BIODEGRADABILITY OF NON-EDIBLE VEGETABLE OILS AND ITS BIOLUBRICANTS: EXPERIMENTS AND EMPIRICAL MODELS

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Abstract:

The environmental concern associated with the use of mineral oil based lubricants has necessitated the search for biodegradable lubricants. Currently, vegetable oils are considered to be alternatives to mineral oils for lubricant base oils due to certain inherent technical properties and their ability to be biodegradable. Whereas, research on biolubricants has advanced, very little has been done on the biodegradability of vegetable oil based lubricants especially on the impact on bioldegradability of the modification processes used for development of biolubricants. The synthesis of biolubricants from jatropha and castor oils using TMP polyol and evaluation of their biodegradability as compared to commercially available mineral oil based lubricant SAE 20/W50 was successfully carried out. The non-edible vegetable oils and lubricants were inoculated with the *Bacillus sp.* CDB-08 bacterial isolated from petroleum contaminated soil and their biodegradability over 28 days at an interval of 7 days was determined using gravimetric and visible ultraviolet spectroscopy methods. The jatropha oil, castor oil, jatropha TMP ester biolubricant, castor TMP ester biolubricant and mineral oil based lubricant after 28 days had 81.48 %, 96.6 %, 81.4 %, 81.4 % and 35.2 % biodegrability respectively. The jatropha oil biodegraded at the rate of 2.345 % per day and had a half-life of 22.2 days. The castor oil biodegraded at the rate of 3.1 % per day and had a half-life of 11.2 days. The jatropha TMP ester biolubricant biodegraded at the rate of 2.7 % per day and had a half-life of 22.5 days. The castor TMP biolubricant biodegraded at the rate of 2.6 % per day and had a half-life of 23.9 days. The mineral oil based lubricant biodegraded at the rate of 1.2 % per day and had a half-life of 40 days. The jatropha and castor oils as well as their synthesised TMP biolubricants are highly biodegradable while the mineral oil based lubricant is not readily biodegradable. The transesterification of jatropha and castor oils with TMP polyol has negligeable effects on their biodegradability.

Keywords: Biodegradability, biolubricants, environmentally-friendly, jatropha oil, castor oil, TMP esters, U-V spectroscopy.

Introduction

The environmental concern associated with the use of mineral oil based lubricants has necessitated the search for biodegradable lubricants. Also, the fluctuation in petroleum oil price and the depleting global mineral oil reserve has given rise to research into the development of more sustainable base stocks for lubricant production. Besides, the negative impact of mineral oil based lubricants on the soil, aquatic life, plants and the health of operators is another driver for biolubricant research.

Currently, vegetable oils are Considered to be alternatives to mineral oils for lubricant base oils due to certain inherent technical properties and their ability to be biodegradable (Garba *et al.*, 2013, Syaima *et al.*, 2014, Menkiti *et al.*, 2015, Kania et al., 2015, and Onuh *et al.*, 2017). Stojilković and Kolb (2016) carried out a study on the tribological properties of biodegradable universal tractor transmission oil using rapeseed, soybean and sunflower oil and compared their properties with a commercial mineral oil based universal tractor transmission oil. all the three vegetable oils had better tribological performance compared to the universal tractor transmission oil. Compared to mineral oils, vegetable oils in general possess high flash point, high viscosity index, high lubricity and low evaporative loss (Erhan and Asadauskas, 2000; Adhvaryu and Erhan, 2002; Mercurio, *et al.*, 2004, and Woma *et al.*, 2019a). Vegetable oils have been found to be less dangerous to the soil, water, flora and fauna during disposal or accidental spillage compared to mineral oil (Mercurio *et al.* 2004; Ajithkumar, 2009., and Awoyale *et al.* 2011). Poor oxidative and hydrolytic stability, high temperature sensitivity of tribological behaviour and poor cold flow properties are reckoned to be the limitations of vegetable oils for their use as base oils for industrial lubricants (Erhan and Asadaukas, 2000; Adhvaryu *et al.* 2005). Woma, *et al.*, (2019b) in a review made detail analysis of the prospects and challenges of vegetable oils as lubricants for industrial applications.

The current effort to overcome the limitations of using vegetable oils as lubricants includes the use of additives, chemical modifications and thermal modifications (Li and Wang, 2015). It has been found that, esterification, transesterification, hydrolysis and thermal cracking of vegetable oils succeeded in altering their chemical bonds and made them more suitable for application as lubricants (Maleque *et al.*, 2003, Menkiti *et al.*, 2015, Zulkifli *et al.*, 2015, Musa *et al*., 2016, Karmakar *et al.*,2017, Onuh et al., 2017, and Kania *et al.*, 2017).

Also, some researchers successfully supressed the poor properties of vegetable oils using chemical additives. The inoculation of 2 wt% ZDDP in corn and canola oils lowered the friction coefficient for both oils (Azhari *et al*., 2015). Quinchia *et al*., (2013) researched tribological potential of vegetable oil-based lubricants containing eco-friendly viscosity modifiers and found that ethyl cellulose (EC) was more competitive than ethylene–vinyl acetate copolymer (EVA) as a viscosity modifier with the best viscosity increments (125% at 40^0C) corresponding to castor oil- ethyl cellulose blend. Erhan *et al.* (2006), studied the resistance to oxygen attacks and cold flow characteristics of vegetable oil based lubricants by adding Zinc diakyl dithiocarbamate (ZDDC) and Antimony diakyl dithiocarbamate (ADDC) to five vegetable oils (refined soya bean oil, mild oleic soya bean oil, high oleic soyabean oil, highly enriched safflower and h sunflower oils) then evaluating their pour point as per American Society of Testing and Materials (ASTM) ASTM D97 method (ASTM, 2002a), oxidation and low temperature stability using differential scanning calorimetry (DSC) and rotating bomb oxidation tests (RBOT) as per ASTM D-2272 (ASTM, 2002b) standard and comparing the result to that of a commercial biodegradable hydraulic fluid. The results showed that the vegetable oils formulated according to the above methods exhibited higher oxidation resistance and better low temperature characteristics compared to the commercial hydraulic fluid and compared at the same level with mineral based lubricants. Similarly, it has been found that vegetable oils blended with some nanoparticles had improved properties (Alves *et al*., 2013, and Shafi *et al.,* 2018).

Biodegradation is the braking down of organic substances in the presence of enzymes secreted by micro-organisms. Organic material can be degraded aerobically, with oxygen or anaerobically, without oxygen. A term related to biodegradation is biomineralisation, in which organic matter is converted into minerals (Diaz, 2008). Whenever any substance is placed in the environment, it begins to undergo degradation due to the action of relevant substrate utilizing microorganisms. Every substance, irrespective of its complexity and toxicity is subject to this process (Aluyor et al., 2009). Biodegradability is assessed by following certain parameters which are considered to be indicative of the consumption of the test substance by microorganisms, or the production of simple basic compounds which indicate the mineralization of the test substance. The widely accepted standards for testing the environmental characteristics of lubricants is shown in Table 1. Aluyor *et al.*, (2009) reviewed the two major methods of biodegradability testing.

Table 1: Commonly accepted standards for testing environmental properties of lubricants (Sander, 2017).

Biodegradability	Toxicity	Bioaccumulation
ASTM D6006: Assessing Biodegradability of Hydraulic Fluids	ASTM D6081: Aquatic Toxicity Testing	OECD 107: Partition Coefficient Shake Flask Method
ASTM D5864: Determining Aerobic Aquatic Biodegradation/OCED 301B: Freshwater Modified Sturm Test	OECD 201: Freshwater Alga and Cyanobacteria, Growth Inhibition Test	OECD 117: Partition Coefficient HPLC Method
ASTM D6139: Determining Aerobic Aquatic Biodegradation, Gledhill Shake Flash/OCED 301D: Freshwater Closed Bottle Test	OECD 202: Daphnia sp., Acute Immob ilization and Reproduction Test	
ASTM D6731: Determining Aerobic Aquatic Biodegradability, Closed Respirometer/OCED 301F: Modified Biodegradation Test	OECD 203: Fish, Acute Toxicity Test	
ASTM D7373: Predicting Biodegradability, Biokinetic Model	OECD 210: Fish, Early-Life Stage Toxicity Test	
OECD 301C: Modified MITI Test	OECD 211: Daphnia Magna Reproduction Test	

O.E.C.D. = Organisation for Economic Co-operation and Development. ASTM = American Society for Testing and Materials

Lubricants must not only meet societal demands but must in addition evolve from a purely technical fulfillment of functions, to fulfil eco-toxicological properties and/or sustainability criteria Shah, *et al.,* (2021). The biodegradability of different lubricant base stocks as per ASTM D5864 standard is shown in Table 2. These values are a summary of the results of an interlaboratory study that tested ten different lubricant base stock samples to evaluate the test method’s reproducibility (Shah, *et al.*, 2021).

Table 2: Biodegradability of different lubricant base stocks as per ASTM D5864 standard
(Wilde *et al*., 2015)

Lubricant Base Stocks	% Ultimate Biodegradation	
	Average	Standard Deviation
Vegetable oil hydraulic fluid	65.0	6.1
Vegetable oil-based grease	56.4	14.7
Low biodegradable synthetic PAO	21.1	8.8
Vegetable oil-aluminum complex grease	19.3	11.9
High biodegradable synthetic hydraulic fluid	59.7	13.6
Mineral oil hydraulic fluid	26.0	6.4
High biodegradable synthetic PAO	58.8	12.2
High biodegradable synthetic ester	70.8	7.8
Moderately biodegradable synthetic PAO	29.5	8.9
Low erucic acid rapeseed	79.3	10.4

Several researchers studied the biodegredebility and oxidative stability of industrial fluids obtained from vegetable oils. These include; as methyl esters (Demirba, 2009); as hydraulic fluids (Abdalla and Patel, 2006; Petlyuk *et al.*, 2004); and as lubricant

(Fernando and Hanna, 2002). Biodegradability studies of vegetable oil based lubricants was also carried out by Luna *et al.*, (2015) using a bio-kinetic model. The result established that the pure castor oil was most biodegradable with half-life of 12 days, followed by biolubricants from castor oil with half- life between 20 to 30 days; but mineral oil had half-life of over 200 days. It was also discovered that there was no much change in biodgrability of lubricants developed by esterification of castor oil using different kinds of alcohols. While the validity of the conclusions of Luna *et al.*, (2015) is in no doubt, the method of test applied (bio-kinetic model) is not generally accepted. Because a manufacturer cannot claim his product is biodegradable unless it has the proven capability to decompose in the most common environment where the product may be disposed within three years through natural biological processes into nontoxic carbonaceous soil, water, carbon dioxide or methane (Aluyor et al., 2009). Thus, there is a need to evaluate the biodegradability of non- edible vegetable oil- based lubricants using methods that similar to natural processes. This work will measure biodegradability of oils inoculated with micro-organism extracted from natural soil and water. Similarly, Abubakar *et al.,* (2020) estimated the biodegradability of biodiesel synthesised from water melon seed (*Citrullus lanatus*) and found that the biodiesel had a biodegradability of 38.45%. The result of Abubakar *et al.*, (2020) is low compared to tests carried out severally that indicates that vegetable oils undergo about 70-100% biodegradation in a period of 28 days (Aluyor et al., 2009).

Whereas, research on biolubricants has advanced, very little has been done on the biodegradability of vegetable oil based lubricants. More worrisome is the fact that researchers have neglected the investigation of the impact on bioldegradability of the modification processes used for development of biolubricants. There is also a dearth of knowledge on the biodegradation of jatropha and castor oil based lubricants. This work seeks to fill this identified gap by quantifying the biodegradability of non-edible vegetable (jatropha and castor) oil based biolubricants. The biodegradability of the castor and jatropha oil based lubricants is also compared with mineral oil based lubricant SAE 20/W50 available in Nigerian market.

Materials and Methods

Materials

Jatropha and castor oils were obtained from Agrienery, Nigeria. Commercially available mineral oil based lubricant SAE 20/W50 was also obtained from Nigerian market. Water sample from drainage channel as well as soil contaminated will used petroleum from a motor cycle workshop were collected. Diethyl-ether (pet-ether) from JHD chemical reagents company limited Guangzhou, 100 mls conical flask, petri dishes and nutrient agar were collected. A visible ultra violet spectrumeter model 752 shown in Figure 1 was also used.

Figure 1: Visible Ultra violet photometer

Synthesis of jatropha and castor oil TMP esters biolubricant

The free fatty acid percentage of the jatropha and castor oils was reduced to less than 1 % by acid catalysed esterification carried according to Abdulkareem *et al*., (2012) and Salimon *et al;* (2014) with slight changes. The esterified jatropha and castor oils were transesterified according to Talib *et al*; (2017) and Kadry (2015) to produce jatropha methyl ester and castor methyl ester.

The TMP biolubricants were synthesised after Musa *et al.*, (2016). The catalyst which is Potassium methoxide (30% w/w KOH in methanol) was prepared by weighing out the Potassium hydroxide (KOH) and dissolving it in methanol at 60^0C. Then each of the jatropha and castor oil methyl esters were transesterified with trimethylolpropane (TMP) at a mole ratio of methyl ester to TMP of 4.0: 1 in the presence of 0.8 % w/w Potassium methoxide catalyst. The transesterification was carried out at 120^0C in a three-neck flask equipped with a digital thermometer, magnetic stirrer and heater positioned in a fume chamber for extraction of methanol as by product as shown in Figure 2. After four hours the jatropha and castor biolubricants were separated from other by-products, washed and dried. The confirmation of the formation of the jatropha and castor biolubricants was confirmed using Fourier infrared spectroscopy (FTIR).

Figure 2: Jatropha and castor oil TMP esters biolubricant synthesis experimental setup

Measurement of biodegradability

The biodegradability test of the oils and lubricants as compared to that of the SAE 20/W50 was carried out according to Ijah and Antai (2003). Sterile sampling bottles were used to collect water sample from a drainage channel and soil sample was collected from petroleum oil contaminated soil in a motor cycle workshop. Microbes (bacteria and fungi) were isolated from the water and soil samples and identified by characterisation based on gram staining and biochemical tests. The oil samples were inoculated with the *Bacillus sp.* CDB-08 bacterial isolated from petroleum contaminated soil and the oils were recovered using diethyl-ether every seven days for 28 days. A control test was also carried out and the extent of the degradation was determined by gravimetric analysis method. The method involved the extraction of the residual oils with 50 ml petroleum ether and measuring its weight. Also, the visible ultra-violet spectroscopy of the residual oil samples was carried out by noting the absorbence reading at 520 nm wavelength. The percentage biodegradability of the oils was also determined by weighing the amount of recovered oil at interval of 7 days over a period of 28 days using equation (1)

$$\%\,biodegradation = \frac{(Wao - Wro)X100}{Wao} \quad (1)$$

Where W_{ao} = weight of the added oil; and W_{ro} = weight of the residual oil after days of bacterial inoculation.

The inoculated oils and lubricant samples were also subjected to visible ultraviolet ray spectroscopy. Samples were collected after every seven days, and subjected to visible U-V spectroscopy at 530 nm and their corresponding absorbance recorded.

Development of biodegradability empirical model

The empirical model of the biodegradability of the oils and lubricants was developed by plotting the biodegradability of the oils and lubricants against time. Then a straight- line fitting the plotted points was produced using Microsoft excel. The linear equation of the line of best fit with a regression square above 0.7 (over 70% fit) was taken to be the empirical model of the biodegradability of the oils and lubricants.

Results and Discussion

Jatropha and castor TMP ester biolubricant yield

The jatropha oil biolubricant produced had 96.95% yield of jatropha TMP esters, while the transesterification of the castor oil methyl ester produced 96.56% yield of castor oil TMP esters. This result is in agreement with the findings of Musa *et al*., (2016).

The presence of jatropha TMP ester was confirmed in the FTIR spectra by a peak found at the wave number 1740.7 cm^{-1} while the presence of castor oil ester TMP was confirmed at the peak of wave number 1736cm^{-1}. The castor oil biolubricant also has a peak showing the retention of the hydroxyl group at 3432.9cm^{-1}wave number.

Biodegradability of jatropha and castor oils

The percentage biodegradability of the jatropha and castor oils as well as that of the commercially available mineral oil based lubricant (SAE 20/W50) over a period of 28 days is shown in Table 3. The visible ultraviolet ray absorbance of the jatropha oil, castor oil and mineral oil based lubricant is shown in Table 4.

Table 3: Biodegradability of jatropha oil, castor oil and mineral oil-based lubricant (SAE 20/W50) over 28 days

Time (days)	% Biodegradability		
	Jatropha oil	Castor oil	SAE 20/W50
14	24.1264559	65.35433071	17.71894094
28	81.4753189	96.60433071	35.23421589

After 28 days of inoculation with bacteria, the castor oil had the highest percentage biodegradation of 96.6 %, followed by jatropha oil with 81.5% biodegradability. The mineral oil based lubricant had only 35.2% biodegradability. The jatropha and castor oils are readily biodegradable since over 60 % of the oils were degraded by the bacterial within 28 days. Conversely, the mineral oil based lubricant is not readily biodegrable. This result is higher than values reported by Wilde *et al.*, (2015), but are within the range of % biodegradability of vegetable oils reported by Aluyor *et al.*, (2009). The use of *Bacillus sp.* CDB-08 bacterial recovered from petroleum oil contaminated soil in this test contributed to the higher % biodegradability recorded as compared to values reported by Wilde *et al.*, (2015). Thus, it is concluded that vegetable oils have far greater % biodegradability than mineral oil based lubricants and the type/source of microorganism used in the biodegradatility test slightly affects the result.

Table 4: Visible U-V spectroscopy absorbence of jatropha oil, castor oil and mineral oil based lubricant

Oil/Lubricant	**Jatropha oil**	**Castor oil**	**SAE 20/W50**
Absorbence after 28 days (nm)	0.297	0.434	0.583

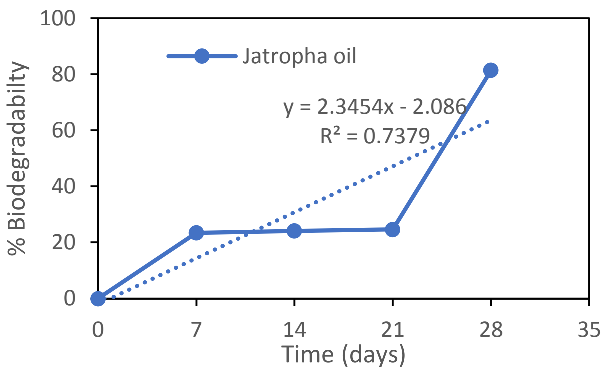
The mineral oil had the highest absorbance of 0.583 nm after 28 days of inoculation with bacteria while the jatropha oil had the lest absorbance of 0.297 nm followed by the castor oil with an absorbance of 0.434 nm. The visible U-V spectroscopy result confirms that the jatropha and castor oils are more biodegradable than the mineral oil base lubricant. The jatropha and castor oils were readily consumed by the bacteria such that their solution became less turbid and absorbed less U-V rays. The mineral oil based lubricant that was not readily consumed had a more turbid solution thereby absorbing more U-V rays.

The rate of biodegradation of jatropha and castor oils

The percentage biodegradability over time of the jatropha oil, castor oil and mineral oil based lubricant is shown in Figure 3. The jatropha oil biodegraded at the rate of 2.345 % per day. The half life (time it took for 50% oil to biodegrade) of the jatropha oil is 22 days, while the ultimate biodegradation time of the jatropha oil is 43.5 days. The empirical model of the rate of biodegradation of the jatropha oil inoculated with *Bacillus sp.* CDB-08 bacterial is given by equation (2)

$$y = 2.3454x - 2.086 \quad (2)$$

Where y is the percentage biodegradability and x is the time in days.



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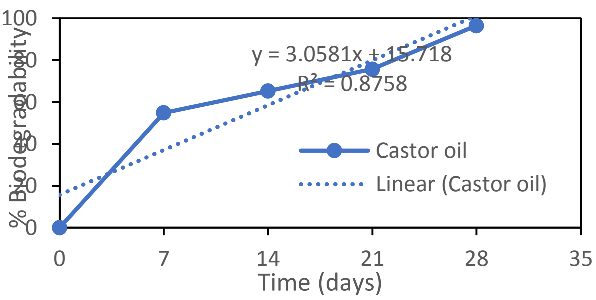

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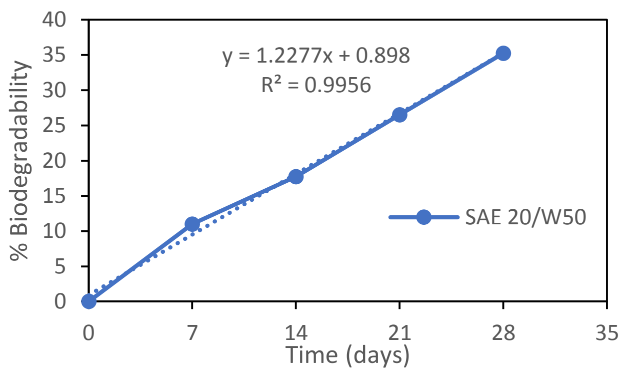


(c)

Figure 3: Percentage biodegradability over time (a) Jatropha oil (b) Castor oil (c) Mineral oil based lubricant (SAE 20/W50)

The castor oil biodegraded at the rate of 3.0581 % per day. The half-life (time it took for 50% oil to biodegrade) of the castor oil is 11.2 days, while the ultimate biodegradation time of the castor oil is 27.56 days. The empirical model of the rate of biodegradation of the castor oil inoculated with *Bacillus sp.* CDB-08 bacterial is given by Equation (3)

$$\boldsymbol{y = 3.058x + 15.718} \quad (3)$$

Where y is the percentage biodegradability and x is the time in days.

The half-life for the castor oil is in agreement with the findings of Luna et al., (2015), that reported half-life of fresh castor oil using biokinetic technique to be 12 days.

The mineral oil based lubricant biodegraded at the rate of 1.2277 % per day. The half life (time it took for 50% oil to biodegrade) of the mineral oil based lubricant is 40 days, while the ultimate biodegradation time of the mineral oil based lubricant is 80.72 days. The empirical model of the rate of biodegradation of the mineral oil based lubricant inoculated with *Bacillus sp.* CDB-08 bacterial is given by equation (4)

$$y = 1.2277x + 0.898 \qquad (4)$$

Where y is the percentage biodegradability and x is the time in days.

The half life of the mineral oil based lubricant is far lower than the over 200 days reported by Luna et al., (2015). This difference in result is due to the difference in the methods used for measuring the biodegradability. Also, the bacterial *Bacillus sp.* CDB-08 biodegrades mineral oils faster than most micro-organisms as reported by Ijah and Antai (2003). Thus, biokinetic technique is good for measuring biodegradation of vegetable oil but might need modification to be applied in mineral oil based biodegradability tests.

Comparison of jatropha oil, castor oil and mineral oil biodegradation process

The biodegradability over time of the jatropha and castor oil as compared to the mineral oil based lubricant is shown in Figure 4. The castor oil degraded at a very fast rate within the first seven days of inoculation with the bacterial *Bacillus sp.* CDB-08. The rate of biodegradation of the castor oil reduced from the 7th to the 21st day and increased after the first 21 days. The jatropha oil biodegraded at a high rate within the first seven days. The rate of biodegradation of the jatropha oil was constant between the 7th and the 21st day, and rapidly increased after the first 21 days.

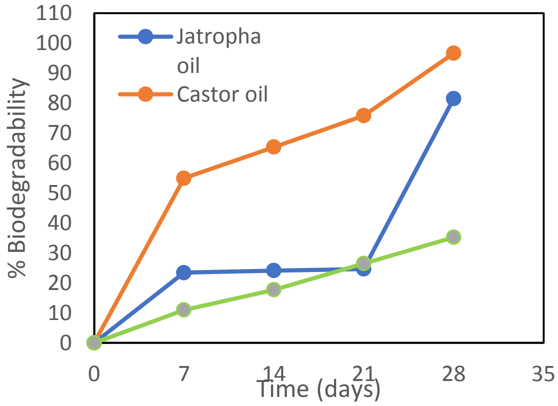


Figure 4: Percentage biodegradability of the jatropha oil, castor oil and SAE 20/W50 lubricant

The mineral oil based lubricant biodegraded at a slow rate. The mineral oil based lubricant biodegraded in the presence of the bacterial *Bacillus sp.* CDB-08 at a constant rate all through the period of the test. Comparatively, the castor oil biodegraded faster than the jatropha and mineral oil based lubricant. Both the jatropha and castor oil biodegraded faster than the mineral oil based lubricant. Whereas the castor oil maintained a higher rate of biodegradation than the jatropha and mineral oil based lubricant all through the test period, interestingly the jatropha and mineral oil based lubricant had the same % biodegradation on the 21st day. Therefore, comparing the biodegradability of vegetable based lubricants with those of mineral oil based lubricants inoculated with micro-organism at 21 days or less may lead to error. Jatropha and castor oils inoculated with the bacterial *Bacillus sp.* CDB-08 biodegrade at the highest rate within the first seven days. Mineral oil based lubricant biodegrades at constant rate while jatropha and castor oils biodegrade at a non-uniform rate.

Similar trend was observed in the absorbance of visible U-V ray as shown in Figure 5. The castor oil maintained a uniform lower absorbance than the mineral oil based lubricant all through the 28 days of the test. The initial absorbance of the jatropha oil was higher than that of the mineral oil based lubricant, but it decreased sharply with time and became lower than the absorbance of the mineral oil based lubricant after 21 days. Both the jatropha and castor oils had little to no change in absorbance within the first seven days of inoculation with the bacterial *Bacillus sp.* CDB-08. Thus, visible ultraviolet spectroscopy is a good, rapid and reproducible method for estimating the anaerobic biodegradability of lubricants inoculated with micro-organisms. The absorbance of ultraviolet rays by vegetable oils inoculated with micro-organism decreases with the increase in percentage biodegradation.

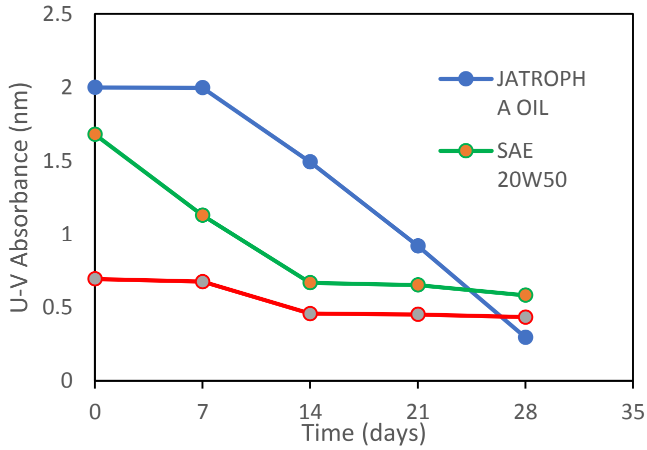


Figure 5: Visible U-V ray absorbance of the jatropha oil, castor oil and SAE 20/W50 lubricant

Biodegradability of jatropha and castor TMP ester biolubricants

The percentage biodegradability of the jatropha TMP biolubricant and castor TMP biolubricant as well as that of the commercially available mineral oil based lubricant (SAE 20/W50) over a period of 28 days is shown in Table 5. The visible ultraviolet ray absorbance of the jatropha TMP biolubricant, castor TMP biolubricant and mineral oil based lubricant (SAE 20/W50) is shown in Table 6.

After 28 days of inoculation with bacteria, the jatropha and castor TMP biolubricants had the same percentage biodegradability of 84%. The mineral oil based lubricant had only 35.2% biodegradability. The jatropha and castor TMP biolubricants are readily biodegradable since over 60 % of the oils were degraded by the bacterial within 28 days. Conversely, the mineral oil based lubricant is not readily biodegrable. This result is within the range of % biodegradability of vegetable oil based lubricants reported by Aluyor *et al.*, (2009).

Table 5: Biodegradability of jatropha TMP ester biolubricant, castor TMP ester biolubricant, and mineral oil-based lubricant (SAE 20/W50) over 28 days

Time (days)	% Biodegradability		
	Jatropha TMP ester biolubricant	Castor TMP ester biolubricant	SAE 20/W50
14	11.665	15.675	17.71894094
28	81.442	81.403	35.23421589

Table 6: Visible U-V spectroscopy absorbence of jatropha TMP biolubricant, castor TMP biolubricant and mineral oil based lubricant

Lubricant	Jatropha TMP biolubricant	Castor TMP biolubricant	SAE 20/W50
Absorbence after 28 days (nm)	0.111	0.175	0.583

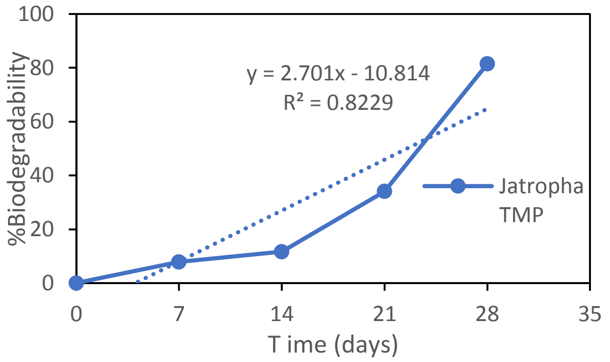
The jatropha TMP biolubricant had the least ultraviolet ray absorbance of 0.111 nm, followed by the castor TMP biolubricant while the mineral oil based lubricant had the highest absorbance of 0.583 nm. The low absorbance of the vegetable oil TMP ester biolubricants corresponded to the high percentage biodegradability of the TMP biolubricants while high absorbance of the mineral oil based lubricant corresponded to its low percentage biodegradability. The jatropha and castor TMP ester lubricants unlike the mineral oil based lubricants were readily consumed by the bacteria such that their solution became less turbid and absorbed less U-V rays.

The rate of biodegradation of jatropha and castor TMP ester biolubricants

The graph of the percentage biodegradability over time of the jatropha TMP ester biolubricant and castor TMP ester biolubricant is shown in Figure 6. The jatropha TMP ester biolubricant biodegraded at the rate of 2.701 % per day. The half-life (time it took for 50% oil to biodegrade) of the jatropha TMP ester biolubricant was 22.5 days and the ultimate biodegradation time was 41 days. The empirical model of the rate of biodegradation of the jatropha TMP ester biolubricant inoculated with *Bacillus sp.* CDB-08 bacterial is given by equation (5).

$$y = 2.701x - 10.814 \quad (5)$$

Where y is the percentage biodegradability and x is the time in days.



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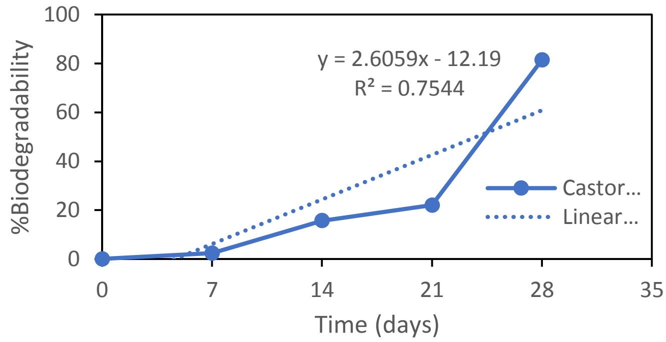


(b)

Figure 6: Percentage biodegradability over time (a) Jatropha TMP ester biolubricant (b) Castor TMP ester biolubricant

The castor TMP ester biolubricant biodegraded at the rate of 2.6059 % per day. The half-life of the castor TMP ester biolubricant was 23.87 days and the ultimate biodegradation time was 43.1 days. The empirical model of the rate of biodegradation of the jatropha TMP ester biolubricant inoculated with *Bacillus sp.* CDB-08 bacterial is given by Equation (6).

$$y = 2.6059x - 12.19 \quad (6)$$

Where y is the percentage biodegradability and x is the time in days.

The half life for the castor TMP ester biolubricant is in agreement with the findings of Luna et al., (2015), that reported half life of castor biolubricants determined using biokinetic test methods to be between 20-26 days. Non edible vegetable oil based biolubricants generally have similar biodegradability and biodegrades through a similar process. The type of alcohol, catalyst, process or type of none edible vegetable oil used to develop non edible vegetable oil TMP ester biolubricants has little effect on their biodegradability.

Comparison of jatropha, castor TMP ester biolubricant and mineral oil biodegradation process

The biodegradability over time of the jatropha and castor TMP ester biolubricants as compared to the mineral oil based lubricant is shown in Figure 7. The visible U-V ray absorbance of the jatropha TMP ester biolubricant, castor TMP ester biolubricant and mineral oil based lubricant is shown in Figure 8.The castor TMP biolubricant degraded at a slow rate within the first seven days of inoculation with the bacterial *Bacillus sp.* CDB-08. The rate of biodegradation rate of the castor TMP biolubricant slightly increased from the 7th to the 21st day and rapidly increased after the first 21 days.

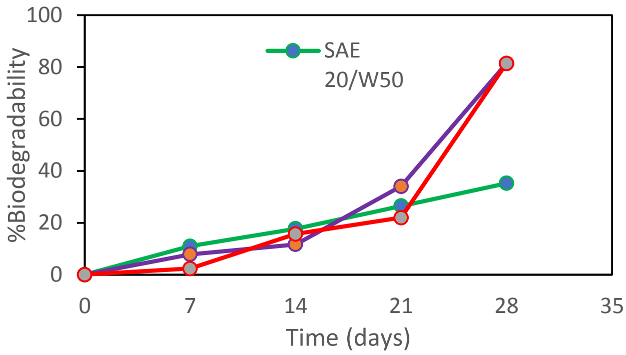


Figure 7: Percentage biodegradability of the jatropha TMP biolubricant, castor TMP biolubricant and mineral oil based (SAE 20/W50) lubricant

The jatropha TMP ester biolubricant biodegraded at a slow rate within the first 14 days. The rate of biodegradation of the jatropha TMP biolubricant rapidly increased after the first 14 days. The mineral oil based biolubricant had a uniform rate of biodegradation which vegetable oil TMP ester biolubricants had non uniform rate of biodegradation. Within the first 14 days of inoculation with *Bacillus sp.* CDB-08, the non-edible vegetable oil TMP ester biolubricants had a lower percentage biodegradation compared to the mineral oil based lubricant; their biodegradation started exceeding that of the mineral oil only after 14 days of inoculation with *Bacillus sp.* CDB-08. Summarily, the mineral oil based lubricant exceeded the vegetable oil TMP ester biolubricants in biodegradation in the first 14 days. Therefore measuring biodegradability over a time lower than 21 days may lead to an erroneous conclusion.

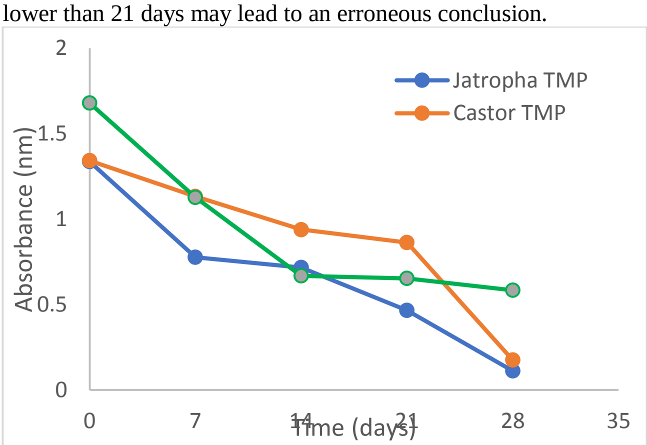


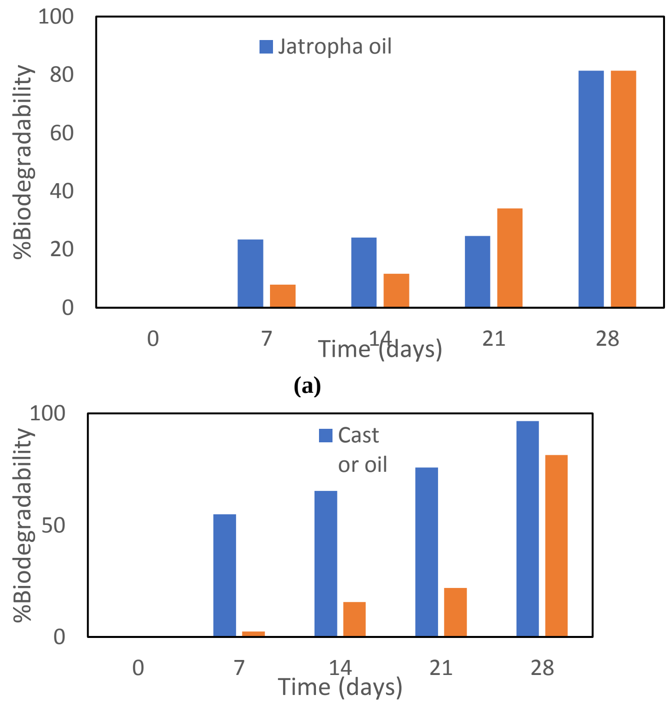
Figure 8: Visible U-V ray absorbance of the jatropha TMP ester biolubricant, castor TMP ester biolubricant and mineral oil based (SAE 20/W50) lubricant

Compared to mineral oil based lubricant, the castor TMP ester biolubricant had higher absorbance of the U-V ray between the 7th and 21st day of inoculation with *Bacillus sp.* CDB-08. Also, the jatropha TMP ester biolubricant had lower absorbance compared to the mineral oil based lubricant.Thus, visible ultraviolet spectroscopy is a good, rapid and reproducible method for estimating the anaerobic biodegradability of lubricants inoculated with micro-organisms. The absorbance of ultraviolet rays by vegetable oils inoculated with micro-organism decreases with the increase in percentage biodegradation.

Effect of transesterification with TMP polyol on biodegradability of jatropha and castor oils

The biodegradability of the jatropha and castor oils as compared to the jatropha and castor TMP esters biolubricants is shown in Figure 9. The percentage biodegradability of the jatropha oil was higher than that of the Jatropha TMP ester biolubricant in the first 14 days. The percentage biodegradability of the jatropha TMP biolubricant was higher than that of the jatropha oil on the 21st day. After the 28th day, the jatropha oil and jatropha TMP biolubricant had the same biodegradability. Thus, transesterification of jatropha oil with TMP polyol does not affect its biodegradability.

The castor oil percentage biodegradability was higher than that of the castor TMP ester biolubricants throughout the period of the test. After 28 days of inoculation with *Bacillus sp.* CDB-08, the castor oil had percentage biodegradability of 96 % while the castor TMP ester biolubricant had a biodegradability of 81 %. Thus, transesterification of castor oil with TMP polyol leads to slight decrease in its percentage biodegradability. This result is in agreement with the findings of earlier researchers like Luna et al., (2015).



(b)

Figure 9: Comparison of biodegradability of vegetable oils and vegetable oil TMP lubricants (a) Jatropha oil and jatropha TMP lubricant (b) Castor oil and castor TMP lubricant

Conclusion

The study of the biodegradability of two non-edible vegetable oils (jatropha and castor oils have been successfully carried out. Non edible vegetable oils and their derived TMP biolubricants have far greater % biodegradability than mineral oil based lubricants and the type/source of microorganism used in the biodegradability test slightly affects the result. Castor has a higher rate of biodegradation than jatropha oil while both oils by far exceed mineral oil based lubricant in the rate of biodegradation. Jatropha and castor oils have non uniform rate of biodegradation. Jatropha and castor oils inoculated with the bacterial *Bacillus sp.* CDB-08 biodegrade at the highest rate within the first seven days. Mineral oil based lubricant biodegrades at constant rate while jatropha and castor oils biodegrade at a non-uniform rate. Measuring of the biodegradability of lubricant sample should be carried out at least over a period of 28 days to avoid error. Visible ultraviolet spectroscopy is a good, rapid and reproducible method for estimating the anaerobic biodegradability of lubricants inoculated with micro-organisms. The absorbance of ultraviolet rays by vegetable oils inoculated with micro-organism decreases with the increase in percentage biodegradation. Both jatropha and castor TMP biolubricants are highly biodegradable and by far exceed the biodegradability of mineral oil based lubricant. Transesterification of non-edible vegetable oils with TMP polyol has negligeable effects on their biodegradability.

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References

Abdalla HS, Patel S (2006). The performance and oxidation stability of sustainable metalworking fluid derived from vegetable extracts. *Proceedings of the Institution of Mechanical Engineers, Part B: J. Engine. Manufacture* 220: 12

Abdulkareem, A.S., Jimoh, A., Afolabi, A.S., Odigure, J.O., and Patience, D. (2012). Production and Characterization of Biofuel from Non-Edible Oils: An Alternative Energy Sources to Petrol Diesel. In Ahmed, A. Z. (Ed.), *Energy Conservation*, 171 -196. doi:10.5772/51341

Abubakar, H., Jauro, A., Abubakar, M. I., Abubakar, A., Yushau, S., Sallau, S., and Yakubu, H., (2020). Production and Biodegradability of Biodiesel from Citrullus Lanatus Seed Oil, *International Journal of Research and Innovation in Applied Science*, V(III), 134-141

Adhvaryu, A., and Erhan, S. Z. (2002). Epoxidized Soybean Oil as a Potential Source of High-Temperature Lubricants, *Ind. Crops Prod.*,15, 247–254.

Adhvaryu, A., Liu, Z., and Erhan, S. Z. (2005). Synthesis of Novel Alkoxylated Triacylglycerols and Their Lubricant Base Oil Properties, *Ind. Crops Prod.*,21, 113–119.

Ajithkumar, G., (2009). *Analysis, Modification and Evaluation of the Cold Flow Properties of Vegetable Oils as Base Oils for Industrial Lubricants*, Cochin University of Science & Technology Kochi-22, India

Aluyor, E.O., Obahiagbon, K.O., and Ori-jesu, M. (2009). Biodegradation of vegetable oils: A review, *Scientific Research and Essay*, 4(6), 543-548

Alves, S.M, Barros, B.S., Trajano, M.F., Ribeiro, K.S.B., and Moura, E. (2013). Tribological Behaviour of Vegetable oil- based lubricants with nano particles of oxides in boundary lubrication conditions, *Tribology International*, 65, 28-36.

American Society for Testing and Materials, (2002a) *ASTM D97–02, Standard Test Method for Pour Point of Petroleum Products*, West Conshohocken, PA, USA, ASTM International

American Society for Testing and Materials (2002b), *ASTM D2272-02, Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel*, West Conshohocken, PA, USA, ASTM International

Awoyale, A.A; Odubiyi ,O.A.and Eloka-Eboka, A. C.(2011). Production and Testing of Biodegradable Grease from Black-Date (Canarium schweinfurthii) *Oil, Journal of Innovative Research in Engineering and Sciences* 2(4), 223-233

Azhari, M.A., Tamar, M.F., Mat Nuri, N.R., and Yusoff, M.R. (2015) Physical Property Modification of Vegetable Oil as Biolubricant using ZDDP, *ARPN Journal of Engineering and Applied Sciences* 10(15), 6525-6528

Demirba A (2009). Biodegradability of Biodiesel and Petrodiesel *Fuels Energy Sources, Part A: Recovery, Util. Environ. Effects*, 31(2), 169- 174.

Diaz, E., (2008). Microbial Biodegradation: Genomics and Molecular Biology, 1st ed., Caister Academic Press. www.horizonpress.com /biod

Erhan, S. Z., and Asadauskas, S**., (**2000), Lubricant Base Stocks from Vegetable Oils, *Ind. Crops Prod*., 11, 277-282.

Erhan, S.Z; Sharma, B.K. and Perez, J. M. (2006). Oxidation and low temperature stability of Vegetable oil-based lubricants, *Industrial Crops and Products*, 24, 292-299.

Fernando S, Hanna M (2002). Oxidation Characteristics of Soybean Oils As Water Pump Lubricants Transactions of the ASAE 45(6): 1715-1719

Garba, Z.N., Gimba, C.E., and Emmanuel, P., (2013). Production and C haracterisation of Transformer Oil, *Journal of Physical Science*, 24(2), 49–61.

Ijah, U. J. J; and Antai, S.P; (2003). The Potential Use of Chicken-drop Micro-organisms for Oil Spill Remediation. *The Environmentalist*, 23, 89-95.

Kadry, G.A. (2015). Biodiesel Production from Jatropha Seeds, *American Journal of Chemical Engineering*, 3(6), 89-98.

Kania, D., Yunus, R., Omar, R., Rashid, S. A., & Jan, B. M. (2015). A review of biolubricants in drilling fluids: Recent research, performance, and applications. *Journal of Petroleum Science and Engineering*, 135, 177–184

Kania, D., Yunus, R., Omar, R., Rashid, S. A., and Jan, B. M., (2017). Performance Evaluation of Polyol Esters from Palm Oils as a Lubricant for Bentonite Suspension Drilling Fluid, *Tribology Online*, 12 (5), 247-250

Karmakar, G., Ghosh, P., and Sharma, B. K., (2017). Chemically Modifying Vegetable Oils to Prepare Green Lubricants, *Lubricity*, 5(44), 1-17

Li, W. and Wang, X. (2015). Bio-lubricants derived from Waste cooking Oil with Improved Oxidation stability and low-termperature properties, *Journal of Oleo Science*, 64(4), 367-374

Luna, F. M. T., Cavalcante, J. B., Silva, F. O. N., and Cavalcante Jr, C. L. (2015). Studies on biodegradability of bio-based lubricants, *Tribology International*, 92, 301–306

Maleque, M. A., Masjuki, H. H., and Sapuan, S. M., (2003). Vegetable Based Biodegradable Lubricating Oil Additives, *Industrial Lubrication and Tribology*, 55(3), 137-143

Menkiti, M., Anaehobi, H., Oyoh, K., and Nnaji, P., (2015). Process Optimization and Kinetics of Biolubricant Synthesis from Fluted Pumpkin Seed, *European Scientific Journal*, 11 (27), 30-47

Mercurio, P., Burns, K. A., and Negri, A., (2004), Testing the Ecotoxicology of Vegetable Versus Mineral Based Lubricating Oils: Degradation rates using tropical marine microbes, *Environ. Pollut.*,129 (2), 165-73.

Musa U., Mohammed I. A, Sadiq M. M., Aliyu, M.A., F. Aberuagba., and Adekunle, J. I.(2016). Statistical Optimization of Biolubricant Production from Jatropha Curcas Oil using Trimethylolpropane as a Polyol, *Proceedings of the World Congress on Engineering and Computer Science, II WCECS.*

Onuh, C.Y., Dosunmu, A., Anawe, P. A. L., Efeovbokhan, V., and Adebisi, A., (2017). Transesterification of Non-edible Vegetable Oil for Lubricant Applications in Water-based Mud. A Review, *International Journal of Applied Engineering Research,* 12 (18), 7397-7401

Petlyuk A, Adams M, Richard J (2004). Oxidation Stability and Tribological Behavior of Vegetable Oil Hydraulic Fluids. Tribology Transactions 47(2): 182- 187.

Quinchia, L. A., Delgado, M.A., Reddyhoff, T., Gallegos, C. and Spikes, H.A., (2013). Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers, *Tribology International* 69, 110–117

Salimon J, Abdullah BM, Yusop RM, and Salih N (2014) Synthesis, reactivity and application studies for different biolubricants. *Chem Centr J.* 8 (1),1–11

Sander, J. (2017). *"Lubricants Can't Be Green . . . Can They?";* Wichita, KS, USA, Lubrication Engineers, Inc.:,; Available online: https://www.lelubricants.com/wp-content/uploads/Green-Lubricants-white-paper.pdf (accessed on 31 January 2021).

Shafi, W. K., Raina, A., and Haq, M. I. U., (2018). Friction and Wear Characteristics of Vegetable Oils Using Nanoparticles for Sustainable Lubrication, *Tribology-Materials, Surfaces and Interfaces*, 1-7

Shah, R.; Woydt, M.; Zhang, S., (2021). The Economic and Environmental Significance of Sustainable Lubricants. *Lubricants,* 9, (21), 1-11

Stojilković, M. and Kolb, M. (2016) Tribological Properties of Biodegradable Universal Tractor Transmission Oil. *Tribology in Industry* 38 (2), 229-234.

Syaima M.T.S., Zamratul M.I.M., Noor I.M. & Rifdi W.M.W.T. (2014). Development of bio-lubricant from Jatropha curcas oils. *Int J Res Chem Metall Civil Eng*; 1(1)

Talib, N; Sasahara, H. and Rahim, E. A. (2017) Evaluation of modified jatropha-based oil with hexagonal boron nitride particle as a biolubricant in orthogonal cutting process, *Int J Adv Manuf Technol*., 92, 371-391. DOI 10.1007/s00170-017-0148-x

Wilde, B.D.; Mortier, N.; Siotto, M.; Briassoulis, D.; Mistriotis, A.; Van der Zee, M., (2015). *Biodegradability Standards Assessment Report;* Knowledge Based Bio-based Products' Pre-Standardization; Delft, The Netherlands, Netherlands Standardization Institute.

Woma, T.Y; Lawal, S.A; Abdurahman, A.S; and Olutoye, M. A; (2019a). Nigeria Jatropha oil as suitable basestock for biolubricant production. *Jurnal Tribologi,* 23, 97-112.

Woma, T.Y; Lawal, S.A; Abdurahman, A.S; Olutoye, M. A; & Ojapah, M .M; (2019b). "Vegetable Oil Based Lubricants: Challenges and Prospects," *Tribology Online,*14(2), 60-70

Zulkifli, N. W. M., Azman, S. S. N., Kalam, M. A., Masjuki, H. H., Yunus, R., and Gulzar, M., (2015). Lubricity of Bio-based Lubricant Derived from Different Chemically Modified Fatty Acid Methyl Ester, *Tribology International*, 93(B), 555-562