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The Feasibility of Waste Workshop Oil for the Formulation Lubricating Grease with-Bio Thickener for Industrial Usage

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Abstract

Environmental concerns have prompted industry to seek alternate green options for lubricating grease formulation. The key problems in generating modified grease include taking into account the chosen thickener as an environmentally friendly material. According to studies, waste oil can be utilized as grease base oil; nevertheless, the variety of waste oil compositions at every disposal influence grease formulation. The current study's main objectives were to formulate lubricating grease utilizing waste motor oil as base oils and to investigate the influence of thickener on the formulated lubricant grease. The base oils were made from filtered and unfiltered waste motor oil obtained from a workshop., beeswax and natural molybdenum disulfide (MoS2) were used as thickener and additives. The grease's physiochemical characteristics were determined and compared to industry standards. The grease was evaluated for consistency, stability, and oil bleeding. Except for the grease containing unfiltered used oil, the prepared greases had a grease consistency of grade 2. Grease modification using an environmentally friendly thickening was successful, although it is regarded a low temperature grease due to the low melting point of beeswax (62°C-65°C).

Keywords: Physico-Chemical, Grease, Lubricant, Thickner, Additives

1.Introduction

Government legislation and increased consumer awareness are influencing the design process of lubricating grease to use more sustainable and ecologically friendly components [Sharma and Sing, 2017]. As a result of this scenario, a new industry revolving around eco-friendly items is fast forming, with consumers showing a higher proclivity to utilize new products and being prepared to pay for green products to protect the environment from bad impacts. Several investigations have been conducted on environmentally friendly lubricating grease using eco-friendly thickeners such as cellulose derivatives and beeswax [Nowak etal.,2019].

Grease is a semi-fluid product which comprises of a thickening agent along with other elements that provide the grease with special properties dispersed in a lubricating base oil. Base oils, thickeners, and additives typically have percentage compositions of 70-95%, 3-30%, and 0-10%, respectively. Many studies on eco-friendly grease have been conducted, with the majority of researchers using vegetable oil as the foundation oil [Madeshwara ,2022]. In contrast, there have been few investigations on thickeners. Thickeners are known to play an important function in grease composition, determining the consistency of the grease. Used oils are typically generated during engine service and maintenance, however they are frequently polluted with contaminants during usage and handling. Furthermore, used oils are frequently identified as a severe pollution concern as a result of irresponsible unlawful dumping and uncontrolled disposal, resulting in groundwater, surface water, and soil contamination [Nagendramma and Kumar,2015].

Used oils are generally generated during the engines service and maintenance however, it is often contaminated with impurities in the course of usage and handling. In addition, used oils often points outas a serious pollution problems due to irresponsible act of illegal dumping and unmanageable disposal resulting in groundwater, surface water and soil contamination[Nagendramma and Kumar,2015]. Thus, in this study, used oils were utilized as one of the base oils to prevent the aforementioned problems.

Beeswax is a natural substance collected from the honeycombs of bees after the honey has been extracted by the process of draining or centrifuging. It is one of the oldest and most significant items utilised by mankind. Beeswax is now used for over 300 different uses. Apart from being utilised by beekeepers, beeswax now finds many uses in cosmetics, pharmacy, food, and other industrial operations, with a global production of roughly 60,000 metric tonnes [Nuru, 2007]. As a result, the demand for beeswax is extremely high and has never been met. Because of its high demand and scarcity in the global market, beeswax adulteration with cheaper materials such as animal fats, plant oils, and petroleum spirits (paraffin wax) has become an issue for beeswax quality.

The fundamental function of beewax as a thickening is to keep lubricant from moving or leaking out due to gravity, and it is sometimes referred to as a sponge that holds the lubricants . Beeswax is a natural substance derived from bee honeycombs after the honey has been extracted by draining or centrifuging. It is insoluble in water, moderately soluble in alcohol, and very soluble in ether. Beeswax was employed as a thickener in grease compositions in this investigation, while natural MSO2 was used as an additive

The quality of beeswax is a prior and a determinant factor in its industial applications. The aplicability of beeswax can also be examined by using physicochemical parameters, such as melting point, density, acid value, Saponification value, ester value, and peroxide value . The physiochemical are commonly used to ascertain the beeswax quality and possible adulterations which are the melting point, Saponification value, acid value, ester value and ester to acid ratio were also tested and compared to standard values [Nuru ,207]. The values for the parameters vaaries in beeswax differ from country to country . These differences might be due to the point of origin of the beeswax because the environmental and geographical parameters also play an important role in the bees adaptation and, as a result, the beeswax Physiochemical properties .

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Lubricating grease reduces surface wear and tear by eliminating direct metal-to-metal contact between rubbing surfaces and lowers metal expansion [Nowak et al.,2019] . Lubricating grease reduces surface wear and tear by eliminating direct metal-to-metal contact between rubbing surfaces and decreases metal expansion owing to frictional heat and material destruction. Grease was made from motor oils and utilised oils, beeswax, and natural MSO2. This study was conducted to formulate grease using various types of base oils and to investigate the influence of thickener on the produced grease.

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2.Methodology:

Materials

Different types of base oils were used which are motor oils and used oils. . Used oil were collected from workshop was selected as alternative of base oils. Beeswax was chosen to act as a thickener. The Freshly harvested honey combs were bought from farmers in Abia state Local Government Area while natural MSO_2 was used as additive

Methods:

Preparation of Beewax

The physiochemical characteristics of the raw materials were determined using procedures detailed in an earlier article [Nuru,2007]. The honey comb was melted in hot water after mechanically removing the honey by hand-pressing it. The wax came to the surface and was scraped away. It was remelted, filtered to remove impurities, molded into the appropriate shape, allowed to dry or solidify for a period of approximately 30 days at room temperature, and then stored**.**

Determination Of Physiochemical Properties of Beewax

All parameters were determined using standard method .AOAC, (1990) method,.

Iodine Value

The Iodine Value (IV) was calculated from the equation

$$IV = \frac{(B - S) \times N \times 12.69}{w_o}$$

Where B = blank titre value,S = sample titre value,N = normality of sodium thiosulphate
w_o = weight of oil sample.

Refractive Index
The refractive index was determined using Abbe Refractometer.

Flash Point
The flash point of oil was obtained using the Pensky Martens flash point tester.

Peroxide Value
The peroxide value (PV) was calculated from the equation

$$Peroxide\ Value\ (PV) = \frac{(S - B) \times N \times (1000)}{w_o}$$

Where B = blank titre value,S = sample titre value,N = normality of sodium thiosulphate
w_o = weight of oil sample

Melting Point
A wax's melting point was the temperature at which it transitioned from a solid to a liquid form. The beeswax was melted by gently warming it in a water bath until it melted, and the melting points were calculated using either the capillary tube method or the drop point method. Melted beeswax was added to a 10 cm long, 2mm internal diameter thin-walled hollow capillary tube until it reached a height of around 1 cm. The beeswax-containing capillary tube was placed into a bath of water that was steadily warmed at 1-2°C/min; the temperature was verified with a thermometer (with an accuracy of 0.1°C) whose bulb had to be as close to the wax column introduced as feasible.

Saponification Value
The wax (2 g) was dissolved in hot toluene (910 ml). Alcoholic potassium hydroxide (25 ml of 0.5 M KOH) was added, and the solution is refluxed for 2 hours. A few dropsof phenolphthalein were added and the residual potassiumhydroxide was titrated with 0.5 M hydrochloric acid. A blankassay or titration was also performed with 25 ml of 0.5 Malcoholic potassium hydroxide plus toluene.

The saponification number was the number of milligrams of potassium hydroxide required to hydrolyze 1 g of wax and determination was made in triplicate. The saponification value,expressed as mg KOH/g, was calculated as follows,

$$SV = \frac{(B - S) \times N \times M}{w_o}$$

Where: B = volume in ml of the standard hydrochloric acid required for the blank,
S = volume in ml of standard hydrochloric acid requiredfor the wax,
N = normality of standard hydrochloric acid, andWo = mass in g of the wax taken for the test.

Acid Value
The acid value was determined as the number of milligrams of potassiumhydroxide needed to neutralize a gram of wax. This was done by by the titration of the wax solution in ethanol– toluene with 0.5 M potassium hydroxide.Blank was also titrated as a control for solvent acidity. Two drops phenolphthaleinwas added as the indicator. The acid value (inmg KOH/g) was calculated with the formula,

$$AV = \frac{TV \times N \times M}{w_o}$$

Where:
V = volume in ml of standard potassium hydroxidesolution used
N = normality of standard potassium hydroxide solution,Wo = mass in g of the wax taken for the test.

Ester Value
The ester value was calculated by subtracting the saponification value from the acid value, and the amount of potassium hydroxide utilised in the saponification of the esters was reported. Calculation : EsterValue = SaponificationValue – AcidValue

Ester to Acid Ratio

The ester to acid ratio or ratio number was the number obtained by dividing the ester value by the acid value. Calculation of result was determined as follows:

Ester to Acid ratio = Ester value/Acid Ratio

A; beehive with wax embedded B. Moulded bee wax C. natural MSO_2- additive

Figure 1: Bio-thickener and Natural additive for grease formulation

3. Technique

Preparation of grease samples

The base oil, bio-thickener(bees wax), and natural additive(MOS_2) ratios were fixed at 15:5:1 for the production of 210g of grease samples. In a 500-mL beaker, 50g of beeswax was slurried with half the amount of base oil (80g) at a continuous stirring rate. The speed of the mixer was varied according to the viscosity of the paste, and mixing was continued for each sample until a smooth paste was formed at a constant temperature of 50°C-60°C. The remaining half of the base oil and natural molybdenum disulfide (MoS2) (10g) were progressively added to the paste, and the process was repeated until all of the components blended together. In compliance with the guidelines, the samples for each formed grease were as follows

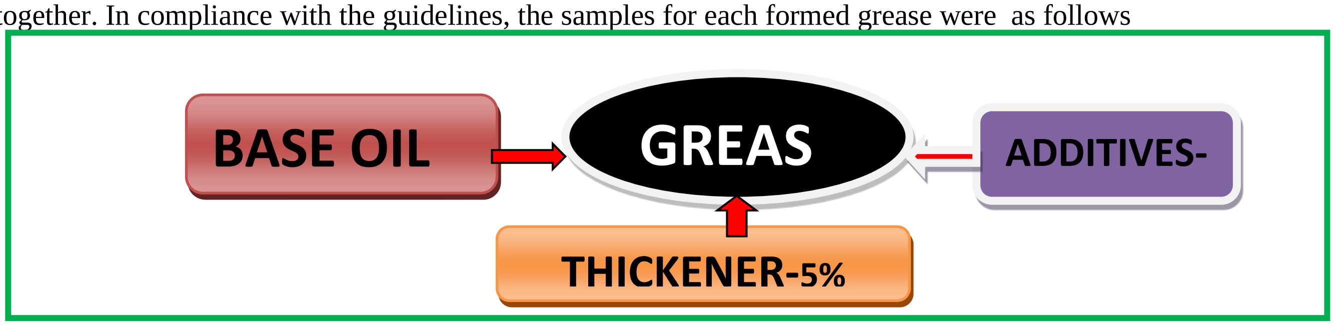


Figure 2 - Grease – formulation

Table 1. Grease samples identification

Type of base oil identification	Sample
Unfiltered- Motor oil	**U MO**
Filtered -Motor oil	**F M O**

The tests was carried out using the SKF Grease Test Kit TGKT 1. A measured volume of grease volume was spread between 2 glass plates for 15 seconds. The consistency of thegrease strain was evaluated using calibrated measuring scale- NLGI grade. The test method was in accordance with ISO 2137 which is the standard methods for determining the consistency of lubricatinggreases when small samples are available. The results of the NLGI for each grease shows their consistency level [SKF,2009].

Table 2. NLGI classification system based on consistency (ASTM D217-17 2017)

NLGI Number	Worked Penetration, tenth of millimeter	Consistency
000	445-475	Very soft
00	400-430	soft
0	355-385	Soft
1	310-340	Soft
2	265-295	Creamy texture (buttery)
3	220-250	Semi-solid
4	175-205	Stiff
5	130-160	Stiff
6	85-115	Hard solid

Ester/Acid Ratio

The ratio of ester values to acids, a criterion, determines if prolonged or excessive heating changes natural beeswax significantly beyond the limitations set for pure beeswax. The eater to acid ratio of the beeswax samples purchased was 80.8, compared to the standard value of 4.4.

Acid value (mgKOH/g)

The acid value is the number of milligrammes of KOH required to neutralise the free acidity in one gramme of bees wax. It is a relative rancidity measure because free acidity is generally produced with the degradation of beeswax glycerides. The acid value of the obtained samples is 0.85 in comparison to the standard value of 24mgKOH/g. This could be related to the impact of agro-ecology on the acidity of beeswax.

Ester Value (mgKOH/g)

The difference between saponification value and acid value, which represent the quantity of KOH consumed during ester saponification, determines the ester value of beeswax, and the result must meet regulatory limits to demonstrate the absence of contamination. The ester value of the beeswax purchased was 68, according to the test results.

Saponification value (mgKOH/g)

The saponification value (number) is the amount of saponifiable matter contained as the number of milligrammes potassium hydroxide required to hydrolyze 1 g of the sample. The saponification value of beeswax reveals the number of acids and ester groups present. The current investigation found an acid value of 69.5 versus the usual value of 105.

Developed Lubricant grease consistency

The results of the testing on each grease sample in accordance with the NLGI consistency grade (Table 2). This grades determines the consistency /appearance of grease at 25°C. Grease with NLGI Grade 2 is appropriate for moderate loaded, medium industrial applications. Grease of this consistency is developed to provide the needed qualities for smooth pumping through a dispensing devices.

When comparing the UMO-based grease to the other samples, a significant difference in consistency was seen in the UMO-based grease, which is of NLGI grade 00 .When UMO-based grease and FMO-based grease are compared, FMO-based grease is created with filtered spent oil. pollutants in unfiltered MOTOR oil (UMO) may impact grease consistency, hence most of these pollutants are eliminated before being employed in FMO-based grease formulation. As a result, it was concluded that increasing the oil-to-thickener ratio can increase the consistency of UMO-based grease [Lught, 2013].

Grease *Stability test*

The test was carried out in line with the Standard Test Method for Oil Separation for Lubricating Grease during Storage (ASTM-D1742).the two grease samples were stored in a closed container and the initial level of the grease is observed and recorded. The samples were left for 2 month room temperature. The amount of oil separated was measured and weighed. the lesser the oil separated, the better the stability/quality of the formulated grease. The sample is considered stable if the amount of the oil separated is less than 4% [Franco, 2015].

Oil bleeding test

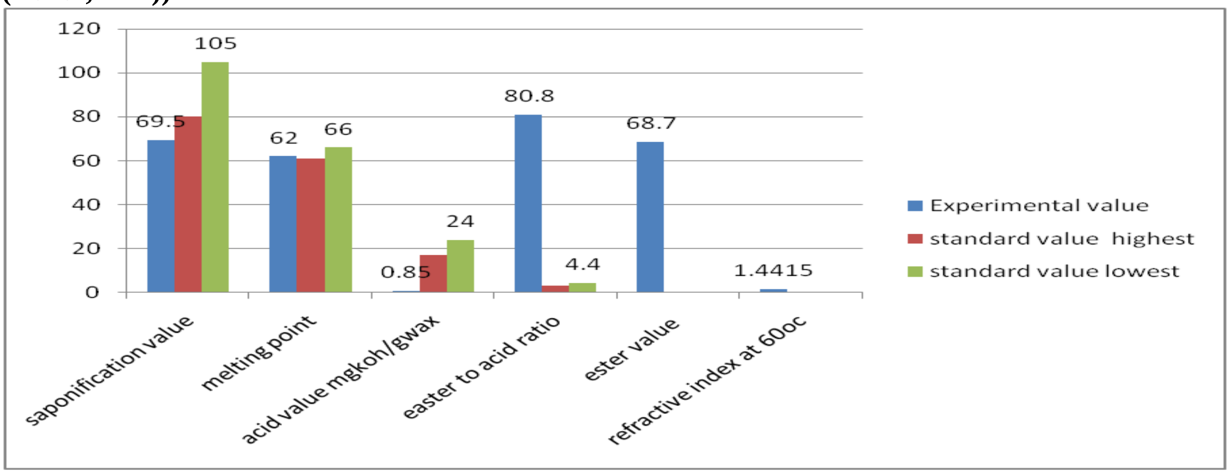
The tests on the sample was performed using SKF Grease Test Kit TGKT 1. A fixed amount of grease was put on a blotter paper . The samples was heated for 3 hours at 60°C fixed temperature according to the operating condition of the test kit [Sharma and Sing,2019]. Thebase oil released from the grease created a stained on the paper. The bleed area and the percentage difference between bleed area of fresh and used samples were calculated by using equation (1) and (2).

$$\text{Bleed}_{\text{Avfresh}} = 0.785 \times (D^2 - 100) \quad (1)$$

$$\%\text{Diff} = 100 \times S_{used} - S_{fresh} / S_{fresh} \quad (2)$$

4. Results and discussion

Figure 3 . Physiochemical properties of Beeswax in comparison to standard value (Nuru ,2007))



The physiochemical properties of beewax is represented above with the peroxide value 70 M.eq.peroxide /kg wax , saponificatio value 69.5 and acid value of 0.85 –mgkoh/gwax with the ester value of 68.7.

Ester to Acid Ratio

The ratio of ester values to acids, a parameter determines whether natural beeswax is changed significantly by prolonged or excessive heating beyond the limits set for pure beeswax. The eater to acid ratio of beeswax samples bought were 80.8 compared to 4.4 stndard value.

Acid Value (mgKOH/g)

The acid value is the amount of KOH milligrams required toneutralize the free acidity present in one gram of bees wax. It is a relative measure of rancidity as free acidity is normally formed during decomposition of beeswax glycerides. The acid value of thecollected samples reveals 0.85 acid value compared to the standard value of 24mgKOH/g This might be due to the influence of agro-ecology over the acid value of beeswax.

Ester Value (mgKOH/g)

The ester value of beeswax determined by the difference between saponification value and acid value which indicate the amount of KOH consumed during saponification of estersand the result must met standard limit to show absence of contamination. The result of ester value examined for the beeswax bought shows an ester value of 68.

Saponification Value (mgKOH/g)

The saponification value (number) is the number of milligrams potassium hydroxide required to hydrolyze 1 g of the sample and is measure the amount of saponifiable matter present. Testing saponification value indicates the number of acids and ester group found in beeswax. The present study indicated the acid value of 69.5 compared to the standard value of 105.

(A)Unfiltered motor oil grease (B) filtered motor oil grease

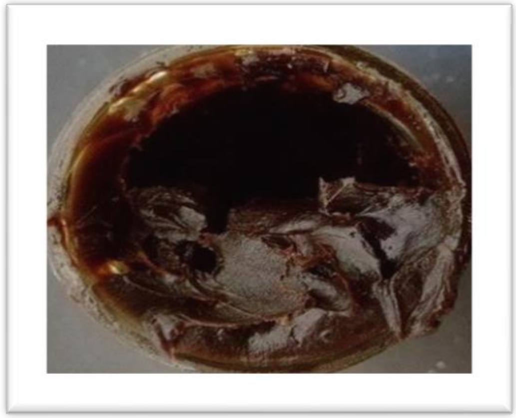


Figure 4: Produced grease appearances

The formulated grease samples prepared were semi-solid and their color depend on the color of base oil which vary from brown yellow to black as in Figure 1. The properties of modified greases are explained below..

Formulated lubricant grease consistency(SKF, 2009)

The outcomes of testing done on grease samples in accordance to the NLGI consistency grade (Table 2). The grades shows the consistency of the greases at 25°C. Grease with NLGI Grade 2 were good for rolling bearings moderately loaded with medium speed usage. Grease of this consistency are formulated f good balance of properties for easy pumping in dispensing systems . Also, most of the multipurpose grease are of this grade of NLGI 2-3 consistency.

Table 3. Consistency of formulated grease.

Sample	NLGI	Consistency
UMO	00	Semifluid
FMO	2	Buttery

UMO-based grease shows consistency of NLGI grade 00. UMO-based grease is softer than the FMO formulated greases. By comparing UMO-based grease and FMO-based grease, FMO-based grease WHICH isformulated with filtered motor oil. The presence of contaminants in the unfiltered motor oil (UWO) might be what affects the grease consistence in which majority of the contaminants was removed before usein FMO-based grease production . Therefore, it was deduced that the UMO-based grease consistencycan be increased by reducing the oil-to-thickener ratio [Nowak etal., 2019].

Oil separation in storage

Greases will tends to release their base oils in storage which is called static oil bleeding. Static grease bleeding can be affectedby storage conditions and is more pronounced if the grease is soft in consistency (NLGI grades 00, 0 and 1) [Syahir etal.,2017]. Grease Oil separation often relates to its base oil and thickener used in combination with the kinematic viscosity of the base oil [21]. The two grease samples were stored in room temperature for 55 days and wereobserved for any changes of the properties. Table 4 shows results for oil separation occurring in toUMO-based grease.

Table 4. Grease oil separation upon storage at 25ºC.

Sample	Oil separated (g)	% losss	Description
UMO	16.20	8.10	Unstable
FMO	-	-	Stable

The UMO-based grease was discovered to be unstable, with more than 4% oil separation. Contaminants in unfiltered used oil can suck base oils out of the thickening system over time . The oil pool on top of the grease, on the other hand, does not render the grease unfit for use. It can be eliminated by either decanting the free oil from the surface or swirling it back into the grease.

Other than UMO-based grease, prepared grease has demonstrated excellent oil separation resistance. The base oil and thickening agent used appear to have strong physically acting bond forces that produce a stable three-dimensional network structure based on the appearance of the FMO grease samples [Rizvi,1996]. Interestingly,filtered used oil-base grease (FMO) has comparable oil separation to fresh motor oil-base grease. This could be due to the pre-treatment of used oil, such as settling, filtration, and dehydration, which removed the majority of the pollutants in the used oil.

The Produced Grease Oil Bleeding analysis

Due to the tendency of softer greases to sweep away during the test, this test method is not suitable for greases softer than NLGI grade 1 consistency. As a result, the testing was inapplicable to UMO-based grease of grade 00. A comparison of grease leaked between fresh and used samples was done. The percentage difference in bleed area (%Diff) between the used and fresh samples was calculated to indicate either the lubricating ability of the grease. Positive results indicate that the grease lubricating ability has improved or vice versa.

According to the data in table 5, the two greases' lubricating ability was reduced. When exposed to high temperatures, FMO-based grease loses its lubricating properties, causing these greases to harden over time. The rate of oil release from the grease increases with time and varies with storage temperature [Lught,2016]. The formulated greases were found to have a low operating temperature range, as specified that the dropping-point temperature of the beeswax-thicken greases was between 52oC and 66oC. The developed grease's high temperature endurance, on the other hand, can be improved by adding the appropriate addition to boost its dropping point temperature qualities.

Table 5. Oil bleeding test at 60ºC.

Sample	DAV fresh (mm)	DAV used (mm)	SFresh (mm^2/s)	SUsed (mm^2/s)	%Diff
UMO	N/A	N/A	N/A	N/A	N/A
FMO	35.50	34.01	910.79	828.91	-8.97

Table 6 displays the results of the tests performed on each of the grease samples. The consistency test, stability test, and oil bleeding test were all performed. To determine the NLGI consistency grade for grease samples, consistency tests were performed. Any changes in grease samples were analysed after 2 months of storage at room temperature in the stability test. Oil bleeding tests were performed for two hours at a constant temperature of 60°C, in which the base oil released from the grease of fresh and used samples caused oil stains on the paper. The diameter of the stained area as well as the bleeding qualities were measured.

Table 6. Overall results of formulated lubricant grease analysis.

Sample	Color	Texture	NLGI	Stability	bleed @ 25ºC
UMO	Black	Semifluid	00	Unstable with 8% oil	Not applicable
FMO	Dark brown	Buttery	2	Stable	-8.98

Conclusion

Beeswax-thickened greases have the potential to be environmentally friendly. According to the results, the majority of the formulated grease were successfully formulated using beeswax as a thickening with an NLGI consistency range of grade 2.This grease can be used as bicycle grease and general purpose bearing grease. While grease with NLGI of grade 00 will be used in gear boxes at low temperatures. However, these greases are not intended to be subjected to high temperatures because they lose their lubricating ability and harden when exposed to high temperatures over an extended length of time.

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