Analysis and Characterization of Waste Lubricating Grease Derived Oil

Motshumi Diphare and Edison Muzenda

***Abstract*—**As a result of the changes that occur during their use, used lubricants differ in chemical and physical composition from virgin oil. In general recycled oils have higher water and sediment compared to virgin oil and relatively higher concentrations of oxidation products and metals. This work was aimed at studying the differences between virgin and recycled oil using atomic absorption (AA), inductive couple plasma (ICP) and Fourier transform infrared radiation (FTIR).

***Keywords*—**Chemical Structure, Oil, Rheological Properties, Viscosity, Waste Grease

I. Introduction

UTILIZING used lubricants as an energy source was shown to be one of the best waste oil management technique [1]. Hence most countries are now focusing on recovering oil from waste lubricants. The characterization of the recovered oil is necessary to determine the level of contamination. The principal source of contamination during application is the chemical breakdown of additives and the subsequent interaction among the resultant components to produce corrosive acids and other undesired substances [2].

Oil characterization can be achieved using Fourier Transform Infrared (FTIR), Atomic Absorption Spectrometry (AAS), Karl Fischer Titration (KFT), Malvern Particle Analyser (MPA) as well as performing calorimetric and emission tests.

FTIR spectroscopy has found extensive use as an alternative technique to standard wet analytical techniques used to determine key oil quality parameters [3] and, more recently, lubricants [4]. In most cases the lubricating grease is subjected to severe and shearing stresses, which results in local degradation of the grease structure and the formation of new chemical species. As a result of the changes that occur during oxidation, oil derived from contaminated grease tend to differ in chemical and physical composition from the oil derived from fresh grease [5]. As lubricants are exposed to air at elevated temperatures, oxidation may take place during operation. As most of the additives have carbonyl groups, oxidation may lead to formation of carboxylic acids which then decrease oil pH and promote corrosion. Hence the degree of oxidation is a good measure of degradation [6]. FTIR spectroscopy can quantify organic chemicals and identify the chemical structure of the molecules under investigation. It is based on the principle that specific molecular functional groups absorb in unique regions of the mid-infrared spectrum, allowing identification of additives, contaminants, oxidation products and breakdown products [7].

Rheological properties of oils influence their application [8]. The rheological properties of lubricating oils and greases depend on the nature and concentration of its components and the microstructure resulting from its manufacturing process [9]. These include viscosity and its dependence on temperature, shear rate and shear stress. Couronn´e, et al, 2003 [10] studied the influence of the thermal degradation of lubricating greases focusing on the rheological and physicochemical characteristics. They showed that lithium based lubricating greases degrades at temperatures around 120 to 150^0C.

AAS can quantitatively determine the chemical elements through the absorption light radiation by free atoms in the gaseous state [11]. Samples such as oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products can be analysed for elements such as barium, chromium, cobalt, copper, lead, molybdenum, nickel silver, vanadium and zinc [12].

II. Materials and Methods

A. Materials

The contaminated high temperature metal bearing grease was supplied by Engine Petroleum (Pty) Ltd.

B. Methods

FTIR – Samples were prepared and placed into an appropriate sample holder. The spectra were obtained in a wave range of 0–4000 cm−1, at 4 cm−1 resolution, in the transmission mode.

ASS – 3g of oil sample was weighed accurately and diluted into a 50 ml flask. The samples for AA measurements were prepared by diluting the solution according to the metal species to be determined using xylene. All reagents used were of analytical grade.

Rheology - Rheological measurements were performed using a Paar Physica controlled stress and shear rheometer, Model UDS 200. Plate geometry was chosen for this study. A

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gap size of 50 µm was used for all measurements. For the study of the flow properties of WGDO, continuous shear and viscosity experiments were performed to study the flow properties of waste lubricating grease derived oil between 60 and 120^0C..

Karl Fischer Titration - Coulometry was used for oils due to their low water content [13]. The titration cell was filled with KF reagent (70 mL analyte plus 30 mL 1-decanol in the anode compartment). The cell contents were first titrated to dryness (conditioned) until a constant drift was achieved (typically <10 µg H_2O/min). A dry syringe was filled with approximately 0.5 to 1 g of sample and then injected into the titration cell.

III. Results and Discussions

FTIR was used to evaluate the chemical modification of waste grease derived oil after being exposed to oxygen at high temperature. Figs. 1 and 2 represent the spectra for fresh grease derived oil (FGDO) and waste grease derived oil (WGDO) respectively. The FGDO spectrum shows two strong absorption bands of long hydrocarbons chains. The first peak in the region of 1080-1375cm-1 represents the CH_3 bend while the second peak in the region of 2950-2800 cm-1 represents alkane C-H stretch. This suggests that the oil contains a very long hydrocarbon chain. The spectrum also showed several very weak absorption bands for additives in the regions of 600-1300 cm-1 and 1500-2000 cm-1.

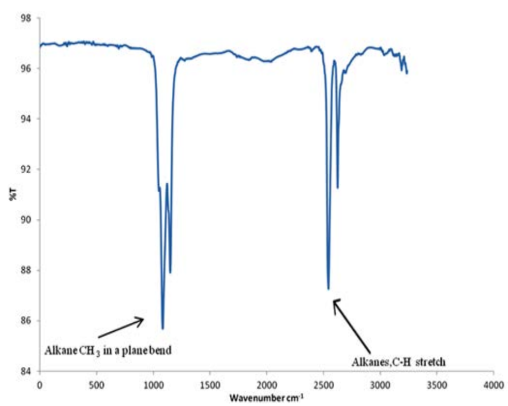

Fig. 1 FTIR spectrum of FGDO

Al-Ghouti et al, 2009 [7] reported that a spectrum band of 1716cm-1 indicated the presence of oxidation products in their characterization study of virgin and recycled used oil. Cann, 2006 [14] reported a similar observation for grease degradation in a bearing simulation device. The WGDO spectrum shows an intense (C=O) band at 1670-1725 cm-1, which is due to oxidation of the oil and small traces of the thickener. Rincon et al, 2007 [15] pointed out that the co-extraction of oxidation compounds together with base oil may be affected by the presence of oil additives in the WGDO. The interactions between oxidation products and additives complicate the separation of oxidation products from the oil.

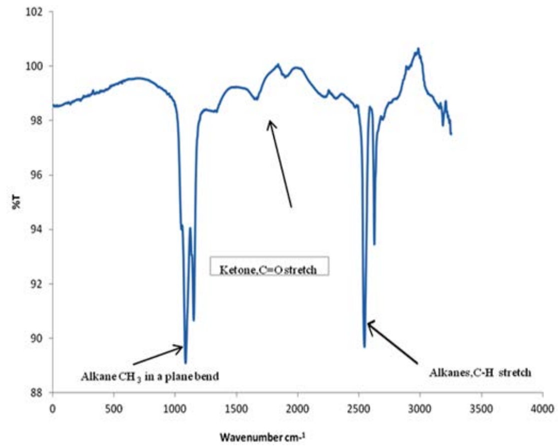

Fig. 2 FTIR spectrum of WGDO

AAS has an extremely good sensitivity in parts-per-million (ppm) range for many metals, a level of contamination that may occur in recycled oils.

Table 1 shows the elemental analysis for fresh lubricating oil (FLO), fresh grease derived oil (FGDO) and waste grease (Si), Aluminium (Al), Iron (Fe) and Nickel (Ni) confirmed mechanical wear and corrosion. The difference in the composition of FLO and FGDO is due to thickener and additives added during manufacturing process of grease. Ahmad et al, 2005 [16] showed that extraction using hydrocarbon solvents is very efficient in removing metal contaminants like iron, copper, nickel, calcium, magnesium and zinc compared to other techniques such as the clay process.

TABLE I
Elemental Analysis of Various Types of Oils

Metal	FLO (mg/L)	FGDO (mg/L)	WGDO (mg/L)
Cu	0.0001	0.0023	0.0560
Si	0.0010	0.0010	0.7560
Al	0.0001	0.0002	0.8230
Fe	0.0001	0.0001	0.9230
Ni	-	-	0.6100

In this work, the rheological behaviour WGDO was studied temperature and stress range [17]. During operation, shear stress / rate is applied to lubricants promoting the reorientation of fibres in the microstructural network resulting in shear-thinning flow [18].This keeps contacting surfaces separated by a lubricant at relatively high velocities.

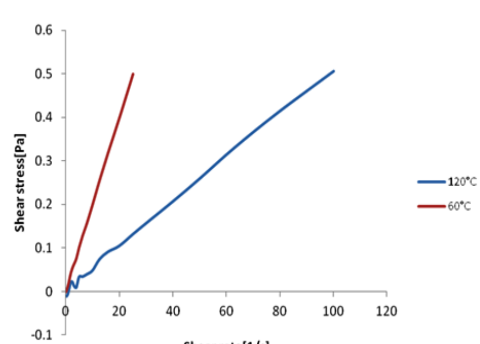

Fig. 3 Newtonian relationship between shear rate and shear stress

Fig. 3 shows a Newtonian behaviour for WGDO at temperatures between 60 and 120^{0}C. The viscosity of non-Newtonian fluids varies with time even at constant rate of shear [19]. Nik et al, 2005 [20] also report a similar trend with corn, canola and sunflower oils. At 60°C, the oil showed slight shear thinning.

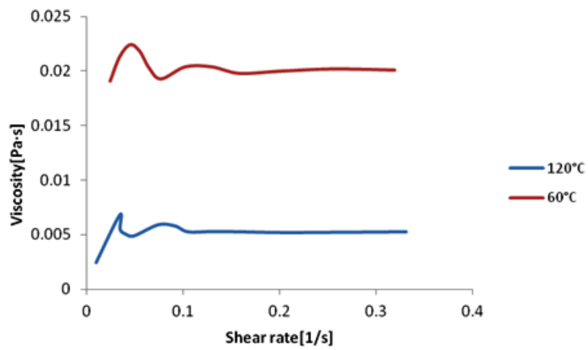

Fig. 4 Relationship between shear rate and viscosity

Fig. 4 shows the variation of the viscosity of WGDO with shear rate at two different temperatures. The oil viscosity slightly increased with increasing shear rate at temperatures between 60°C and 120°C. Similar observation was also reported by Al-Zahrani and Al-Fariss, 1998 [21] for waxy oils. Al-Zahrani, 1997 [22] reported that when shear is applied to the fluid, it breaks down the internal structure rapidly and reversibly. Reference 23 reported that the oil behaves as dilatant fluid around 120°C and as a Newtonian fluid at about 60°C.

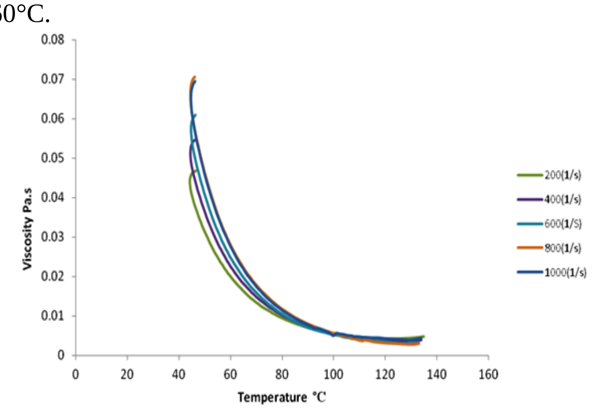

Fig. 5 Effect of temperature on viscosity

TABLE II
PROPERTIES OF WASTE GREASE DERIVED OIL COMPARED TO OTHER OILS

Fuel	Density @ 20°C	Calorific value	Sulphur	Moisture
Paraffin-oil	773 kg/m^3	43.1-46.2 MJ/kg	-	-
Diesel	800 kg/m^3	46.1 MJ/kg	500 ppm	0.05%
IFO	946 kg/m3	45.568MJ/kg	-	0.10%
WGDO	891kg/m^3	44.806 MJ/kg	4.23ppm	0.066%
FGDO	908kg/m^3	45.319 MJ/kg	3.77ppm	0.3488%

IFO = Industrial Furnace oil, WGDO = Waste grease derived oil, FGDO = Fresh grease derived oil

Fig. 5 shows that the variation of viscosity of WGDO with shear rate. The shear rate was varied from 200 to 1000 1/s, with a viscosity convergence at 100°C. The decrease in viscosity with temperature can be attributed to the presence of several polymers. Reference [23] also reported the same behaviour for SAE 20W-50.An increase in temperature increases molecular interchange and reduce attractive forces between molecules. However, in liquids, the reduction in attractive forces is much more significant than the increase in molecular interchange resulting in a decrease in viscosity with temperature [24].

The properties of paraffin oil, diesel and industrial furnace oil (IFO) in Table II were obtained from literature [25]. When compared to other fuels, WGDO can be used as an alternative fuel because of its calorific value and sulphur content of 44.806 MJ/kg and 4.23ppm respectively. The sulphur content is much lower than that of standard diesel which is at 500 ppm. Reference [25] also performed a similar comparative study with aim of using grease derived oil with a calorific value of 38.8 MJ/kg as second grade fuel for diesel oil.

The waste grease considered in this study can be used as second grade fuel for paraffin-oils, industrial furnace oil and grease oil. A major drawback with WGDO in diesel engines or in industrial blast furnaces is their high viscosity which causes poor fuel atomization and inefficient mixing with air in combustion chambers [26]. As WGDO is very viscous, blending with diesel can make it suitable for use as furnace oil. This is vital during high temperature and pressure atomisation in combustion chambers.

According to Murugan et. al, [27] high viscosity fuels atomise into larger droplets with higher momentum and are more likely to collide with the relatively cooler liner wall. This extinguishes the flame and increases the soot deposits and emission. The oil extracted from grease can be utilised as feedstock for grease manufacturing particularly lower grease product grades.

IV. CONCLUSION

Solvent extraction is not adequate for complete purification of waste grease derived oil. Physical and chemical analysis can be used to check the quality of the oil. Oxidation was observed to occur at a band length of 1716 cm-1while additives were identified at 1670 – 1725 cm-1.

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