Zubaidy *et al*, 2010 [18]. The recovery behaviour was also reported by Rincon *et al*, 2005 [19]. At lower solvent to oil ratio, solvent becomes saturated with base oil resulting in reduced oil recovery while at higher solvent/oil ratio maximum oil could be extracted and oil free sludge is obtained.

The combined oil recovered was within a range of 69.3 and 74.2% of the original grease feed. The amount of solvent recovered oil varied from 82.6% to 88% of the original amount. Solvent loss likely occurred through evaporation during mixing, decantation and from entrainment with the remaining sludge removed during decantation. A closed process should be capable of increasing the solvent recovery.

IV. CONCLUSIONS

Oil recovery from waste lubricating grease by degradation-flocculation followed by solvent extraction has been found to be one of the competitive processes for the recycling of waste lubricating grease. In this study, the performance of degrading agent at different concentration for oil recovery has been studied. The optimum concentration was found to be 30%. Various solvent to oil extraction ratios were studied. The optimum solvent to oil ratio was found to be 1:7. Combined oil recovery was found to be within a range of 69.3 and 74.2%. The amount of solvent recovered varied from 82.6% to 88% of the original amount.

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