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Effect of copper (II) oxide nanoparticle enrichment on the chemo-physical properties of sandbox bio-lubricant

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ABSTRACT

The service life and efficiency of the machine depend on the performance and quality of the lubricating oils. Lubricants quality also plays an important role in reduction of fuel consumption. Addition of nanoparticles to the lubricants can improve the properties of the oils due to their very high surface area which made them to be extremely reactive.This study investigated effect of copper (II) oxide nanoparticle additive on chemo-physical properties of bio-lubricant produced from sandbox seed oil. The nanoparticle enriched bio-lubricantwas developed by adding varying concentrations of copper (II) oxide nanoparticle to the sandbox oil. American Society for Testing and Materials (ASTM) standards was used to analyze the chemo-physical properties of the bio-lubricant. The results indicated that thekinematic viscosities of the copper (II) oxide nanoparticle-enriched bio-lubricant at 40^{o}C and 100^{o}C, free fatty acid, acid values and iodine values are higher than that of ordinary sandbox bio-lubricant without nanoparticle. Saponification value, viscosity index, cloud point, flash and fire points of the nanoparticle-enriched bio-lubricant are lower compared to that without nanoparticle. FTIR analysis also revealed that the molecular structure of sandbox oil was not damaged by addition of copper (II) oxide nanoparticle. The obtained results are conformed to the Society of Automotive Engineers standards. The study revealed that the added copper (II) oxide nanoparticle improved the chemo-physical properties of the bio-lubricant produced for better lubricating performance in the automotive engines.

Keywords: Nanoparticle, copper (II) oxide, bio-lubricant, chemo-physical, sandbox.

I. INTRODUCTION

Bio-lubricants are becoming an important alternative to mineral oil based lubricants due to improvement in awareness of environmental pollution caused by mineral lubricants. They possess better properties like renewability, environmental friendliness, biodegradability, non-toxicity, excellent lubricity, high fire point and flash point, high viscosity index, low volatility and low vapour emissions [1]. Vegetable oils are nowadays considered as viable bio-resource and promising candidates for the development of bio-based lubricants because they have some basic chemo-physical properties which make them suitable to be used for lubricant production. According to [2], vegetable oil based lubricants are becoming more attractive everyday due to their environmental benefits. The increase in demand for more non-edible oils from vegetable sources to complement others has led to employing sandbox seed oil as alternative raw material for lubricant production. Sandbox seed oil is highly neglected non-edible oil available at little or no cost of purchase. Reference [3] reported that it has no specific use and no commercial value presently, as the seeds are discarded as waste. Sandbox oil is a promising alternative oil because it is environmentally friendly, renewable, cheap, and easily manageable [4]. It contains high content of unsaturated fatty acid such as oleic acid. Oleic acid has been proved as the most ideal monounsaturated fatty acid for bio-lubricant. This makes the oil suitable for bio-lubricant production because of presence of double bond will lower the melting point, which would enhance the low temperature performance of the bio-lubricants.

The base oil alone rarely meets all the requirements of the lubricant, and is therefore enriched with additives to provide the properties required in a lubricant operation for desired effectiveness and comply with the specifications in terms of viscosity, friction, ageing, oxidation, foaming etc.

Lubricant additives are materials added to lubricants to effect changes in their chemical and physical properties. They are chemical components or blends that provide one or more functions in the fluid at a specific treat rate, generally from 0.1 – 35%. The basic roles of lubricants additives according to [5] are to reduce wear of the engine parts exposed to very high pressure, and reduce or eliminate internal rust and corrosion. Reference [6] reported that additives often improve existing properties, suppress undesirable properties, and introduce new properties to the base oils. The compatibility of additives in lubricant is important in the lubricant selection. Compatible additives should have their individual properties supportive in a lubricant's performance.

Nanoparticles are emerging lubricant additives with wear and friction reduction potentials. Reference [7] observed that the lubricating behaviour of nanoparticles depends on their concentration, shape and size. There are many reasons for the motivation of using nanoparticles as lubricant additives. The most important advantage according to [8] is their teeny sizes that empower the nanoparticles to enter the cavities of contact area, which result in the positive lubrication effect. Nanoparticle additives can easily mix with lubricating oil due to its mini-scale size to enhance the lubricating properties of the oil [9].They provide large surface area to improve interaction with the surface material of friction pairs forming a protective film due to their high surface area to volume ratio, thereby reducing wear and friction [10].

Copper (II) oxide (CuO) nanoparticle has been observed by [11] to have potentials as anti-wear additives in a chemically modified rapeseed oil tested in high frequency reciprocating rig (HFRR) under boundary lubrication conditions. Reference [12]also reported copper (II) oxidenanoparticle to be insusceptible to oxidation which makes them to be effective high temperature additive. Reference [13] evaluated the tribological characteristics of lubricant from coconut oil using copper (II) oxide nanoparticle as additive and their results show that optimum concentration of the nanoparticle in the lubricant reduces the pin surface roughness to a low value after sliding. As the quantity of the nanoparticle increases beyond the optimum level, wear rate as well as coefficient of friction increased.Reference [14] studied the tribological and thermo-physical properties of bio-based copper (II) oxide nano-lubricant which contains surfactant at elevated temperatures and observed that improvement in the properties like viscosity and fire point is more obvious for nano-lubricant with surfactant-modified copper (II) oxide nanoparticle than the corresponding nano-lubricant with unmodified copper (II) oxide nanoparticle. Reference [15]reported the tribological evaluation of copper (II) oxide nanoparticle additivesand observed that the nanoparticle achieved maximal friction and wear reductions in the test conditions. Reference [16]also reported that copper (II) oxide nanoparticle has potentials as anti-wear additives in the chemically modified rapeseed oil.

The main effects provided by nanoparticle-enriched lubricant as listed by [8] are: ball bearing effect between the contact surfaces, protective film to prevent friction and coating the rough surface, polishing effect and mending effect.Generally, majority of the studies agreed that the nanoparticles improved the chemo-physical properties of lubricants. They can significantly improve the wear-reduction capability, friction-reducing property and pure oil load carrying capacity [17]. They provide large surface area to improve interaction with the surface material of friction pairs forming a protective film due to their high surface area to volume ratio, thereby reducing wear and friction [10]. Nanoparticles also provide a repairing effect by filling the surface roughness points and forming a thin physical tribofilm during the frictional process to divide the rubbing faces. This study investigated the effect of copper (II) oxide nanoparticle enrichment on chemo-physical properties of sandbox bio-lubricant.

1.1 Chemo-physical Properties of Lubricant

Chemo-physical properties of lubricant that are important to lubricity, according to [8], include: viscosity, viscosity index, density, specific gravity, acid value, iodine value, saponification value, cloud point, pour point, flash point and fire point.

1.1.1 Viscosity

Kinematic viscosity is defined as the resistance of liquid to flow [18]. It is described as the thickness of oil obtained by measuring the amount of time taken for a given oil to pass through an opening of a specified size. Viscosity influences the capacity of the lubricant to separate contacting areas in relative motion within the operating pressure and temperature. An ideal lubricant for most purpose is one that has a constant viscosity entirely when there is change in temperature.

1.1.2 Viscosity index

Viscosity index is a very important lubricity propertywhich shows how lubricants behave when temperature changes and relates the kinematic viscosity of the lubricant to that of two reference lubricants with known viscosity sensitivity to temperature[19].Bio-lubricants with a high viscosity index will have minimal changes in viscosity at higher temperature. Reference [20] reported that lubricants with high viscosity index will remain stable and not varies much in viscosity over the temperature range which allows for consistent in the performance of engine within the standard working conditions. The viscosity index can be calculated using this formula:

$$\mathrm{VI} = \frac{\mathrm{L-U}}{\mathrm{L-H}} \mathrm{x}\, 100$$

Where:
VI = Viscosity index
U = Oil’s kinematic viscosity at 40^{o}C
L = Values of kinematic viscosity at 40^{o}C for oils of lowest viscosity index (0)
H = Values of kinematic viscosity at 100^{o}C for oils of high viscosity index (100)

1.1.3 Density and specific gravity

Reference [21] described density as a property used to determine the exact fuel volume necessary to supply adequate combustion. It is the mass of a lubricant per its unit volume. Bio-lubricant has high density and less compressible than petroleum based lubricant regardless of the feedstock. Specific gravity is defined by [11]as the mass of certain lubricant volume at a certain temperature divided by the mass of equal volume of laboratory distilled water at another temperature.

1.1.4 Flash and fire points

Flash and fire points show the volatility, fire resistance and maximum temperature up to which lubricant can be used, thereby help in safety and shipping classification of a material. Flash point is the minimum temperature at which lubricant gives sufficient vapours to ignite momentarily when a flame of standard dimension brought near the surface of the lubricant for a prescribed rate in apparatus of specified dimension [22]. In other words, it is the temperature at which oil gives off enough vapour which ignites when exposed to flame or a spark. Flash point measures the readiness of the oil to ignite momentarily in air and varies inversely with the volatility of fuel. It is used in safety and shipping classification of a material. Bio-lubricants generally have higher flash points in comparison with petroleum based lubricant as reported by [23]. This shows that bio-lubricant is safe for transport, handling and storage purpose. Reference [24] described fire point of a lubricantas the lowest temperature at which sufficient vapour is produced continuously for burning after ignition for at least 5 seconds. The fire point is generally 5 - 10^{o}C higher than the flash point. Good lubricants should have fire and flash points above its operating temperature.

1.1.5 Cloud and pour points

Refernce [22] described cloud point as temperature at which crystallization of solid occur in the form of cloud when oil is cooled. It expresses low temperature stability of lubricant. At this temperature, mixture start to separate into two phases and wax precipitation is visible in the lowest part of the container. Pour point is one of most critical properties which determine the performance of lubricants. It indicates the suitability of oils in cold condition. It is that temperature at which the oil ceases to flow after cooling. Oil used in engine working at low temperature should have low pour point; otherwise it will make the engine to jam. The cloud and pour points of bio-lubricant varies significantly with feedstock depending on fatty acid compositions.

II. MATERIALS AND METHOD

2.1 Materials and Equipment

The materials and reagents used in this research included: sandbox (Hura crepitans)oil, methanol, potassium hydroxide, trimethylolpropane (TMP), oleic acid (OA), copper (II) oxide (CuO) nanoparticle, conventional lubricant SAE 40 and Anton Paar ball-on-disc tribometer (model TRN)**.**

2.2 Methods

This study involved materials collection and preparation, production of copper (II) oxide nanoparticle enriched bio-lubricant, and characterization of the nanoparticle-enriched sandbox bio-lubricant.

2.2.1 Materials collection and preparation

Sandbox (Hura crepitans)seeds were collected in Wukari town, Taraba State while commercially available copper (II) oxide nanoparticle and other chemicals were obtained from Bristol Scientific Company Ltd, Lagos. The nanoparticle used was produced by M/S Sigma-Aldrich, USA. The seeds were cleaned, manually dehulled and milled using milling machine. The oil was extracted in a Soxhlet extractor by solvent extraction. After the extraction, the oil was recovered from the mixture by evaporating the residual extracting solvent in an oven set at 50^{o}C and then stored in bottles.

2.2.2 Production of copper (II) oxide nanoparticle enriched bio-lubricant

Copper (II) oxide nanoparticle-enriched bio-lubricant was produced in accordance with the method described by [19], using sandbox oil as base oil. A double transesterification process; methyl ester synthesis and bio-lubricant synthesis, was involved. In the first transesterification, methyl ester of the oil was produced by mixing the oil sample with methanol using potassium hydroxide as catalyst. The ratio of weight of the oil – methanol was 3:1 and potassium hydroxide of 0.5% w/w of the oil was used. During the second transesterification, bio-lubricant synthesis was achieved by adding trimethylolpropane (TMP) to the sandbox methyl ester to produce the desired bio-lubricant. The copper (II) oxide (CuO) nanoparticle used as additive was added in different concentrations of 0.75 wt% and 1.50 wt% to the bio-lubricant. In order to prevent agglomeration during dispersion process and improve the dispersion stability of the nanoparticle oleic acid was added to bio-lubricant. The bio-lubricants were coded as:**SB10** (Sandbox oil),**SBL10**(Sandbox bio-lubricant), **SBCuO10** (Sandbox oil + 0.75 wt% CuO)and **SBCuO15**(Sandbox oil + 1.5 wt% CuO).

2.3 Characterization of the Bio-lubricant

The chemo-physical properties of the sandbox oil and nanoparticle-enriched bio-lubricant produced were determined using standard methods.

2.3.1 Fourier transform infrared (FTIR) analysis

FITR analysis of the oil and bio-lubricant was done to determine the functional groups present in them and its degradation was analyzed in accordance with the method adopted by [25] using PerkinElmer Spectrum 400 FTIR spectroscopy instrument with a data acquisition system. The bio-lubricant samples were placed between the infrared source and detector. These infrared radiations are required to pass through the lubricant samples to be transmitted and provide corresponding spectra. The transmittance spectra for bio-lubricant samples were analyzed for functional groups and related peaks were determined. A background spectrum was obtained as reference before FTIR measurements was conducted. The crystal surface was cleaned and properly installed before obtaining the background spectrum. The spectra were obtained over a spectral range of 650 - 4000 cm^{-1} at 8 cm^{-1} spectral resolution. The transmittance spectra mode was chosen for data analysis.

2.3.2Dispersion stability analysis

Dispersion stability analysis of the nanoparticle in the bio-lubricant was done in accordance with [16] by measuring the optical absorbance spectrum with the aid of T60U Ultra-Violet (UV) visible spectrophotometer. The spectrophotometer has wavelength accuracy of ± 2 nm and a repeatability of 1 nm. The bio-lubricants were examined for dispersion stability of the nanoparticle in the oil using 500 nm wavelength. The samples were place in glass cuvettes and blank sandbox oil was used as a reference solution. The cuvettes were placed in the spectrophotometer and the dispersion stability test was carried out. The dispersion stability test lasted for two weeks (336 hours). The absorbance level of visible light was measured using visible spectroscopy over different time intervals. The rate at which changes in the absorbance level of visible light was recorded to measure the dispersive capability of the samples.

2.3.3 Determination of density and specific gravity

Density and specific gravity were determined in accordance with [26]. Bio-lubricant of 5 ml was poured into a weighed beaker and weighed. The density was determined from the sample weight by using the ratio of weight of the bio-lubricant to the known volume (5 ml) and specific gravity using equations (1) and (2) respectively.

$$\text{Density} = \frac{m}{v} \qquad (1)$$

$$\text{Specificgravity} = \frac{A}{B} \qquad (2)$$

Where

m = sample mass (g)
A = Weight of a unit volume of the oil (kg)
B = Weight of equal volume of water (kg)
v = sample volume (cm^{3})

2.3.4 Determination of refractive index

The degree of refraction of a beam of light that occurs when it passes from one transparent medium to another known as refractive index was determined in accordance with [27]. Digital Abbe's refractometer Model DRA-1 was used for the measurement of the lubricant's refractive index. The oil was smeared on the lower position of the refractometer, after some adjustment, the refractive index was read directly at room temperature (25^{o}C).

2.3.5 Determination of saponification value

Saponification value of the bio-lubricant was determined in accordance with [28]. Bio-lubricant of 10g was weighed into 250ml conical flask. Potassium hydroxide solution of 25 ml was added using pipette. The flask content was thoroughly stirred and then connected to reflux condenser to boil for one hour for complete saponification. The cooled content was titrated with hydrochloric acid of 0.5M using phenolphthalein indicator. The value was calculated using:

$$\text{SAPvalue} = \frac{56.1\,(B-S)N}{W} \quad (3)$$

Where
B = Titre value of hydrochloric acid used for the blank (cm^3)
S = Titre value of hydrochloric acid used for the sample
W = Sample weight (kg)

2.3.6 Determination of iodine value

Reference [29] method was used to analyze iodine value of the bio-lubricantsby dissolving 0.1g of oil in 15ml of carbon tetrachloride and stirring. The solution was mixed with 25ml Wij's solution and stayed in the dark at room temperature for 30 minutes. Distilled water of 100ml and 20ml of 10% (w/v) of potassium iodide were then added to the mixture. This was later titrated with 0.1ml sodium thiosulphate using 10% (w/v) starch indicator. The titration continued until light blue colour was observed. The iodine value was calculated using equation (4).

$$\text{Iodinevalue} = \frac{12.69(B-S)N}{W} \quad (4)$$

Where:
B = Titre value of sodium thiosulphate used for blank
S = Titre value of sodium thiosulphate used for sample
N = Normality of sodium thiosulphate
W = Sample weight (kg)

2.3.7 Determination of acid value

Reference [30] method was used to determine the acid value of the bio-lubricant. Bio-lubricant of 1g was weighed into 25ml of isopropyl alcohol in a 250ml conical flask. The solution was titrated using 0.1M potassium hydroxide (KOH) and 3 drops of phenolphthalein was added with constant stirring until a persistent colour appeared. The titre value obtained was used to calculate the acid value using the equation (5) given by [19].

$$\text{Acidvalue} = \frac{56.1\ VN}{W} \quad (5)$$

Where
V = Titre value of potassium hydroxide used (cm^3)
N = Normality of potassium hydroxide
W = Sample weight (kg)

2.3.8 Determination of free fatty acid (FFA)

Free fatty acid is the value of specified fatty acid in oil. Itwas analyzed using [29] method. Bio-lubricant of 5g was weighed into 100 ml of hot neutralized ethanol and 3 drops phenolphthalein indicator was added and titrated with 0.1M sodium hydroxide. Free fatty acid was calculated using equation (6).

$$\text{FFAvalue} = \frac{28.05\ VN}{W} \quad (6)$$

Where
V = Titre value of sodium hydroxide used (cm^3)
N = Normality of sodium hydroxide
W = Sample weight (kg)

2.3.9 Determination of kinematic viscosity and viscosity index

Kinematic viscosity was determined in accordance with [31] method using Smart series rotational viscometer TSML 21105. The viscosity was measured at three different temperatures 28°C, 40°C and 100°C. At a start a proper viscometer spindle was chosen. The samples were transferred to a beaker large enough to hold the viscometer spindle. The beaker was placed on a heating mantle set to a desired temperature, while the temperature of the samples was raised. The viscosity was read at the desired temperature. The spindle was joined to the upper coupling by holding the coupling between the forefinger and thumb while the spindle was cautiously rotating counter-clockwisely. The knob was set to the minimum speed. The spindle was immersed into the sample up to the middle of the identification in the shaft. The viscometer was turned on and allowed to run until a constant reading (usually 5 to 10 revolutions) was attained. The viscosity of the bio-lubricants was determined using equation (7) reported by [24]:

$$\text{Viscosity} = \text{readingobtainedx}\,\frac{\text{factorforthespindle}}{\text{speed}} \quad (7)$$

The viscosity index which is used to measure change in the viscosity with variation in temperature was measured in accordance with [32].This method used the lubricant's kinematic viscosities at 40°C and 100°C. The temperature of oil sample was raised to the desired level by heating the oil with constant stirring using a heating mantle. Equation (8) was used for the calculation of viscosity index values for the bio-lubricants.

$$\text{ViscosityIndex} = \frac{L-U}{L-H} \times 100 \qquad (8)$$

Where:
U = Oil's kinematic viscosity at 40°C
L = Values of kinematic viscosity at 40°C for oils of lowest viscosity index (0)
H = Values of kinematic viscosity at 100°C for oils of high viscosity index (100)

2.3.10 Determination pour and cloud points

Pour and cloud points were determined in accordance with [33]. The lubricants were poured into a test tube and placed in a refrigerator to solidify. The lubricants were removed after they solidify and the temperature at which the solidified oil starts to melt and flow was measured using thermometer.The lowest temperature at which movement was observed is the pour point. The temperature at which a cloud of crystals first appear when the lubricant is cooled is the cloud point.

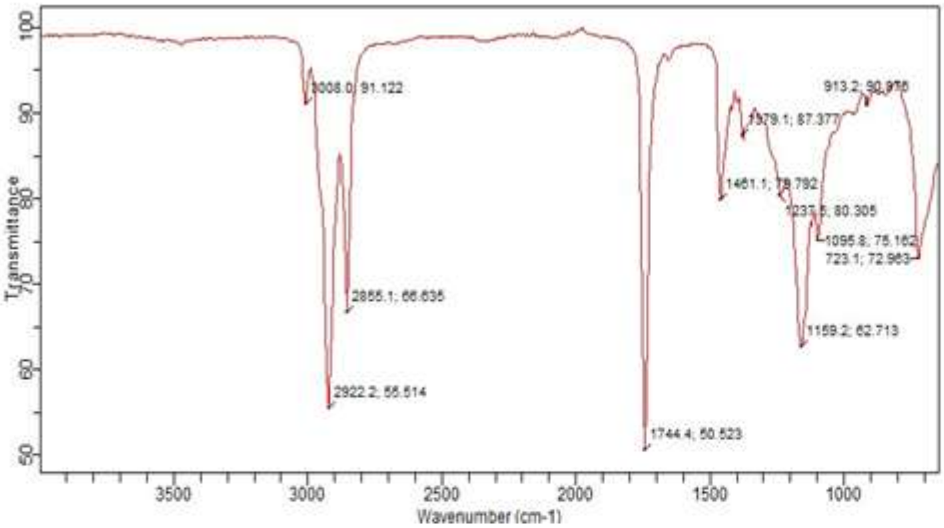


Fig. 1(a) Sandbox oil (SB10)

2.3.11 Determination of flash and fire points

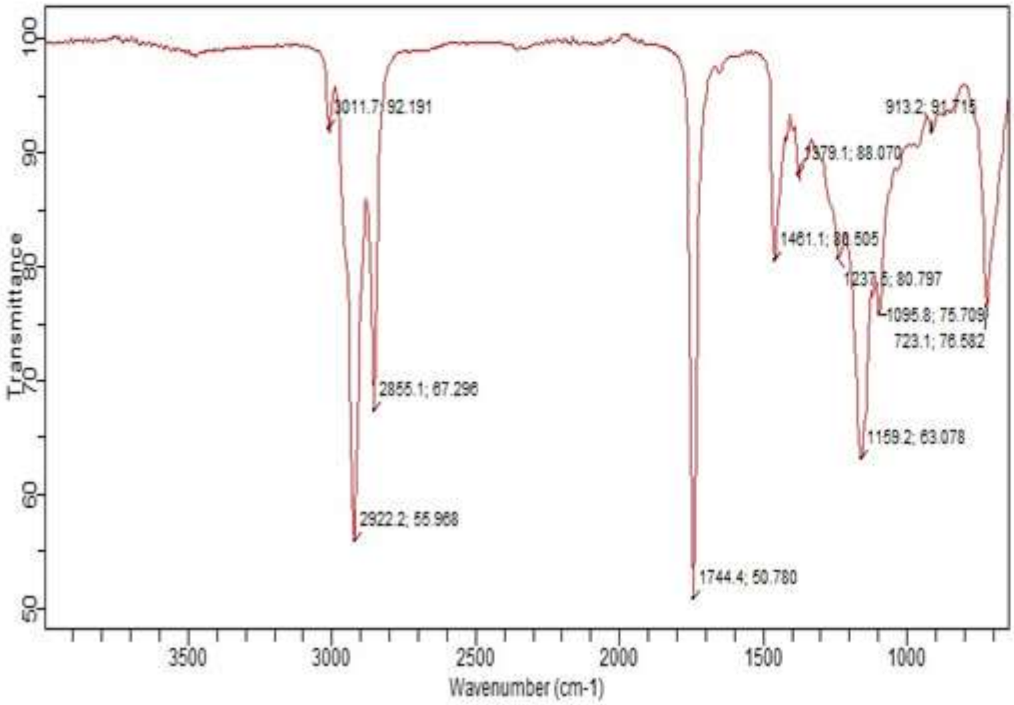
Flash and fire points were measured in accordance with [34]. The lubricant was poured into a metal container and heated at 5°C interval with a flame being passed over the surface of the sample. The temperature at which an instantaneous flash occur was taken immediately and recorded as flash point while the fire point is that temperature at which the vapour of the lubricant burns constantly for 5 seconds when flame is brought near. Fire point is always higher than flash point by 5°C.

III. RESULTS AND DISCUSSION

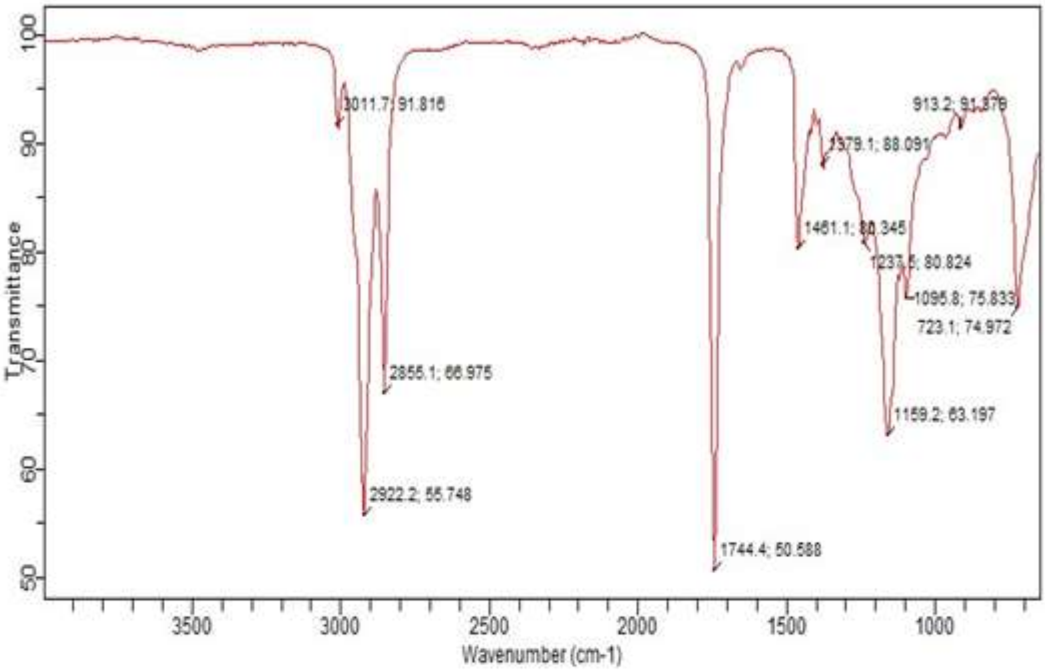
FTIR spectra

There are two interesting spectral regions in a complete characterization of the vibrational activity of oil in the FTIR spectra for sandbox oil shown in Figure 1(a). In the first region at 1500 - 700 cm^{-1}there are observations of vibrational activity in the conjugated bond and bending vibration of aliphatic compounds, while the second region at 3800 - 2800 cm^{-1} the activity of fatty acid stretching vibration and hydroxide were observed. The wavelength range of various functional groups reported by Khan et al, 2019 is shown in Table 1. Figure 1(b) – (c) show that the FTIR spectra of the formulated copper (II) oxide nanoparticle-enriched bio-lubricant were consistent with that of sandbox oil having similar vibrations
with slight shift in vibrational bands and with little contrast in intensities. This means that the molecular structure of the sandbox oil was not damaged by addition of nanoparticle. The presence of a weak band at 3008 cm^{-1} similar to the unsaturation C-H stretching indicating the presence of carbohydrate; while vibration absorption band observed at 1744.4 cm^{-1} similar to carbonyl (C=O) indicating the presence of fats, 1159.2 cm^{-1} corresponding to the vibration of the C-O, indicating the presence of ester and its shoulders at 1105 cm^{-1} and 1235 cm^{-1}; a broad band at 723 cm^{-1} corresponding to Cu-O stretching indicating the presence of metal oxides and 3500 cm^{-1} corresponding to stretching of the hydroxyl group (O-H), indicating the presence of water and phenol. Reference [23] reported similarresultsfor bio-

lubricants from jatropha seed oil and sesame seed oil respectively.



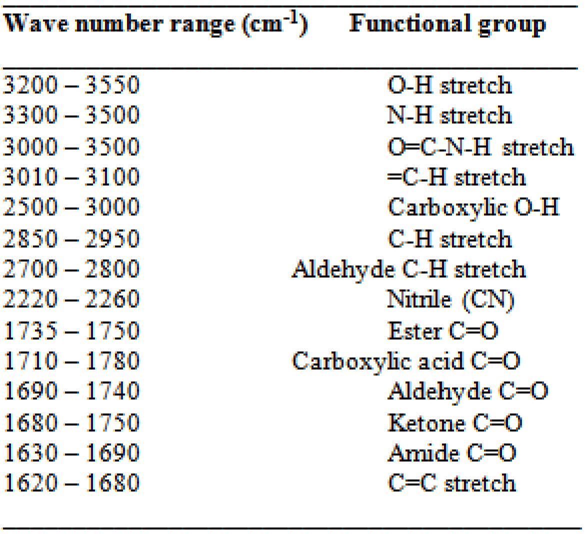
(b) Sandbox oil + 0.75 wt% CuO (SBCuO10)



(c) Sandbox oil + 1.5 wt% CuO (SBCuO15)

Figure 1: FTIR spectra for sandbox oil and formulated bio-lubricant

Table 1: Range of wavenumber (cm^{-1}) of various functional groups in FTIR



Wave number range (cm^{-1})	Functional group
3200 – 3550	O-H stretch
3300 – 3500	N-H stretch
3000 – 3500	O=C-N-H stretch
3010 – 3100	=C-H stretch
2500 – 3000	Carboxylic O-H
2850 – 2950	C-H stretch
2700 – 2800	Aldehyde C-H stretch
2220 – 2260	Nitrile (CN)
1735 – 1750	Ester C=O
1710 – 1780	Carboxylic acid C=O
1690 – 1740	Aldehyde C=O
1680 – 1750	Ketone C=O
1630 – 1690	Amide C=O
1620 – 1680	C=C stretch

Dispersion stability

Dispersion stability is highly desirable for reliable lubrication performance. The optical absorbance profile for lubricant samples dispersed with copper (II) oxide nanoparticle additive is presented in Figure 2. For long stationary applications as well as consistent performance, stable bio-lubricant suspensions are needed. The higher the value of optical absorbance, the stable will be dispersion of nanoparticle as reported by [35]. The UV- spectrometry analysis of the samples revealed a steady absorbance decrease with an increase in ageing time. The nanoparticle additive used in the lubricating oil showed good stability and solubility in the lubricant. It was readily dispersed in the oil at room temperature and remained unchanged for several days. The optical absorbency profile shows a continuous improvement in dispersion stability with stable trends when nanoparticle added was increased from 0.75 wt% to 1.50 wt%. Bio-lubricant enriched with 1.50 wt% copper (II) oxide nanoparticle showed better dispersion stability than 0.75 wt% enrichment. The dispersion stability was observed to be a function of concentration of the nanoparticle added to the oil, as a rapid decline in absorbance occurred for lubricants containing higher concentrations of nanoparticle. This was as a result of increase in tendency of agglomeration and sedimentation at higher concentrations of nanoparticle. These observations were reported previously by [36]where copper (II) oxide nanoparticle was added to bio-based lubricants. Generally, there is a linear relationship between the absorbance and concentration of nanoparticle in the bio-lubricant.

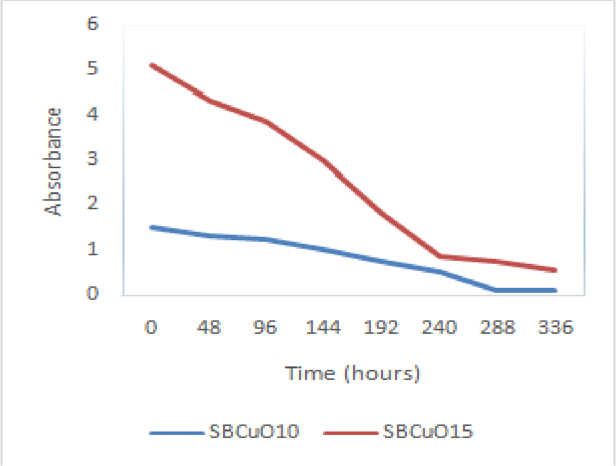


Figure 2: Optical absorbance profiles of the bio-lubricants

Note: SBCuO10: Oil + 0.75 wt% CuO
SBCuO15: Oil + 1.50 wt% CuO

Density

Density plays a critical role in the functioning of a lubricant and the performance of moving parts of a machine. The higher the density of a lubricant, the thicker it becomes, which increases the time it will take for particles to settle out of suspension.The density of the sandbox oil was 0.93 g/cm^3, while that of SBCuO10 was 0.89 g/cm^{3}and for SBCuO15 it was 0.90 g/cm^3. This shows that they are less dense than water and in case of contamination with water; water will settle below the lubricant and will be subsequently drained off. There is slight decrease in density of the bio-lubricants when compared with that of the sandbox oil (from 0.93 g/cm^3 to 0.89 g/cm^3) due to series of modification the oil passed through during the trans-esterification processes, thereby making the bio-lubricant less dense than the oil. The obtained results are in line with 0.92 g/cm^3 reported by [24] for jatropha bio-lubricant and 0.915 g/cm^3 reported by [37] for soybean and sunflower oils.

Specific gravity

When comparing the specific gravity of the nanoparticle-enriched bio-lubricants with crude sandbox oil, it was observed that the specific gravity increased. The specific gravity of SBCuO10 increased by 2.20% while SBTiO150 increased by 2.44%.This may be as a result of series of modification the oil undergoes through trans-esterification processes. It can be deduce from these results that the sandbox oil and bio-lubricants are more likely to mix well with water since their specific gravities are close to that of water.

Refractive index

Refractive index, according to [38], increases with increase in saturation and the chain length of fatty acid. Refractive index of the sandbox oil was 1.4679, SBCuO10 had1.4697, SBCuO15 had 1.4691, while the refractive index of SAE 40 was 1.4815. This shows that copper (II) oxide nanoparticle-enriched bio-lubricants are more saturated than sandbox oil. These values lie within the standard range of 1.3000 – 1.7000 as reported by [39] and comparable to that of conventional lubricant SAE 40.

Saponification value

Crude sandbox oil had saponification value of 245.98 mg KOH/g, SBCuO10 had 190.74 mg KOH/g, and SBCuO15 had 179.52 mg KOH/g while that of conventional lubricant SAE 40 was 213.18 mg KOH/g as shown in Figure 3. Due to the esterification reaction which reduced the free fatty acid content, there was decrease in the saponification values of the nanoparticle-enriched bio-lubricants compared to crude sandbox oil.This was so because saponification value is said to have strong positive correlation with free fatty acids content. The higher the free fatty acids, the higher the saponification value and vice versa as reported by [38]. The high saponification values indicate the presence of high percentage of free fatty acids which might lead to foam formation. The obtained values aligned with186.11 mg KOH/g, 182.75 mg KOH/g and 191.20 mg KOH/g reported by [24]for moringa, castor and cotton bio-lubricants respectively.

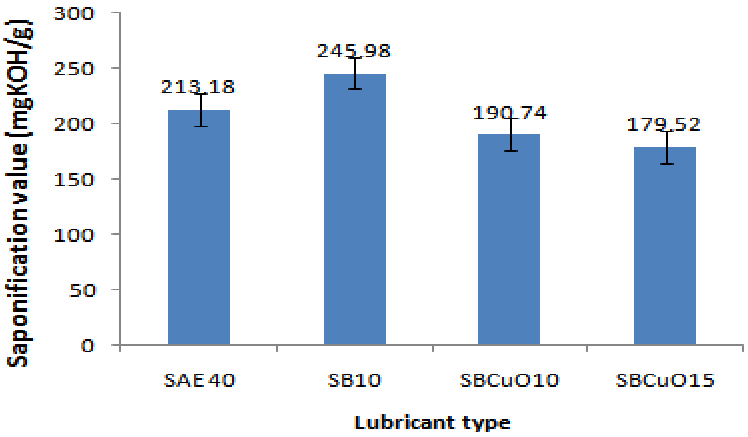


Figure 3: Effect of nanoparticle enrichment on saponification value

Note:
SAE 40: Conventional lubricant
SBL100: Sandbox bio-lubricant

Iodine value

Iodine value is the measurement of unsaturation fats and oils. High iodine value means high degree of unsaturation fats and oils. The higher the iodine value, the less stable, softer, more reactive and susceptible to oxidation the oil will be. The conventional lubricant SAE 40 had iodine value of 102 $gI_2/100g$, while that of crude sandbox oil, SBCuO10 and SBCuO15 were 177.66 $gI_2/100g$,152.16 $gI_2/100g$ and 150.76 $gI_2/100g$ respectively as presented in Figure 4. The values show that there was decrease in the iodine value of the bio-lubricants compared to that of crude sandbox oil. Oils with high iodine value according to [38] have lower melting point and performs better in cold weather. The iodine value of sandbox oil was high due to fact that the oil contains unsaturated glycerides, which have the ability to absorb a definite amount of iodine. These values aligned with the iodine value of 174.9 $gI_2/100g$ for jatropha bio-lubricant and 185.6 $gI_2/100g$ for moringa bio-lubricant reported by [24] in a previous research work and 102.9 $gI_2/100g$ obtained for conventional lubricant SAE 40.

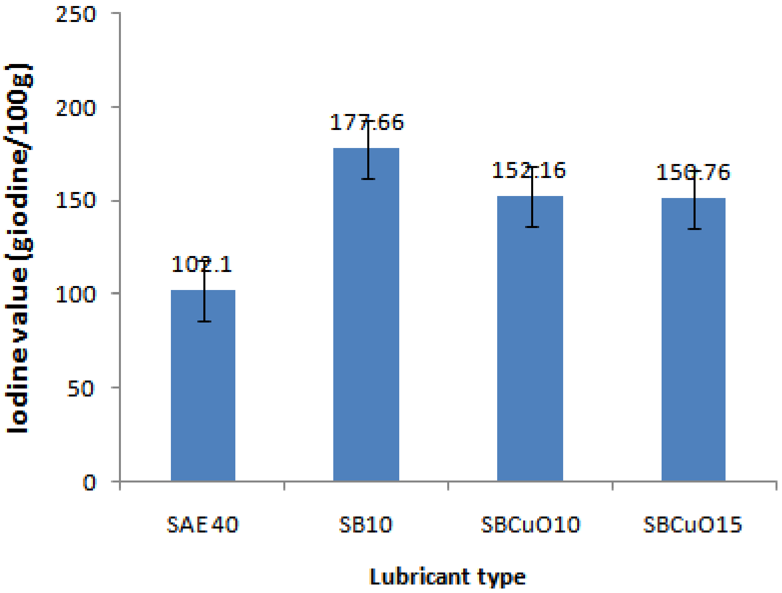


Figure 4: Effect of nanoparticle enrichment on iodine value

Acid value

Acid value is the number of grams of potassium hydroxide required to neutralize one gram of oil. A high acid value is not recommended for bio-lubricants due to oxidation which can accelerate wear and rust formation as well as corrosion. The acid value of the crude sandbox oil was 1.68 mgKOH/g, SBCuO10 had 1.82 mgKOH/g, SBCuO15 had 2.31 mgKOH/g, while the acid value for conventional lubricant SAE 40 was 4.40 mgKOH/g as shown in Figure 5. These values show that there was increase in the acid value of the nanoparticle-enriched bio-lubricants compared to that of crude sandbox oil.In comparison with the conventional lubricant SAE 40, the bio-lubricants have lower acid values which make it of higher quality. This is because the lower the acid value of oil, the higher the quality. The values were above 0.50 mgKOH/g set as lower value for bio-lubricant in both European (EN 14214) and American standards (ASTM D6751) as reported by [38]. The results obtained aligned with the findings of [39] who reported acid values of 1.60 mgKOH/g for neem oil bio-lubricant and 3.90 mgKOH/g for jatropha oil bio-lubricant.

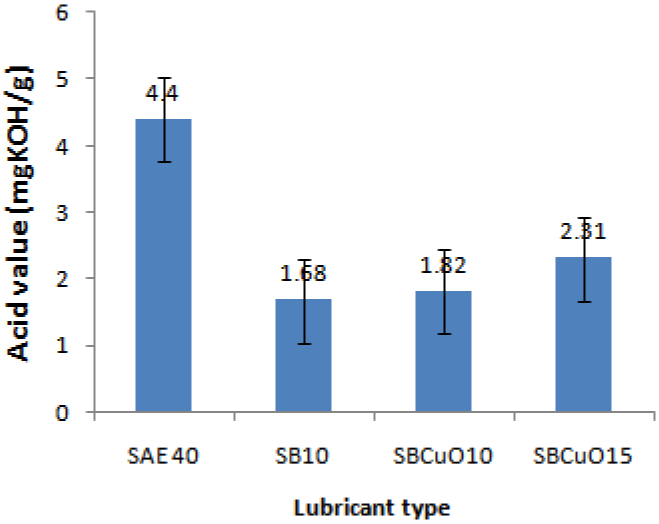


Figure 5: Effect of nanoparticle enrichment on acid value of the bio-lubricants

Free fatty acid

The free fatty acid content of the crude sandbox oil reduced from 14.03 mgKOH/g to 8.42mgKOH/g (SBL10) as a result of series of modification the oil undergoes through trans-esterification processes. But addition of 0.75 % w/w and 1.50% w/w copper(II) oxide nanoparticle to the sandbox bio-lubricant increased the fatty acid to 8.57 mgKOH/g and 9.10 mgKOH/g respectively from 8.42 mgKOH/g. Reference [19] recommended that oil used in transesterification reaction should contain not more than 1% free fatty acid. The values obtained are comparable with previous work by [9] and [24] where the free fatty contents of the crude jatropha oil, moringa oil, castor oil and cotton oil reduced due to esterification of the oil with methanol.

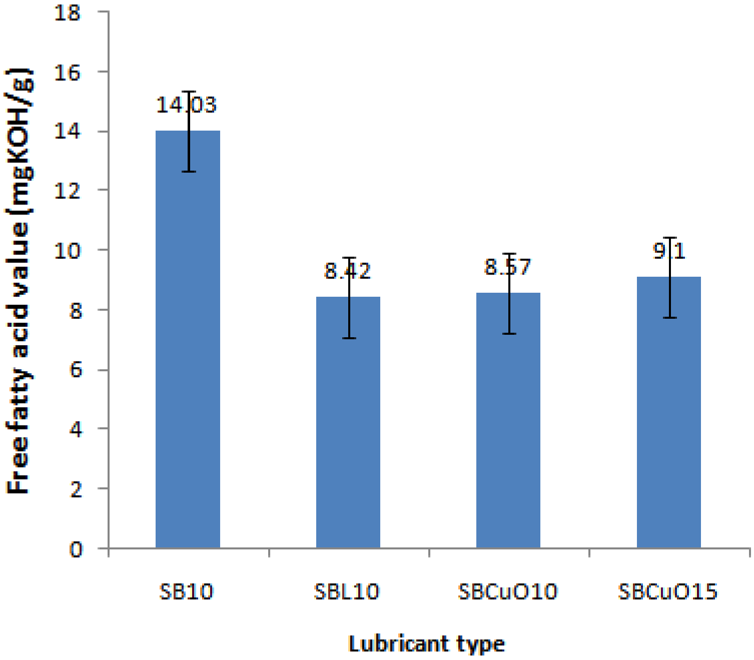


Figure 6: Effect of nanoparticle enrichment on free fatty acid

Viscosity

The viscosities of copper (II) oxide nanoparticle-enriched bio-lubricants were higher in comparison with that of sandbox oil but lower than that of conventional lubricant SAE 40 as shown in Figure 7. The viscosities of the crude sandbox oil were 29.80 cSt and 7.90 cSt at 40°C and 100°C respectively while that of conventional lubricant SAE 40 were 56.00 cSt and 7.70 cSt at 40°C and 100°C respectively. The viscosities of the copper (II) oxide nanoparticle-enriched bio-lubricants at 40°C were 35.40 cSt and 40.90 cSt and 8.40 cSt and 9.10 cSt at 100°C for SBCuO10 and SBCuO15 respectively. Theseconform to the ISO viscosity classification recommended for automobiles applications reported by Arianti and Widayat (2018) for ISO VG32 specifications of > 28.80 cSt at 40°C and 4.10 cSt at 100°C.In previous research works, [40] reported 42.85 cSt and 42.80 cSt at 40°C and 10.00 cSt and 11.2 cSt at 100°C respectively for conventional lubricant SAE 30. Reference [41] also reported viscosity of 42.8 cSt at 40°C for SAE 30. Reference [6] reported viscosities of 92.45 cSt at 40°C and 12.32 cSt at 100°C for conventional lubricant SAE 40. Reference [23] reported viscosities in the range of 39.1 – 54.1 cSt for palm and palm kernel oils based bio-lubricants and 43.9 cSt for jatropha oil based bio-lubricant at 40°C as well as in the range of 7.7 – 9.8 cSt and 8.7 cSt at 100°C. Reference [42] reported viscosities of 40.5 cSt and 7.80 cSt for canola oil based bio-lubricant. The reports show a good comparison between sandbox oil based lubricant and other seed oil based lubricants.

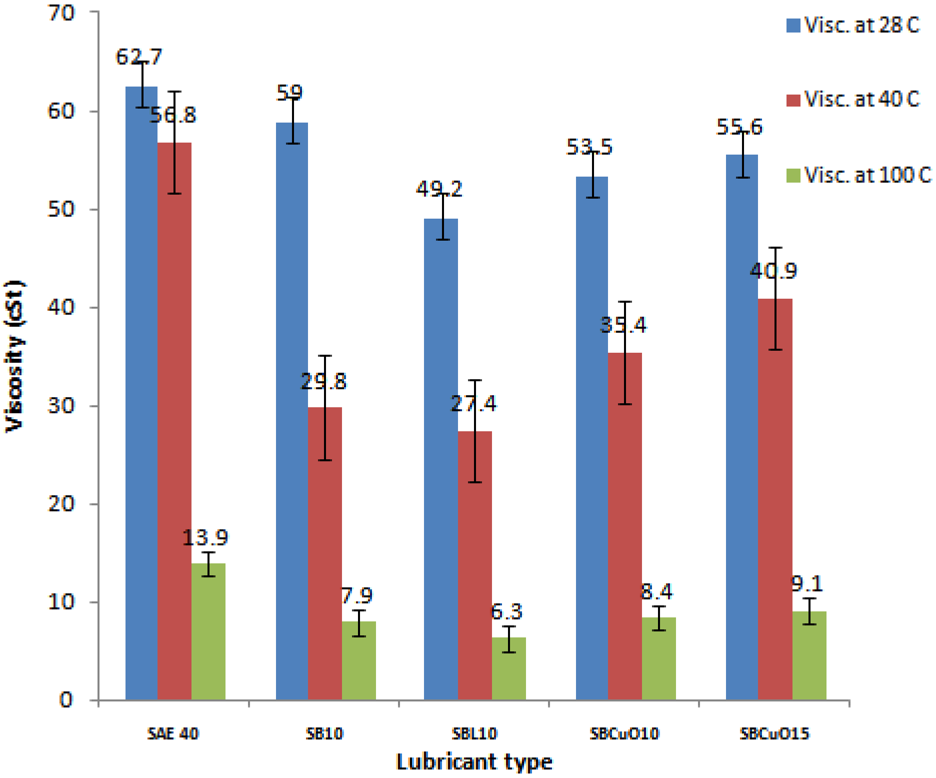


Figure 7: Effect of nanoparticle enrichment and temperature on viscosity of the bio-lubricants

Viscosity index

The viscosity indexeswere 172.96, 169.31, 163.93 and 158.71 for the crude sandbox oil, SBL10, SBCuO10 and SBCuO15 respectively,while that of the conventional lubricant SAE 40 was 161.22 as shown in Figure 8, which could meet the requirement of the ISO VG32 lubricant since it is within the ISO viscosity range 32 standard. The results show that there was decrease in the viscosity index of the nanoparticle-enriched bio-lubricants compared to that of crude sandbox oil. The standard viscosity index required for lubricants can vary from 30 to 240 for automobiles[43]. The high viscosity indexes obtained will allow the lubricants to keep their lubrication properties at higher temperatures which show that the lubricants were good lubricants. This is because a good multipurpose lubricant maintains a constant viscosity throughout temperature changes. Comparing these results with other research works, [23], [19] and [42] reported viscosity indexes of 187.00, 170.00 180.00 and167.00 and for palm oil, soybean oil, jatropha oil and palm kernel based lubricants respectively. Viscosity indexes of 134.00 for jatropha oil based bio-lubricant, 127.00 for moringa oil based bio-lubricant and 113.00 for cotton oil bio-lubricant were also reported by [24].

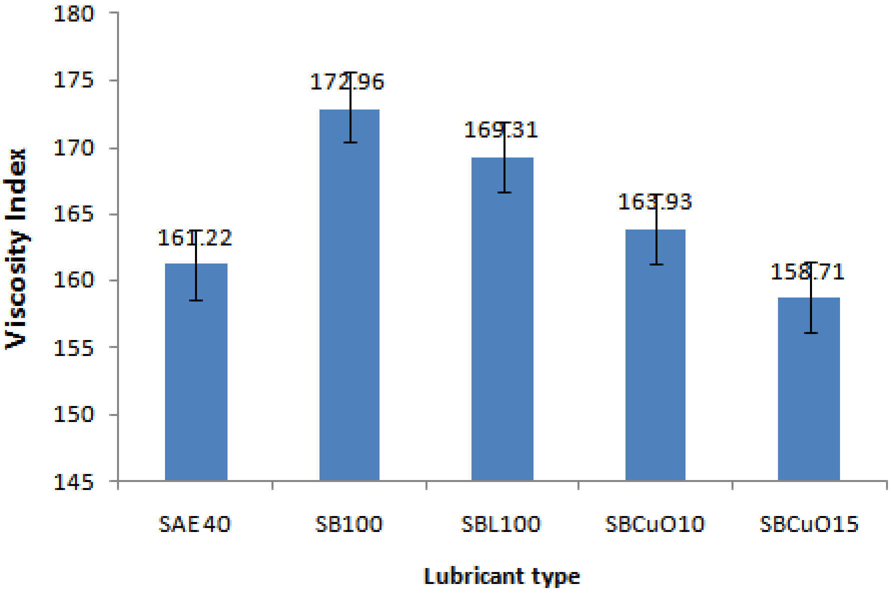


Figure 8: Effect of nanoparticle enrichment on viscosity index

Pour point

The pour point of the sandbox oil improved from – 3^{o}C to – 4.0^{o}C for the nanoparticle-enriched bio-lubricant (SBCuO10) and to – 4.5^{o}C for SBCuO15. Comparing the pour points of the bio-lubricants with that of conventional lubricant SAE 40 which had a pour point of 3^{o}C, the nanoparticle-enriched bio-lubricants were more preferred due to low pour points.

Cloud point

Low temperature fluidity is the most essential property for lubricants to perform in environments that are extremely cold [42]. The cloud pointof the sandbox oil improved from 11^{o}C to 4.5^{o}C as shown in Figure 9. These were due to the transesterification reaction and nanoparticles added to the lubricant. These, according to [23], might be as a result of the presence of polyol group and the absence of beta-hydrogen in the bio-lubricant produced when the methyl ester reacted with trimethylolpropane.The values obtained were consistent with the pour points and cloud points of other bio-lubricants as reported in previous studies. Reference [23] reported an improvement in the pour point of crude jatropha oil from – 7^{o}C to – 12^{o}C for jatropha oil based bio-lubricant. Reference [39] reported pour points of 1.30^{o}C for neem based bio-lubricant, 0.20^{o}C for jatropha based bio-lubricant and -30^{o}C for mineral oil SAE 50. Reference [19] reported improved pour points of jatropha oil from 5^{o}C to – 7^{o}C for its bio-lubricant.

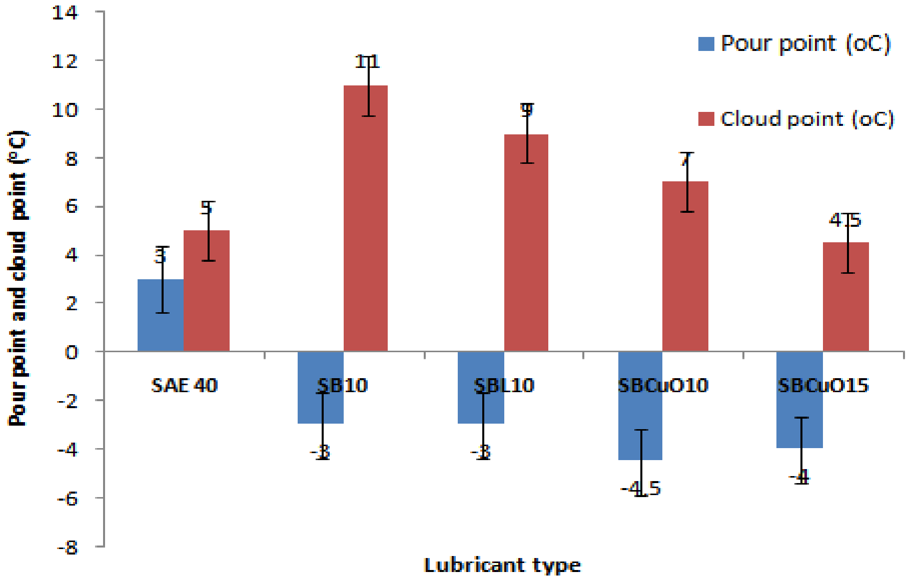


Figure 9: Effect of nanoparticle enrichment on pour and cloud points

Flash and fire points

The flash and fire points of the nanoparticle-enriched bio-lubricant were relatively lower than that of sandbox bio-lubricant as a result of the addition of nanoparticle. The flash and fire points of the sandbox bio-lubricant and SBCuO15 bio-lubricant were higher than that of crude sandbox oil as shown in Figure 10. The results show that the bio-lubricants have very good flash and fire points. These high points suggest their potential for high temperature applications. The values indicate that the bio-lubricants can be used in both humid and temperate regions and transported safely with minimum risks of explosion. The values are similar to the values reported previously by [19].Reference [7]reported flash point of 256^{o}C for soybean oil based bio-lubricant.Reference [39] reported flash points of 262^{o}C for neem based bio-lubricant and 274^{o}C for jatropha based bio-lubricant.

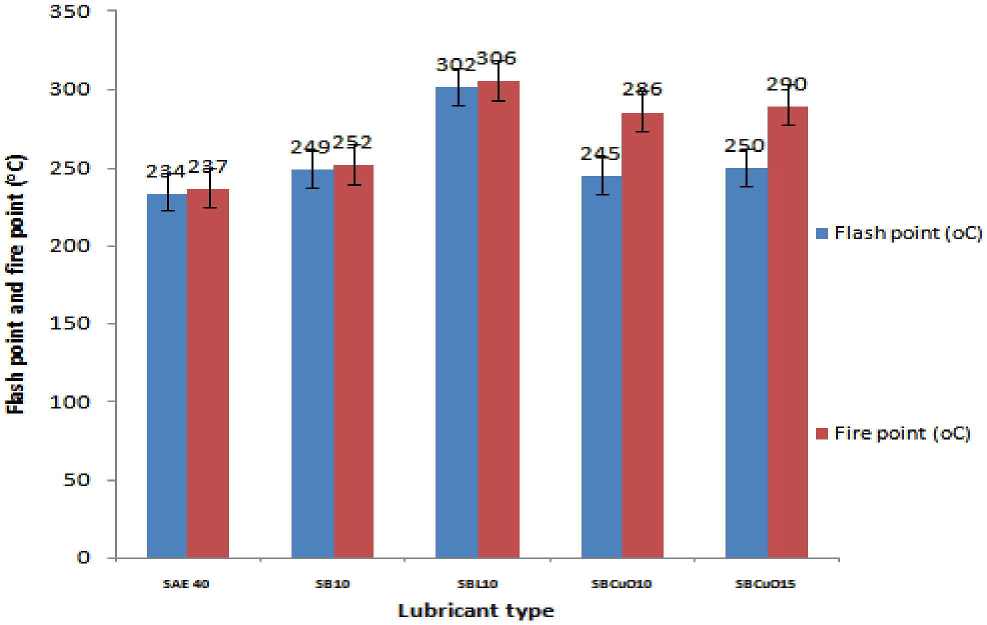


Figure 10: Effect of nanoparticle enrichment on flash and fire points

IV. CONCLUSION

The quality of lubricant plays a vital role in effective reduction of friction between the contact surfaces of engine parts (piston ring assembly, bearings and valve train). Addition of copper (II) nanoparticle to sandbox bio-lubricant enhanced the chemo-physical properties of the sandbox bio-lubricant. The nanoparticle-enriched bio-lubricant produced exhibited good chemo-physical properties and could be favourably used in automobile application as engine oil to improve the lubrication of the moving parts. These properties conformed to the specified standards of the International Standard Organization (ISO). The bio-lubricant can be used as alternative lubricant in automobile engine.

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