Effect of Titanium Oxide Nanoparticle Enrichment on Chemo-Physical Properties of Bio-Lubricant from Sandbox Seed Oil

C.A. POPOOLA[1], K.K. IKPAMBESE[2]
[1] *Department of Food Science and Technology, Federal University Wukari, Nigeria.*
[2] *Department of Mechanical Engineering, University of Agriculture, Makurdi, Nigeria.*

Abstract- This study investigated effect of titanium oxide nanoparticle additive on chemo-physical properties of bio-lubricant from sandbox seed oil. Titanium oxide nanoparticle-enriched sandbox bio-lubricant was developed by adding varying concentrations of the nanoparticle to the sandbox lubricant. Chemo-physical properties of the bio-lubricant were analyzed in accordance with the American Society for Testing and Materials (ASTM) standards. FTIR analysis revealed that the molecular structure of sandbox oil was not damaged by addition of titanium oxide nanoparticle. Results from this study also indicated that the kinematic viscosities of the nanoparticle-enriched bio-lubricants at 40 and 100ºC, iodine values, acid values, and free fatty acid values are higher than that of sandbox bio-lubricant without nanoparticle. Viscosity index, saponification value, cloud point, flash and fire points of the nanoparticle enriched bio-lubricants are lower compared to sandbox bio-lubricant without nanoparticle. These results are found to conform to the SAE standards. The study revealed that addition of titanium oxide nanoparticle to the sandbox oil improved the chemo-physical properties of the bio-lubricant for better lubricating performance in the automotive engines.

Indexed Terms- Sandbox; titanium oxide; nanoparticle; chemo-physical; bio-lubricant.

I. INTRODUCTION

The growing international concerns about environmental pollution associated with the use and disposal of mineral oil-based lubricants have inspired research on alternative lubricants with focus on the formulation and development of biodegradable, renewable and eco-friendly lubricants. Agrawal *et al.* (2017) and Abere (2017) reported that vegetable oils can be used as an alternative to mineral oil or petroleum based lubricant as they provide important environmental benefits with excellent performance in many applications and possess several advantages which include biodegradability, lower toxicity, lower volatility, higher lubricity, higher flash point and viscosity index. 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. Many studies, according to Naik and Galhe (2016), have confirmed that the presence of monounsaturated fatty acids in vegetable oils, such as oleic and palmitic, makes it to be considered as the best feedstock for lubricants. These oils, according to Amdebrhan *et al.* (2015), contain three hydroxyl groups and long chain unsaturated free fatty acids attached at the hydroxyl group by ester linkages that assist in dissolving more of a substance. The unsaturated free fatty acid which is the position and ratio of carbon-to-carbon double bond, three, two and one double bonds of carbon chain is named as a linolenic, linoleic and oleic fatty acid components respectively.

Vegetable oil-based lubricant according to Agrawal *et al.* (2017) is becoming more attractive everyday due to its environmental benefits. Ahmed *et al.* (2014) reported that vegetable oils have a capability to contribute towards the goal of controlling environmental pollution, security and energy independence since they are biodegradable and nontoxic. The increasing need to search 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. Giwa *et al.* (2016) 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 (Adewuyi, 2014). 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 chemical components or blends that provide one or more functions in the fluid at a specific treat rate, generally from 0.1 – 35%. Charoo *et al.* (2017) observed that addition of additives to base oil improve the tribology of lubricant to large extent. Nanoparticles are emerging lubricant additives with wear and friction reduction potentials. Patil *et al.* (2014) and Ali *et al.* (2016) 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 Ali and Xianjum (2015) 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 (Singh *et al.,* 2018).

Titanium oxide nanoparticle as lubricant additive has good performance on relatively low toxicity, non-volatility, anti-oxidant features and pleasant odour according to Jatti (2015). Titanium (Ti) atoms of TiO_2 during reaction coordinate with either two or three oxygen atoms to form TiO_2 group and TiO_3 group, they are therefore hybridized to a planar or three-dimensional structure. Many research works have investigated the effect of titanium oxide nanoparticle additive on the properties of lubricants (Koshy *et al.,* 2015). Battez and Rodriguez (2016) observed that the adhesion and transfer of the nanoparticles speed up self-reduction, surface adjustment and formation of TiO_2 tribofilm that reduced the pressure, temperature, wear as well as friction coefficient in the contact area. Le and Lin (2017) reported that titanium oxide (TiO_2) nanoparticle additive could increase the applicable load, reduce the friction force, and increase the anti-wear capacity of the lubricant. The effect of titanium oxide nanoparticle dispersed in lubricating oil obtained by sonication process in the absence of surfactant was also reported by Afzal *et al* (2017). Binu *et al.* (2014) reported the improvement in capacity to carry load of journal bearing using TiO_2 nanoparticle lubricant additive as compared to plain oils without nanoparticle additive. Laad and Jatti (2018) investigated the tribological characteristics of titanium oxide nanoparticle additive in petroleum based engine oil and found that addition of TiO_2 nanoparticle to engine oil reduces wear rate and friction significantly, thereby improves the lubricating characteristics of the lubricant. The dispersion analysis also confirms that titanium oxide nanoparticle in the lubricant are stable and have good solubility. Battez and Rodriguez (2016) when examined the lubricating properties of the lubricant containing titanium dioxide nanoparticle additive, discovered that titanium dioxide show a good tribological properties.

Generally, majority of the studies agree that the nanoparticle improved the tribological properties of lubricant by deposition at the contact area thereby creating a protective layer. They can significantly improve the wear-reduction capability, friction-reducing property and pure oil load carrying capacity (Su *et al.,* 2018). 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 (Lopez, *et al.,* 2015). 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. The main effects provided by nanoparticle-enriched lubricant as listed by Thirumalaikumaran (2017) are: ball bearing effect between the contact surfaces, protective film to prevent friction and coating the rough surface, polishing effect and mending effect.

This research work investigates the effect of titanium oxide nanoparticle enrichment on chemo-physical properties of bio-lubricant from sandbox seed oil.

1.1 Chemo-physical Properties of Lubricant

Chemo-physical properties of lubricant that are important to lubricity 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

Bello *et al.* (2013) defined kinematic viscosity as the resistance of liquid to flow. It is the oil thickness obtained by measuring the amount of time taken for a given oil to pass through an opening of a specified size. An ideal lubricant for most purpose is one that has a constant viscosity entirely when there is change in temperature. The capacity of the lubricant to separate contacting areas in relative motion is connected to its viscosity within the operating pressure and temperature. It is important to note that many base oils are Newtonian fluids, but the additives change fully developed lubricant to non-Newtonian fluid which makes the viscosity of the lubricant to change with the shear rate, while the temperature remains constant.

1.1.2 Viscosity index

Abere (2017) and Bilal *et al.* (2013) described viscosity index as a very important lubricity property, which 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. High viscosity index of bio-lubricant implies that changes in viscosity at higher temperature will be minimal. Wikipedia (2018) 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 by ASTM D2270 (1995):

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

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

Silitonga *et al.* (2013) 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 is denser and less compressible than petroleum-based lubricant regardless of the feedstock. The effect of density in engine operation is very important to injector nozzle. Specific gravity, according to Abere (2017) is 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 point and fire point

Flash point is the temperature at which oil gives off enough vapour which ignites when exposed to flame or a spark. Chandan *et al.* (2017) described it as the lowest temperature of oil at which it reacts with oxygen to produce an ignitable mixture. It measures the readiness of the oil to ignite momentarily in air and varies inversely with the volatility of fuel. The flash point is used in safety and shipping classification of a material. Menkiti *et al.* (2017) reported that bio-lubricants generally have higher flash points in comparison with petroleum-based lubricant. This means that bio-lubricant is safe for transport, handling and storage purpose. Mohammed (2015) described fire point of a lubricant as the lowest temperature at which sufficient vapour is produced continuously for burning after ignition for at least 5 seconds. Generally, the fire point is 5 - 10^{o}C higher than the flash point. The flash and fire points tell the volatility, fire resistance and maximum temperature up to which oil can be used, thereby help in safety and shipping classification of a material. Good lubricants should have fire and flash points above its operating temperature.

1.1.5 Cloud point and pour point

The cloud point as well as pour point is important for low temperature application. Mohammed (2015) and Chandan *et al.* (2017) described cloud point as temperature at which a cloud of wax crystals first appear when the lubricant is cooled. At this temperature, mixture start to separate into two phases and wax precipitation is visible in the lowest part of the container. Abere (2017) stated that the cloud point of lubricants is determined on base oils, which measures the suitability of the base oil for the purpose. Pour point is one of most critical properties which determine the performance of lubricants. It is that temperature at which the oil ceases to flow after cooling. Chandan *et al.* (2017) described it in other words as the lowest temperature at which oil flows as its container is tilted for a prescribed period. It indicates the suitability of oils in cold conditions. Oil used in engine working at low temperature should have low pour point; otherwise, it will make the engine to jam. Generally, bio-lubricant has higher cloud point and pour point than petroleum-based lubricant as observed by Silitonga *et al.* (2013). The cloud point and pour point 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), titanium oxide (TiO_2) nanoparticle, conventional lubricant SAE 40 and Anton Paar ball-on-disc tribometer (model TRN).

2.2 Methods

This work was subdivided into: materials collection and preparation, characterization of sandbox oil, chemical modification of sandbox oil to produce bio-lubricant, production of 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 nanoparticle and other chemicals were obtained from Bristol Scientific Company Ltd, Lagos. The titanium oxide nanoparticle 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 using n-hexane as extracting solvent. 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 Formulation of titanium oxide nanoparticle enriched bio-lubricant

Titanium oxide nanoparticle-enriched bio-lubricant was formulated in accordance with the method described by Bilal *et al.* (2013), using sandbox oil as base oil. The formulation involves a double transesterification process; methyl ester synthesis and bio-lubricant synthesis. During the first transesterification, an intermediate product, 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. Bio-lubricant synthesis was achieved during the second transesterification by adding trimethylolpropane (TMP) to the sandbox methyl ester to produce the desired bio-lubricant. Titanium oxide (TiO_2) nanoparticle used as additive was added in different concentrations of 0.75 wt% and 1.50 wt% to the bio-lubricant. Oleic acid was added to prevent nanoparticle agglomeration during dispersion process and improve the dispersion stability of the nanoparticle. The bio-lubricants were produced using different concentration of nanoparticle additive and they were coded as: SB100 (Sandbox oil), SBL100 (Sandbox bio-lubricant), SBTiO75 (Sandbox oil + 0.75 wt% TiO_2) and SBTiO150 (Sandbox oil + 1.5 wt% TiO_2).

2.3 Characterization of the Bio-lubricant

The standard methods were used to determine the chemo-physical properties of the sandbox oil and formulated nanoparticle-enriched bio-lubricant.

2.3.1 Fourier transform infrared (FTIR) analysis

The FITR analysis was performed on the oil and bio-lubricant to determine the functional groups present in them and analyze its degradation in accordance with the method adopted by Khan *et al.* (2019) and Laachari *et al.* (2015) using PerkinElmer Spectrum 400 FTIR spectroscopy instrument with a data acquisition system. The bio-lubricant sample was placed between the infrared source and detector. These infrared radiations are required to pass through the lubricant sample 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.

2.3.2 Determination of elemental composition

The elemental composition of the oil and bio-lubricant was determined in accordance with AOAC (2000) method using line source PG-990 Atomic Absorption Spectrophotometer (AAS). The instrument is fully automated for flame or ghaphite furnace analysis. It uses two background correction system, self-reversal method and deuterium lamp method. The burner of the spectrophotometer was ignited by allowing air to mix with acetylene gas from the gas cylinder in good proportion. After the ignition, the spectrophotometer calibration was done immediately with distilled water and standard solution. The sample's aerosol was then aspirated through nebulizer into flame for analysis. Analysis was done for every element of interest at their specific wavelength using hollow cathode lamp of the element under investigation. The result was displayed on the computer and recorded.

2.3.3 Dispersion stability analysis

The analysis of dispersion of nanoparticle in the bio-lubricant was done in accordance with Gulzar (2017) by measuring the optical absorbance spectrum using T60U Ultra-Violet (UV) visible spectrophotometer. The spectrophotometer has wavelength accuracy of ± 2 nm and a repeatability of 1 nm. The bio-lubricant samples were spectroscopically studied for dispersion stability of 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.

2.3.4 Determination of density and specific gravity

The density and specific gravity were determined in accordance with ASTM D1298-17 (2017). 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) as well as specific gravity using equations (1) and (2) respectively.

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

$$Specific\ gravity = \frac{A}{B} \quad (2)$$

Where

m = sample mass (g)

v = sample volume (cm^3)

A = Weight of a unit volume of the oil (kg)

B = Weight of equal volume of water (kg)

2.3.5 Determination of cold flow properties (pour point and cloud point)

Pour point and cloud point were determined in accordance with ASTM D97-05 (2005). The lubricant was poured into a test tube and placed in a refrigerator to solidify. The lubricant was removed after it solidifies 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.

2.3.6 Determination of kinematic viscosity and viscosity index

The kinematic viscosity was measured in accordance with ASTM D445-15a (2015). This method covers the determination of kinematic viscosity using Smart series rotational viscometer TSML 21105. The viscosity was measured at three different temperatures 28ºC, 40ºC and 100ºC. At a start a proper viscometer spindle (3) 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 (3) reported by Mohammed (2015):

$$Viscosity = reading\ obtained\ x\ \frac{factor\ for\ the\ spindle}{speed} \quad (3)$$

The viscosity index was determined in accordance with ASTM D2270-04 (2004). This was determined using Smart series rotational viscometer TSML 21105. Viscosity index is used to measure change in the viscosity with variation in temperature. The viscosity index of an oil may be determined if its viscosity at any two temperatures is known. This method provides the lubricant's kinematic viscosities at 40ºC and 100ºC. The temperature of oil sample was raised to the desired level by heating the oil with constant stirring using a heating mantle. Equation (4) was used for the calculation of viscosity index values for the bio-lubricants.

$$Viscosity\ Index = \frac{L-U}{L-H}\ x\ 100 \quad (4)$$

Where:

U = Oil's kinematic viscosity at 40ºC

L = Values of kinematic viscosity at 40ºC for oils of lowest viscosity index (0)

H = Values of kinematic viscosity at 100ºC for oils of high viscosity index (100)

2.3.7 Determination of flash and fire points

The flash and fire points measurement of the bio-lubricant were done in accordance with ASTM D93-02a (2003). The lubricant was poured into a metal container and heated at 5ºC 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 a flash point.

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 flash point plus 5ºC up to 400ºC.

2.3.8 Determination of iodine and peroxide values

The iodine and peroxide values of the bio-lubricant were analyzed using AOAC (2000) methods by 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. It was then titrated with 0.1ml sodium thiosulphate using 10% (w/v) starch indicator. The titration continued until light blue colour was observed. The iodine value and peroxide value were then calculated using equations (5) and (6) respectively.

$$Iodine\ value = \frac{12.69(B-S)N}{W} \quad (5)$$

$$Peroxide\ value = \frac{0.1(S-B)N}{W} \quad (6)$$

Where

$B = Titre\ value\ of\ sodium\ thiosulphate\ used\ for\ blank$

$S = Titre\ value\ of\ sodium\ thiosulphate\ used\ for\ sample$

$N = Normality\ of\ sodium\ thiosulphate$

$W = Sample\ weight$

2.3.9 Determination of free fatty acid (FFA)

Free fatty acid is the value of specified fatty acid in oil. The value was measured in accordance with AOAC (2000). 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 (7).

$$FFA\ value = \frac{28.05\ VN}{W} \quad (7)$$

Where

$V = Titre\ value\ of\ sodium\ hydroxide\ used\ (cm^3)$

$N = Normality\ of\ sodium\ hydroxide$

$W = Sample\ weight\ (kg)$

2.3.10 Determination of acid value

Acid value was determined in accordance with ASTM D 664-18 (2018). 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 (8) given by Bilal *et al.* (2013).

$$Acid\ value = \frac{56.1\,VN}{W} \quad (8)$$

Where

$V =$ $Titre\ value\ of\ potassium\ hydroxide\ used\ (cm^3)$

$N = Normality\ of\ potassium\ hydroxide$

$W = Sample\ weight\ (kg)$

2.3.11 Determination of saponification value

Saponification value of the bio-lubricant was determined in accordance with ASTM D5558-95 (2001). 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:

$$SAP\ value = \frac{56.1\,(B-S)N}{W} \quad (9)$$

Where

$B =$ $Titre\ value\ of\ hydrochloric\ acid\ used\ for\ the\ blank\ (cm^3)$

$S =$ $Titre\ value\ of\ hydrochloric\ acid\ used\ for\ the\ sample\ (cm^3)$

$N = Normality\ of\ hydrochloric\ acid$

$W = Sample\ weight\ (kg)$

2.3.12 Determination of ester value

The ester value of the bio-lubricant was obtained as a difference between the saponification value and the acid value in accordance with AOAC (2000) method.

$$Ester\ value = SAP\ value - AV \quad (10)$$

Where

$SAP\ value = Saponification\ value$

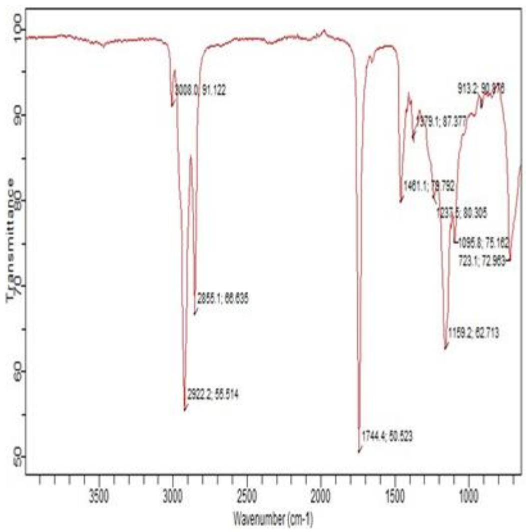
$AV = Acid\ value$

2.3.13 Determination of refractive index

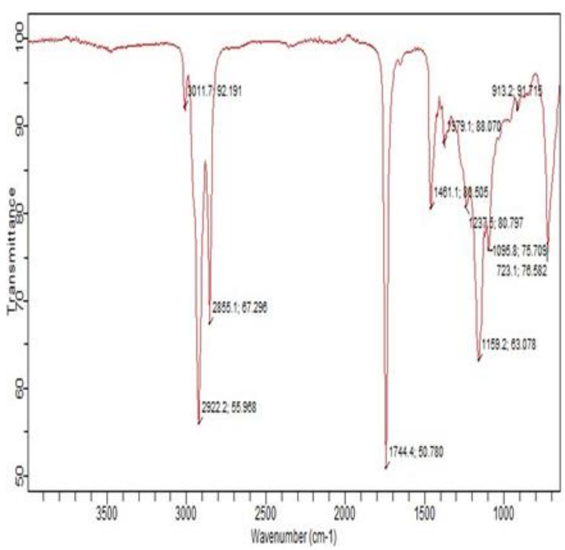
Refractive index of the lubricant which is the degree of refraction of a beam of light that occurs when it passes from one transparent medium to another was determined in accordance with ASTM D1218-01 (2001). Digital Abbe's refractometer Model DRA-1 was used for the measurement of the lubricant's refractive index. The oil was smeared on the lower position of the refractometer, after some adjustment, the refractive index was read directly at room temperature (25ºC).

III. RESULTS AND DISCUSSION

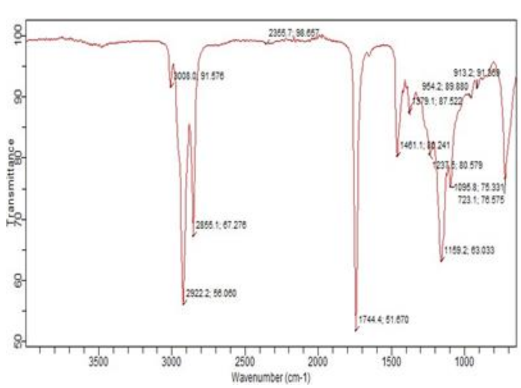
In the FTIR spectra for sandbox oil shown in Figure 1(a), there are two interesting spectral regions in a complete characterization of the vibrational activity of oil as reported by Laachari *et al* (2015). The first region is a region at 1500 - 700 cm^{-1} where there are observations of vibrational activity in the conjugated bond and bending vibration of aliphatic compounds, while the second region is at 3800 - 2800 cm^{-1} where the activity of fatty acid stretching vibration and hydroxide are observed. The range of wavelength of various functional groups reported by Khan *et al*, 2019 is presented in Table 1. The FTIR spectra of the formulated nanoparticle-enriched bio-lubricant as shown in Figure 1(b) – (c) are consistent with that of sandbox oil having similar vibrations with slight shift in vibrational bands and with little contrast in intensities. This suggests that the molecular structure of the sandbox oil was not damaged by addition of nanoparticle. The presence of vibration absorption band observed at 1744.4 cm^{-1} similar to carbonyl (C=O) indicating the presence of fats , while a weak band at 3008 cm^{-1} similar to the unsaturation C-H stretching indicating the presence of carbohydrate; 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 Ti-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. These values were similar to the previous studies by Menkiti *et al.* (2017) and Ocholi *et al.* (2018) for bio-lubricants from jatropha seed oil and sesame seed oil respectively.



(a) Sandbox oil



(b) SBTiO150



(c) SBTiO75

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

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

Wavenumber 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

The optical absorbance profile for lubricant samples dispersed with titanium oxide nanoparticle additive is as shown in Figure 2. Stable bio-lubricant suspensions were required for long stationary applications as well as consistent performance. The UV- spectrometry studies of the samples showed a steady absorbance decrease with an increase in ageing time. According to Ilie and Covaliu (2016), the higher the value of optical absorbance, the stable will be dispersion of nanoparticle. Dispersion stability is highly desirable for reliable lubrication performance. The titanium oxide nanoparticle additive used in the lubricating oil showed good stability and solubility in the lubricant. They were 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%. Lubricant with 1.50 wt% titanium oxide additive showed better dispersion stability than other lubricant sample. 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 are in line with the previous works by Laad and Jatti (2018) and Gulzar (2017) where titanium oxide and copper (II) oxide nanoparticles were added to bio-based lubricants. Generally, there is a linear relationship between the absorbance and concentration of nanoparticle in the bio-lubricant. The degree of absorbance is proportional to the amount of particles per unit volume, and this can be used to denote variations in supernatant particle concentration in the solution with time.

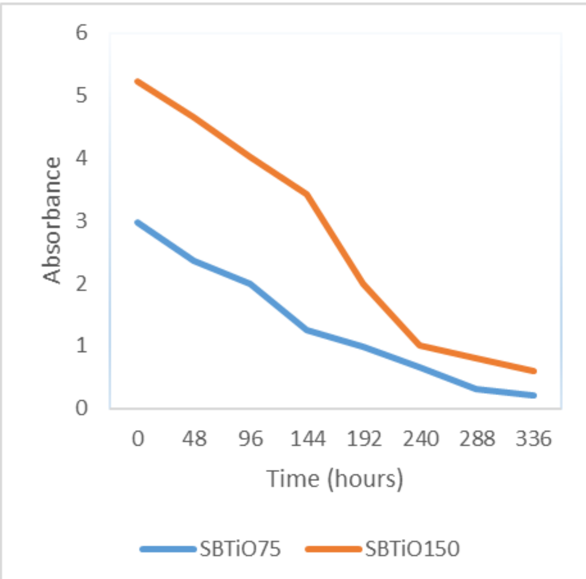


Figure 2: Optical absorbance profiles of the bio-lubricants

Note: SBTiO75: Oil + 0.75 wt% TiO_2
SBTiO150: Oil + 1.50 wt% TiO_2

The amount of various elements in pure sandbox oil is relatively small compared with the formulated nanoparticle-enriched bio-lubricant as shown in Table 2. It is good to note that pure sandbox oil contained copper, iron, and magnesium, among others which according to Bahari (2017) are metallic elements used to determine the quality of vegetable oil before converting it to bio-lubricant. The presence of potassium helps in friction reduction in engine and as cleaner and neutralizer. The metal additives usually used in lubricants act as anti-wear or friction reduction media. They formed protective film by chemical or physical absorption on the contacting metal surface, leading to the sliding friction reduction. Each of the elements has their own specific heat capacity; their presence may lead to the improvement on capability of lubricant in absorbing heat from its surrounding as reported by Bahari (2017). The addition of the nanoparticle to the pure oil improved the values of these elements. But, some elements present in the lubricant may be unnecessary due to its negative effect to the heat capacity and viscosity of the lubricant.

Table 2: Elemental compositions of the formulated bio-lubricants

Element	SB100 (ppm)	SBTiO75 (ppm)	SBTiO150 (ppm)
Magnesium	1.98	2.00	2.15
Potassium	1028	1072	1080
Copper	0.30	0.30	0.30
Iron	0.13	0.14	0.15
Zinc	0.47	0.51	0.53
Lead	0.88	2.05	2.11
Sodium	1520	1596	1620
Manganese	1.86	2.71	2.79
Chromium	1.50	8.89	9.10
Nickel	0.61	0.65	0.68

Note: SB100: Sandbox oil only
SBTiO75: Oil + 0.75 wt% TiO_2
SBTiO150: Oil + 0.75 wt% TiO_2

Density of sandbox oil and bio-lubricants ranged between 0.90 g/cm^3 and 0.93 g/cm^3 which mean that they are less dense than water. Hence, in case of contamination with water, water will settle below the lubricant and will be subsequently drained off. Density plays a critical role in the functioning of a lubricant and the performance of moving parts of a machine. There is slight decrease in density of the bio-lubricants when compared with that of the sandbox oil 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 values are in line with 0.89 g/cm^3 obtained for conventional lubricant SAE 40 and 0.86 g/cm^3 reported by Farhanah and Syahrullail (2015) and Sakinah *et al.* (2016) for lubricant SAE 40, as well as 0.92 g/cm^3 reported by Mohammed (2015) and Bilal *et al.* (2013) for jatropha bio-lubricant and 0.915 g/cm^3 reported by Trajano *et al.* (2014) for soybean and sunflower oils.

Specific gravity of the sandbox oil and nanoparticle-enriched bio-lubricants ranged between 0.93 and 0.98, while that of SAE 40 was 0.86. These values are within the range for lubricants and are comparable to Okolie *et al.* (2012). The specific gravity of the nanoparticle-enriched bio-lubricants was observed to increase compared to that of crude sandbox oil sample, SBTiO75 increased by 2.15% while SBTiO150 increased by 5.38%. This may be as a result of series of modification the oil undergoes through trans-esterification processes. It can be inferred from these data 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 of the sandbox oil was 1.4679, SBTiO75 had 1.4706, SBTiO150 had 1.4699, while the refractive index of SAE 40 was 1.4815. This shows that titanium oxide nanoparticle-enriched bio-lubricants are more saturated than sandbox oil. Refractive index, according to Yerima, *et al.* (2018), increases with increase in saturation and the chain length of fatty acid. These values are satisfactory as they lie within the standard range of 1.3000 – 1.7000 as reported by Aji *et al.* (2015) and comparable to that of conventional lubricant SAE 40 and previous works of Okolie *et al.* (2012) and Aji *et al.* (2015).

Saponification value for the sandbox oil was 245.98 mg KOH/g, 210.10 mg KOH/g for sandbox bio-lubricant, 201.96 mg KOH/g for titanium oxide nanoparticle-enriched bio-lubricants (SBTiO75 and SBTiO150), while that of conventional lubricant SAE 40 was 213.18 mg KOH/g as presented in Figure 3. There is decrease in the saponification values of the nanoparticle-enriched bio-lubricants compared to crude sandbox oil by 18% due to the esterification reaction for the free fatty acid reduction using methanol. The reason being that saponification value is said to have strong positive correlation with free fatty acids content. According to Yerima *et al.* (2018), the higher the free fatty acids, the higher the saponification value and vice versa. The high saponification values indicate the presence of high percentage of free fatty acids which might lead to foam formation. The obtained values are comparable to 198.76 mg KOH/g reported by Mohammed (2015) for crude jatropha oil, 193.04 mg KOH/g for moringa oil, 196.35 mg KOH/g for castor oil and 194.75 mg KOH/g for cotton oil which reduced to 193.15 mg KOH/g, 186.11 mg KOH/g, 182.75 mg KOH/g and 191.20 mg KOH/g for jatropha, moringa, castor and cotton bio-lubricants respectively. The values also align with 198.76 mg KOH/g reported by Bilal *et al.* (2013) for crude jatropha oil.

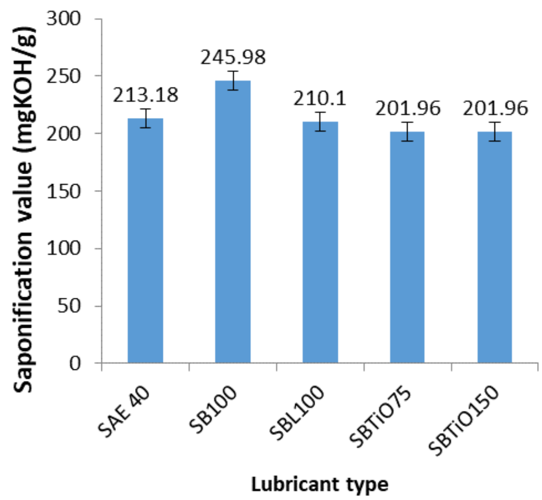


Figure 3: Effect of nanoparticle enrichment on saponification value of the bio-lubricants

Note:
SAE 40: Conventional lubricant
SB100: Sandbox oil only
SBL100: Sandbox bio-lubricant
SBTiO75: Oil + 0.75 wt% TiO_2
SBTiO150: Oil + 1.50 wt% TiO_2

Iodine value of conventional lubricant SAE 40 was 102 $gI_2/100g$, while that of crude sandbox oil, sandbox bio-lubricant, and nanoparticle-enriched bio-lubricants SBTiO75 and SBTiO150 were 177.66 $gI_2/100g$, 148.96 $gI_2/100g$, 166.03 $gI_2/100g$ and 175.65 $gI_2/100g$ respectively as shown in Figure 4. This shows that there is decrease in the iodine value of the bio-lubricants compared to that of crude sandbox oil. Iodine value is the measurement of fats and oils unsaturation. 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. Oils with high iodine value according to Yerima *et al.* (2018) have lower melting point and performs better in cold weather. The iodine value of sandbox oil was high, owing to the fact that the oil contains unsaturated glycerides, which have the ability to absorb a definite amount of iodine. These values are comparable to 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 Mohammed (2015) in a previous research work and 102.9 $gI_2/100g$ obtained for conventional lubricant SAE 40.

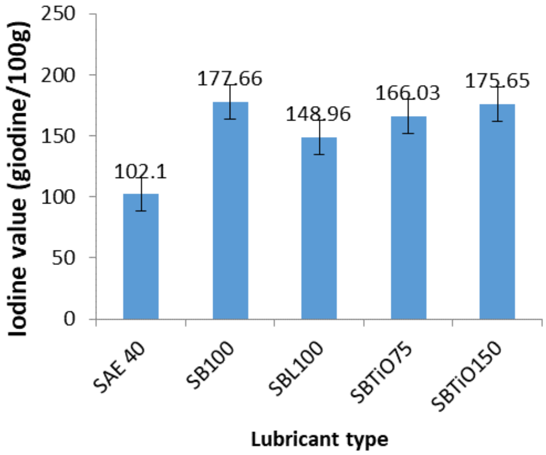


Figure 4: Effect of nanoparticle enrichment on iodine value of the bio-lubricants

Acid value of the crude sandbox oil and bio-lubricants which is the number of grams of potassium hydroxide required to neutralize one gram of oil ranged between 1.68 mgKOH/g and 2.93 mgKOH/g as presented in Figure 5, while the acid value for conventional lubricant SAE 40 was 4.40 mgKOH/g. This shows that there is decrease 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 makes it of higher quality. This is very good because the lower the acid value of the oil, the higher the quality. 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 results obtained are in agreement with the findings of Aji *et al.* (2015) where acid values of 1.60 mgKOH/g for neem oil bio-lubricant and 3.90 mgKOH/g for jatropha oil bio-lubricant were reported. The acid values of all the samples 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 Yerima *et al.* (2018).

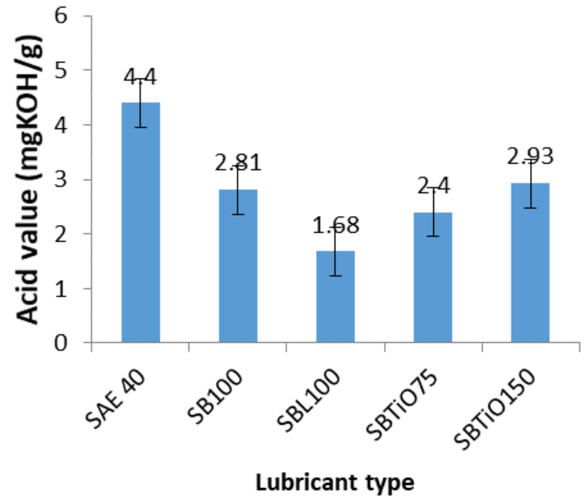


Figure 5: Effect of nanoparticle enrichment on acid value of the bio-lubricants

Free fatty acid values for the crude sandbox oil and bio-lubricants ranged between 8.42 mgKOH/g and 14.03 mgKOH/g as shown in Figure 6. The free fatty acid content of the crude sandbox oil reduced from 14.03 mgKOH/g to 8.42 mgKOH/g as a result of series of modification the oil undergoes through trans-esterification processes. But addition of 0.75 % w/w titanium oxide nanoparticle to the sandbox bio-lubricant increased the fatty acid by 2.3%, while that of 1.50% w/w titanium oxide nanoparticle increased the value by 8.2%. Bilal *et al.* (2013) recommended that oil used in transesterification reaction should contain not more than 1% free fatty acid. The values obtained are in-line with previous work by Singh (2015) and Mohammed (2015) 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.

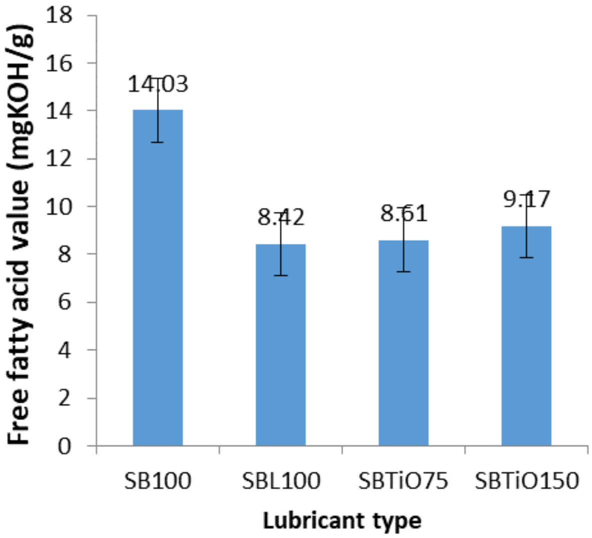


Figure 6: Effect of nanoparticle enrichment on free fatty acid of the bio-lubricants

Viscosities of nanoparticle-enriched bio-lubricants are 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 nanoparticle-enriched bio-lubricants at 40°C were 38.50 cSt and 47.60 cSt and 8.60 cSt and 9.40 cSt at 100°C for SBTiO75 and SBTiO150 respectively. The lubricant SBTiO75 conforms to the ISO VG32 specifications of > 28.80 cSt at 40°C and 4.10 cSt at 100°C, while SBTiO150 conforms to ISO VG46 specifications of > 41.4 cSt at 40°C and 4.10 cSt at 100°C according to ISO viscosity classification recommended for automobiles applications as reported by Arianti and Widayat (2018) and Aji *et al.* (2015). In earlier works, Bahari (2017) reported viscosities of 92.45 cSt at 40°C and 12.32 cSt at 100°C for conventional lubricant SAE 40. Hassan *et al.* (2016a) and Hassan *et al.* (2016b) 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. Abdul-Fattah *et al.* (2017) also reported viscosity of 42.8 cSt at 40°C for SAE 30. Menkiti *et al.* (2017) 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.

In other research work, Bilal *et al.* (2013) reported viscosities of 55.17 cSt and 10.96 cSt for jatropha oil based bio-lubricant at 40°C and 100°C respectively. Mohammed (2015) reported viscosities of 45.57 cSt for jatropha oil based bio-lubricant, 62.73 cSt for moringa oil based bio-lubricant and 46.46 cSt for cotton oil based bio-lubricant at 40°C as well as 7.60 cSt for jatropha oil based bio-lubricant, 9.27 cSt for moringa oil based bio-lubricant and 7.14 cSt for cotton oil based bio-lubricant at 40°C. Sripada (2012) reported viscosities of 40.5 cSt and 7.80 cSt for canola oil based bio-lubricant. These reports show a good comparison between sandbox oil based lubricant and other seed oil based lubricants.

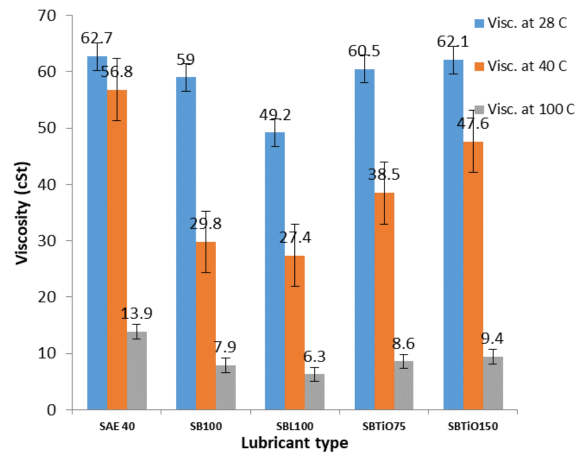


Figure 7: Effect of nanoparticle enrichment and temperature on viscosity of the bio-lubricants

Viscosity index of the bio-lubricants and sandbox oil ranged between 149.29 and 172.96 while the viscosity index of the conventional lubricant SAE 40 was 161.22 as shown in Figure 8, which could meet the requirement of the ISO VG46 lubricant since it is within the ISO viscosity range 46 standard. This shows that there is 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 according to Garces *et al.* (2011) can vary from 30 to 240 for automobiles. The high viscosity indexes obtained will allow the lubricants to keep their lubrication properties at higher temperatures. A good multipurpose lubricant maintains a constant viscosity throughout temperature changes. In comparable with other research works, Asrul *et al.* (2013), Mohammed (2015) and Singh *et al.* (2018) reported viscosity index of 125, 162 and 110 respectively for conventional lubricant SAE 40, Hassan *et al.* (2016a) and Hassan *et al.* (2016b) reported viscosity index of 267.68 for SAE 30, Bilal *et al.* (2013), Menkiti *et al*. (2017), Sripada (2012) and Ahmed *et al.* (2014) reported viscosity indexes of 180.00, 187.00, 167.00, 204.00 and 170.00 for jatropha oil, palm oil, palm kernel, canola oil and soybean oil based lubricants respectively. Mohammed (2015) reported 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.

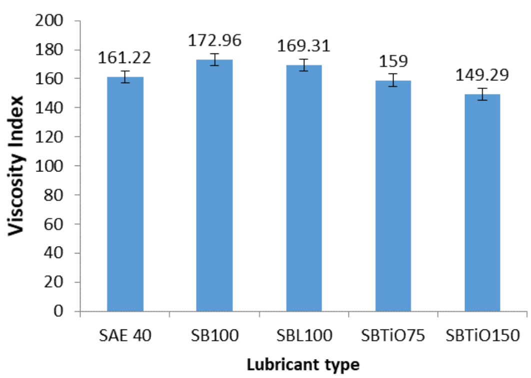


Figure 8: Effect of nanoparticle enrichment on viscosity index of the bio-lubricants

Pour point of the sandbox oil improved from -3°C to – 4.0°C for the titanium oxide nanoparticle-enriched bio-lubricant. The pour points of the bio-lubricants when compared with that of conventional lubricant SAE 40 which had a pour point of 3°C are more preferred. The reason for low pour point value obtained for SAE 40 is due to its higher viscosity compared to other bio-lubricants. Cloud points improved from 11°C – 0.50°C as shown in Figure 9. These improvements were due to the transesterification reaction and nanoparticle additive. These 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 (TMP) as reported by Menkiti *et al.* (2017). These values are consistent with the pour point and cloud point values of other bio-lubricants as reported by Menkiti *et al.* (2017), Bilal *et al.* (2013) and Sripada (2012) from previous studies. Low temperature fluidity according to Sripada (2012) is the most essential property for lubricants to perform in environments that are extremely cold. In their work, Menkiti *et al.* (2017) reported an improvement in the pour point of crude jatropha oil from – 7°C to – 12°C for jatropha oil based bio-lubricant. Bilal *et al.* (2013) reported improved pour points of jatropha oil from 5°C to – 7°C for its bio-lubricant. Aji *et al.* (2015) reported pour points of 1.30°C for neem based bio-lubricant, 0.20°C for jatropha based bio-lubricant and -30°C for mineral oil SAE 50. Singh *et al.* (2018) reported pour point of -21°C for mineral oil SAE 40. Shah *et al.* (2019) also reported pour point of -15°C and cloud point of -20°C for mineral oil SAE 40.

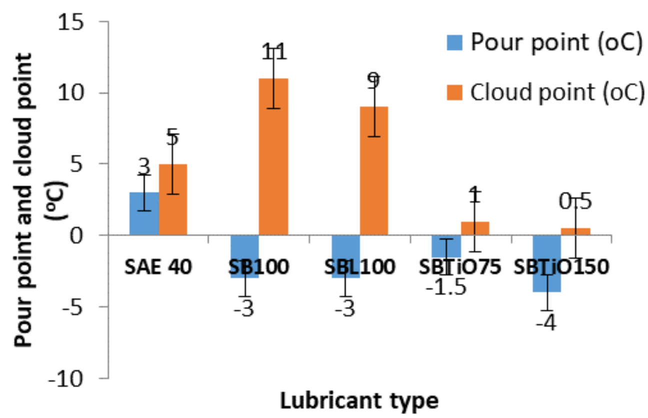


Figure 9: Effect of nanoparticle enrichment on pour and cloud points of the bio-lubricants

The flash points and fire points of titanium oxide nanoparticle-enriched bio-lubricant was found to be relatively lower than that of sandbox bio-lubricant due to the addition of nanoparticle additive. The flash and fire points of the sandbox bio-lubricant and SBTiO150 bio-lubricant were higher than that of crude sandbox oil as shown in Figure 10. It is clear from the results obtained that the bio-lubricants have very good flash and fire points as they can be compared with conventional lubricant SAE 40. The values indicate that the bio-lubricants can be used in both humid and temperate regions and transported safely with minimum risks of explosion. These values are similar to the values of previous work by Ettefaghi *et al.* (2013) and are in agreement with them. Ahmed *et al.* (2014) reported flash point of 256°C for soybean oil based bio-lubricant. Singh *et al.* (2018) reported flash point of 200°C for mineral oil SAE 40. Shah *et al.* (2019) also reported flash point of 204°C and fire point of 209°C for mineral oil SAE 40. Aji *et al.* (2015) reported flash points of 262°C for neem based bio-lubricant, 274°C for jatropha based bio-lubricant and 234°C for mineral oil SAE 50.

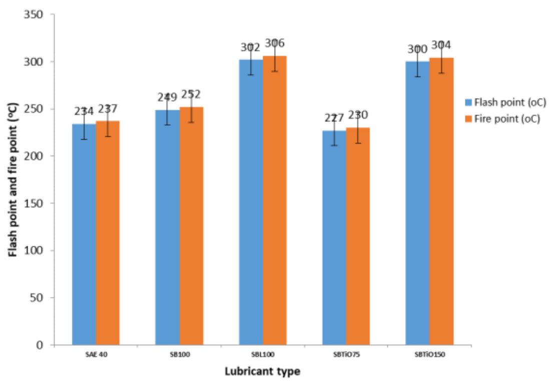


Figure 10: Effect of nanoparticle enrichment on flash and fire points of the bio-lubricants

CONCLUSION

The chemo-physical properties of the sandbox oil were enhanced with the addition of titanium oxide nanoparticle. The titanium oxide nanoparticle-enriched bio-lubricant exhibited good chemo-physical properties and could be favourably used in automobile application as engine oil.

Sandbox oil is a potential vegetable oil that can be used as alternative lubricant feedstock in automobile engine oil production. This is because it has good chemo-physical properties besides the advantages of vegetable oil like renewability, biodegrability, and non-toxic.

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