

PRELIMINARY STUDY AND CHARACTERIZATION OF SLUDGE FROM USED ENGINE  
OIL FOR HIGH TEMPERATURE GREASE PRODUCTION

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ABSTRACT

The recovery of sludge from used lubricating oil was examined utilizing a blend of two solvent mixtures. The activity of these solvent extraction blends {toluene, butanol and ethanol (A)} and {Hexane, isopropanol and methanol (B)} on the used engine oil was evaluated experimentally, after which the used oil and sludge recovered was characterized for their physiochemical properties. The results confirm solvent mixture (B) gave good efficiency with the highest percent sludge removal. The physical properties of the used lubricating oil and sludge recycle oil were measured and compared, the results show the change in the properties of sludge after treatment and sludge sample recovered from solvent mixture (B) have good properties and efficiency.

**Keywords:** Used Engine Oil, Lubricant Sludge, Solvent Mixtures, Waste to Wealth, Physiochemical Properties.

INTRODUCTION

Access to lubricants is essential to any modern society and not only does lubrication reduce friction and wear by interposition of a thin liquid film between moving surfaces, it also removes heat, keeps equipment clean, and prevents corrosion (Hamawand *et al.*, 2013). In addition, increase in the price of crude oil and environmental concerns, have put pressure on the industries thereby necessitating the need to find alternatives of mineral oils used for the production of lubricants (Battersby, 2005).

Grease is a semi-solid lubricant consisting of a thickening agent dispersed in a liquid lubricant such as mineral oil (petroleum oil), synthetic oil (silicon oil) or vegetable oil. Simply, grease is made up of three essential components which are the base oil, thickener and additives (Kholijah *et al.*, 2012). The thickeners in lubricating grease are the component that sets grease apart from fluid lubricants. Thickeners are molecules, polymers, or particles that are partially soluble in lubricating fluid; they arrange themselves in such a way that they impart a semi-solid consistency to the grease. Many different types of chemical compounds can be used to thicken grease. Simple soaps are the most common grease thickeners, examples are; lithium 12-hydroxystearate and calcium stearate. Grease can also be thickened with non soap materials. Common non soap thickeners include polyurea, organophilic clay, fumed silica, fluoropolymers, and others. Fumed silica powder is used in relatively few grease products because it has no defined melting point and can be used in high temperature applications (What Is the Thickener in Lubricating Grease, 2017).

Lubricating sludge is a waste generated during the solvent extraction recycle process of waste lubricant oil. This recycle process is usually performed to recover a significant amount of base oil from the used oil. Solvent extraction process followed by adsorption is a more effective process for recycling of waste lubricating oils to recover sludge (Kamal and Khan, 2009). Osman *et al.*, (2017), reported that there is more effective sludge removal capabilities by using different solvents which help to determine the maximum percentage of sludge formed by the waste oil.

Currently, many researches were being done to search for alternative sources for grease production due to the increase of crude oil prices in the world market and the depletion of the source. Thus, this will definitely affect the price of base oil as main component in grease. In this work therefore, instead of using mineral oil as the base oil, silicone oil which is a more economic choice and is more abundantly available was used. That is why, this research would have a significant impact in the production of grease as it proves that sludge which is a waste, could be turned into wealth and thus reducing the pollution problem and at the same time reducing the cost of grease production.

## METHODS

**Processing and Treatment of Raw Materials (Used engine oil):** The sample of used engine oil (premium motor oil SAE-40) was collected from a car Mechanic workshop in Minna, Niger state, Nigeria. The sample was directly drained from a car which was due for service and change of oil. Pretreatment of waste lubricating oil was carried out by filtration, solid particles and some seen impurities were removed from waste engine oil and moisture content also removed by heating. The filtration was done using a funnel with a filter paper placed in it, and then a vacuum pump was connected to the filtering flask to which the funnel was fixed with the aid of a rubber stopper. The used engine oil was also treated by heating to a temperature of over 100°C for one hour, for the purpose of evaporating the water and the volatile substances in the used oil.

### Sludge separation from used engine oil

- For the first sludge separation, 300 ml of toluene, 300 ml of 1-butanol, 300 ml of ethanol and 2.6 g of potassium hydroxide were added into a beaker containing 500 mL of used engine oil in a closed vessel. The whole mixture in a beaker was placed on a magnetic stirrer and stirred for one hour. Then, the beaker was covered with an aluminium foil and set aside for 24hours, for settling filtration system to remove solvent from the sludge. The collected Sludge A was mixed well manually, and was further treated by heating to a temperature of over 100°C for one hour, to evaporate any moisture content and volatile substances in the sludge, before it was stored in a plastic container at room temperature for future use. This is sample A.
- For the second sludge separation the same method was employed where, 0.576 mL of hexane, 864 mL of isopropyl alcohol, 300ml of methanol and 2.6 g of potassium hydroxide were added into a beaker containing 500 mL of used engine oil. The remaining steps should be repeated as was used to prepare A. The resulting sample is B.

The percentage sludge removal on equal amount of used engine oil with the two solvent mixture separations was determined by weighing the sludge and the total mixture of used oil and solvent mixture used for separation. After the mass of sludge in the two separations process was calculated, the weight percent was therefore determined, seen in Table 2.

$$M_S = M_T - M_R \quad (1)$$

where  $M_S$  = Mass of sludge

$M_T$  = Mass of Total mixture

$M_R$  = Mass of Raffinate

**Characterization of used engine oil and sludge:** The used engine oil and sludge was tested to characterize the following physical and chemical properties it has attained due to the different operational conditions and pollutant contaminations during its service period.

#### i. Density

The density ( $\rho$ ) of the used oil sample was estimated by dividing a known mass of the oil to its volume. Briefly, 10 ml of the used oil was measured and weighed, the result was shown in Table1. The density of the oil was derived from the following equation (Hamawand *et al.*, 2013).

$$\rho = \frac{M}{V} \quad (2)$$

where  $\rho$  = density of Sample ( $\text{kg}/\text{m}^3$ )

$M$  = mass of sample (kg)

$V$  = Volume of sample ( $\text{m}^3$ )

#### ii. Viscosity

Viscosity ( $\mu$ ) was measured using a Cannon-Fenske (Fisher Scientific, Pittsburgh, PA) glass capillary kinematic viscometer in a constant temperature bath in accordance with ASTM D445. Kinematic viscosity is determined by measuring the time ( $t$ ) for a known volume of liquid flowing under gravity to pass through a calibrated glass capillary viscometer tube. The manufacturer of the Cannon- Fenske type viscometer tubes supplied calibration constants ( $c$ ) at a range of temperature 40°C and 100°C respectively (Udonne, 2011).

Kinematic viscosity ( $\mu$ ) in (m<sup>2</sup>/sec) was calculated from the following equation and the result was shown in Table 1.

$$\mu = C \cdot t \quad (3)$$

where;  $\mu$ =viscosity (m<sup>2</sup>/sec)

C=Constant of U-tube=7.328

t= time (sec)

### iii. Specific Gravity

Specific gravity (SG) is used to relate the weight or density of liquids to that of water. Specific gravity is a unit less measurement that is derived as a ratio of either the weight of another liquid divided by the weight or density of water (g/l). Temperature must also be taken into account when determining specific gravity, since density changes in relation to temperature (Hamawand *et al.*, 2013).

$$S.G = \frac{\rho_s}{\rho} \quad (4)$$

where S.G= Specific Gravity

$\rho_s$ =density of sample (kg/m<sup>3</sup>)

$\rho$ =density of water (kg/m<sup>3</sup>)

### v. Flash Point

Flash Point was analyzed using closed cup flash point method (ASTM D93). 75 milliliters of the sample was measured into a closed cup. It was agitated and heated at a fixed rate. At periodic intervals, the cup was opened and a source of ignition was brought over the apex of the cup. The flash point represents smallest temperature that the vapors above the liquid ignite when an ignition source is brought into contact (Aseem and Pankaj, 2016).

### v. Acid / Neutralization Number

The Neutralization Number or Total Acid Number (TAN) of the used oil was conducted using ASTM D974. It is the quantity in milligrams of potassium hydroxide (KOH) per gram of oil necessary to neutralize acidity. Two grams of used oil sample was weighed and mixed with 100 mL of the titration solvent (toluene and isopropyl alcohol containing a small amount of water) and 0.5 mL of the indicator solution (*p*-naphtholbenzein) and swirled until the sample was entirely dissolved by the solvent. The mixture assumes a yellow-orange colour and titrated with 0.1 M KOH solution in increments and mixed vigorously near the end point i.e. green colour. To observe the end point of dark-colored oil, the flask is shaken vigorously to produce momentarily slight foam and the colour change occurs under a white fluorescent. The neutralization number or Total Acid Number (TAN) result as shown in Table 1 was calculated as shown below: (Osman *et al.*, 2017)

$$\text{TAN} \frac{(\text{mg KOH})}{(\text{g sample})} = \frac{[(A-B) \times M \times 56]}{W} \quad (5)$$

where; A = KOH solution required for titration of the sample, (mL),

B = KOH solution required for titration of the blank, (mL),

M = molarity of the KOH solution, and

W = sample used, (g).

### vi. Coking Test

During a coking test (ASTM D524), the carbon residue was determined by weighing the residue after the oil had been heated to a high temperature in the absence of air. Three grams of used oil was measured on a crucible and put into a tubular stainless steel apparatus which was inserted into a tubular furnace. The apparatus was then flashed with N<sub>2</sub> gas so as to make the environment inside inert. The test was conducted at 550°C for thirty minutes. Finally the remaining residue was measured to calculate its percentage out of the total sample (Osman *et al.*, 2017).

$$\% \text{ Carbon Residue} = \left( \frac{M_{cr}}{M_{is}} \right) \times 100 \quad (6)$$

where  $M_{cr}$  = Mass of carbon residue  
 $M_{is}$  = Mass of initial sample

#### vii. Ash Content

There was some quantity of incombustible material present in a lubricant which can be determined by measuring the amount of ash remaining after combustion of the oil in a furnace (ASTM D482). Measured amount of used oil was put in a crucible and kept for five hours in the furnace at 800°C. The result as shown in Table 1, indicate the ash content of the sample. Mass of the remaining ash was measured and its percentage is calculated by dividing it with initial mass of the sample (Osman *et al.*, 2017).

$$\% \text{ Ash} = \left( \frac{M_a}{M_{is}} \right) \times 100 \quad (7)$$

where  $M_a$  = Mass of ash  
 $M_{is}$  = Mass of initial sample

#### viii. Water Content

Water content is the amount of water present in the lubricant. It is estimated by putting a measured amount of sample in an oven at 120°C for an hour. The dehydrated sample is then weighed to calculate the loss as shown in Table 1 (Hamawand *et al.*, 2013).

$$\% \text{ Water} = \frac{M_{is} - M_f}{M_{is}} \times 100 \quad (8)$$

where  $M_f$  = Mass of final water content  
 $M_{is}$  = Mass of initial sample

#### ix. Metal Content

The metallic content analysis was performed by atomic absorption spectrometry (AAS), using a fast sequential atomic absorption spectrometer. Before the analysis the used engine oil sample was heated to 60 °C and stirred to ensure homogeneity of the sample, it was then mixed with ten volumes of kerosene. Sets of organometallic standards of metal Zn, Cu, Fe, Pb. Cyclohexylbutyric acid salts were prepared and metal concentrations were determined by introducing the test solutions of engine oil samples into the flame of the atomic absorption spectrophotometer and recording the responses. Metal concentrations were determined from the calibration curve that was obtained from standard solutions. Standard solutions for all metals in engine oil samples were prepared according ASTM D 4628-2, as shown in Table 1 (Hamawand *et al.*, 2013).

#### x. FTIR Spectroscopy

In the FTIR test the used oil sample was used to measure and determine functional group contained in the samples at a given time and temperature. It describes also a technique that could be applied to investigate the degradation of the used oil. A sample mass of 40 mg was heated in the crucible at a heating rate of 20°C/min from 50 to 950°C in an inert atmosphere (nitrogen).

The gas evolving from STA6000 was transferred via gas transfer line. This transfer line allows the transfer of combustion of pyrolysis products from thermal analyzer to FTIR 100 through the gas flow cell. Spectrum time base was used to analyze the sp files collected during the testing to analyze the spectrum (Collected continuously for over 3600 s) as shown in figure 1 ( Von-Fuchs and Diamond, 2002).

## RESULTS AND DISCUSSION

### Characterization of Used engine Oil and sludge Samples

The used engine oil was tested to determine its degradation effects and contamination level in comparison on the environment. Results from analyses that are used to characterize the experimental samples are given in Table 1.

**Table 1:** Used engine oil and sludge sample characterization results

Properties	Standard Engine oil (premium motor oil SAE-40)	Used engine oil sample (premium motor oil SAE-40)	Oil sludge(A)	Oil sludge (B)
Flash Point °C	>200	132	148	163
Kinematic Viscosity@ 40 °C (cSt)	105	126.41	233.19	306.25
Kinematic Viscosity@ 100 °C(cSt)	15.1	16.9	58.12	72.35
Specific Gravity	0,890	0.884	0.896	0.960
Ash Content (%)	-	4.9	5.1	4.7
Moisture Content (%)	-	4.22	3.68	1.9
Carbon Content (%)	-	4.68	12.96	4.91
(TAN) mg KOH/g(sample)	-	5.62	11.06	6.38
Density @ 27 °C, g/L	890	884	896	960
Metal Contents (mg/L)				
• Cu	-	5.2103	3.3962	3.3908
• Pb	-	29.3228	51.7146	33.2978
• Fe	-	9.0164	10.6740	13.1420
• Zn	-	0.4052	0.4398	0.4111

From Table 1, for used engine oil and sludge analyses, it can be seen that there is a significant property alteration due to the substantial deterioration of the used oil during its application period. As stated by Udonne (2011), a lower flash point indicates fuel contamination, while sludge (B) has a more significant increase in flash point, indicating less fuel contaminant. Increased density, specific gravity and viscosity show possible oxidation and polymerization products dissolved and suspended in the oil and sludge with sludge (B) showing high values. This according to Kholijah *et al.*, (2012,) indicate more of soap-like polymerization product needed in the thickening effect of sludge for the production of grease. Similarly, the moisture content refers to contamination from extraneous source; Ash content indicates contamination from incombustible solid particles of dirt, dust, grit and metallic fragments and, the value of Ash content shows the presence of metallic impurities which have been reduced by 5% in case of Sludge B, showing the removal of salts, while carbon residue indicates contamination with soot and carbon originating from incomplete fuel combustion and oil component breakdown. However the value was reduced in the case of sludge B compared to A as shown on Table 1 and these results are in agreement with the report of Osman *et al.*, (2017). Total acid/neutralization number indicates contamination from organic acids, soaps of heavy metals; and finally metal contents show contamination from engine parts tearing and wearing while the acid value is also reduced in the case of sludge (B) compared to (A) as shown in the Table 1. Since the recovery and use of sludge for the production of grease is our primary objective in this research study, sludge (B) has a better property rating compared to sludge (A). Therefore this shows that the properties of the sludge recovered as shown in sludge B possesses the desired characteristic for high temperature grease. It is envisaged that the processes used to produce sludge B can be applied in formulation of grease production in this research study.

#### Study of solvent mixtures and its solubility on the recovery of sludge from used oil.

An important experimental measurement of the solvent separation process is normally represented by the amount of sludge removed from the used oil. This may be expressed as the percentage sludge removal (PSR) which is the mass of sludge removed in gram/100 g of used oil.

# Preliminary Study and Characterization of Sludge from Used Engine Oil for High Temperature Grease Production

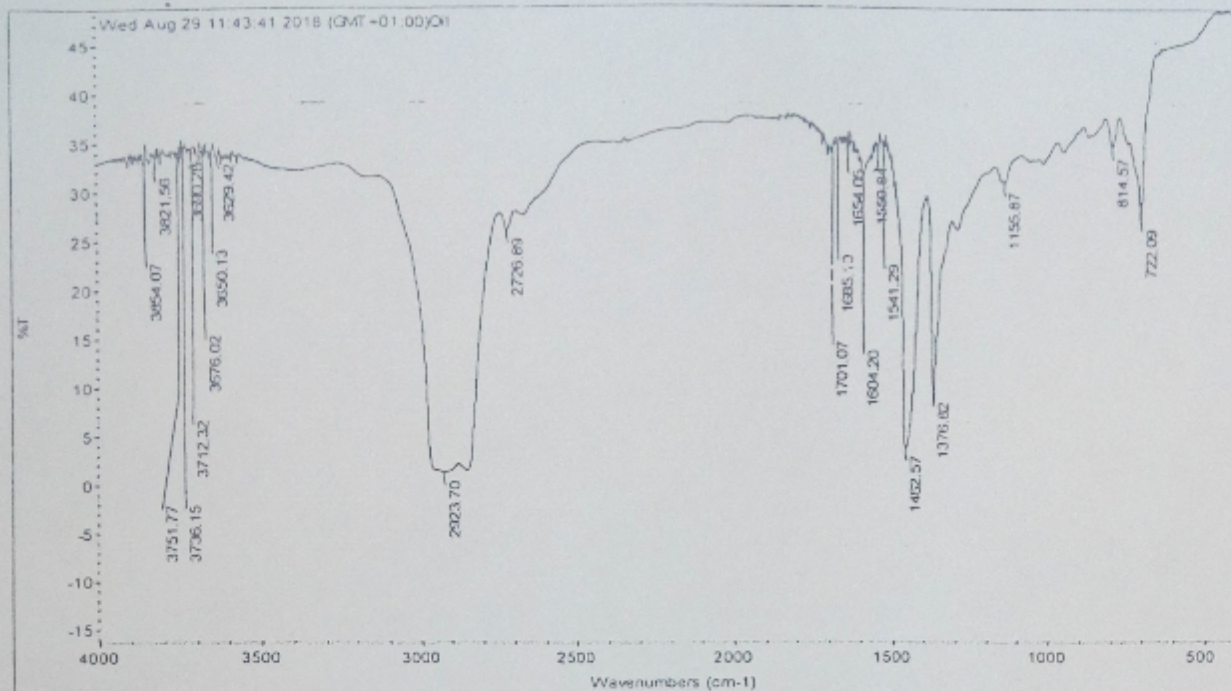


Figure 1: Results of FTIR analyses of used engine oil and sludge

The experimental results indicate that the effect for sludge removal capability of solvent mixtures A and B are shown on Tables 2 and Table 3. It is found that mixture B removed maximum sludge percent (52%) and mixture A removed lower percent (36.7%). This result is attributed to the solubility of solvent mixture B which is higher 23.2 (g/m<sup>3</sup>) as against that of solvent mixture A, 21.5 (g/m<sup>3</sup>). Also, the dielectric constant of solvent mixture B is higher than the other solvent mixture A as given in Table 3. These results indicate that as chain length of carbon atoms in the solvent and polarity decreases, its ability to eliminate sludge increases, although the solvent become more miscible in the oil as shown in Table 2 and 3. It is clear that solvent mixture B has higher solubility and dielectric constant. Therefore, B has maximum efficiency for sludge removal. Hexane, Isopropyl and Methanol removes the heavy components more than the other solvent mixture because its dielectric constant is higher. The more percent of sludge removal recovery means good efficiency of solvent separation process. This is in agreement with the observation of Osman *et al.*, (2017).

Table 2 Effect of different solvent mixture on the recovery of sludge from used oil.

	Solvent mixture A	Solvent mixture B
Sludge wt%	36.7	52
Raffinate wt %	63.3	48
Colour of sludge	Brown	Dark brown

Table 3 Solubility and dielectric constant of two solvent mixtures

	Solubility (J/m <sup>3</sup> )	Dielectric constant
Toluene + Butanol and Ethanol(A)	21.5	6.982
Hexane + Isopropyl and methanol (B)	23.2	6.994

## FTIR Analyses of Used engine Oil and sludge.

The IR results of the used engine oil as shown in Figure 1 shows that there are no peaks between 1700 cm<sup>-1</sup> to 1750 cm<sup>-1</sup> which indicates the absence of secondary oxidation products in the used engine oil sample. However, IR spectra for used engine oil showed peaks at 814.57, 1155.87 and 2726.89, 2923.70 cm<sup>-1</sup> which represent primary oxidized products at high temperatures. The used oil also shows that there are aldehyde components at 2726.89 cm<sup>-1</sup> and carboxylic acids at 814.57 and 1155.87 cm<sup>-1</sup> which are present in it. The carboxylic acids and aldehyde components are not desirable in the used oil because they form hydrogen bond to water molecule, thereby causing reaction of oil and water, and at room temperature they have the characteristic of causing the oil to have sharp or unpleasant odour (Boudreaux, 2012).

The IR results of Sludge A as shown in Figure 1 shows that there are no peaks between  $1700\text{ cm}^{-1}$  to  $1750\text{ cm}^{-1}$  which indicates the absence of secondary oxidation products in the sludge sample.

IR spectra for Sludge A showed peaks at  $1129.58$ ,  $1188.70$ ,  $1315.83$ ,  $1469.56$ ,  $1664.40$ ,  $2362.97$ ,  $2855.64$ ,  $2969.41$  and  $3443.28\text{ cm}^{-1}$  which represent primary oxidized products at high temperatures. The sludge sample also shows that there are aldehyde components at  $2855.64\text{ cm}^{-1}$  and carboxylic acids at  $1129.58$ ,  $1188.70$ ,  $1469.5$  and  $2362.97$ . Also peak at  $3443.28\text{ cm}^{-1}$  which shows presence of alcohols and phenols present in it. These are not desirable for sludge used for grease production because it can react to moisture content because of its solubility in water and also the presence of alcohols and phenols indicating fuel contamination (Abu-Ella *et al.*, 2015). If this sludge sample A is used for Grease production, high temperature antioxidant additive like phenyl alpha-naphtylamine (PANA), may be required to break the hydrocarbons for effective grease production (Rudnick, 2009).

The IR results of Sludge B as shown in Figure 1 also shows that there are no peaks between  $1700\text{ cm}^{-1}$  to  $1750\text{ cm}^{-1}$  which indicates the absence of secondary oxidation products in the sludge sample. IR spectra for Sludge B showed peaks at  $582.84$ ,  $1382.30$ ,  $2089.93$  and  $3446.68\text{ cm}^{-1}$  which represent primary oxidized products at high temperatures. The sludge sample shows the absence of aldehyde components and carboxylic acid which is desirable for thickener used in grease production. Sludge B proves to be the best sludge sample after sludge separation and pretreatment compared to the used engine oil sample, because it shows no aldehyde and carboxylic acid in the peaks.

### CONCLUSION

The Mixture solvent (B) has the maximum efficiency for sludge removal from used lubricating oil and its physical properties have been enhanced to a reasonable extent for efficient use in the production of grease.

### ABBREVIATIONS

AAS	=	Atomic absorption spectroscopy
ASTM	=	American Society for Testing and Materials
FTIR	=	Fourier transform Infrared
NLGI	=	National Lubricating Grease Institute
PSR	=	Percentage Sludge Removal
PANA	=	Phenyl Alpha-Naphtylamine

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