International Journal of
Advances in Scientific Research and Engineering (ijasre)

E-ISSN : 2454-8006

DOI: 10.31695/IJASRE.2021.33932

Volume 7, Issue 2
February - 2021

Characterization of Palm Oil as Base Feedstock for Bio-lubricant Production

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ABSTRACT

Petroleum-based lubricants have dominated the range of lubricants in industrial and domestic machinery. With the global call to the reduction in fossil fuel consumption and the finite nature of petroleum deposit, interest is increasing in finding alternative lubricants that are environmentally friendly and cost-effective. One of such alternatives is lubricant from biomaterials (biomass). In this study, the characterization of palm Oil (oil) as a base oil for bio-lubricant production is carried out with a view to determining the inherent properties of the oil necessary for its use as the base oil for bio-lube production. Three samples of raw palm oil were sourced from open markets within the South-West, South-East and South-South regions in Nigeria. Each of the samples was divided into two in which one half was bleached and the other used as supplied. Prior to bleaching, the sample was degummed, neutralized and then bleached to improve their qualities. Kaolin clay was used to produce the bleaching agent used to bleach the samples. The raw and bleached samples were analysed for their respective lubricating characteristics. The physicochemical properties were tested for and compared with two commercial petroleum-based lubricants. The results show that raw palm oil has inherent lubricating properties that could enable its use as the base oil for bio-lubricants production. It was also observed that irrespective of the source of the oils, all the raw palm oil samples have similar viscosity with the same pattern of viscosity variation with temperature. Furthermore, there was a positive bleaching effect on all the properties of the oils such as improved colour, acid levels, reduced volatile content, high flash point and density.

Key words: Bio-lubricant, Base oil, Biodegradable oil, Palm oil, Lubrication, Viscosity index.

1. INTRODUCTION

Lubricants are essential for the operation of many domestic and industrial machines or engines and have been in use for a very long time now. Lubrication is required for safe and reliable operation of machines and engines at their required operating conditions. It allows for smooth sliding of moving parts, reducing wear and friction which in turn reduces energy loss (Mobarak, et al., 2014). Conventionally, lubricants are made from petroleum by-products and it has dominated the lubrication industry. For instance, about 38 million tons of lubricants, representing approximately 85% of lubricants used in 2005, originated from petroleum based oils (Darfizzi&Jumat, 2013). There are social and environmental consequences of using these lubricants which include inability to decompose naturally, land and water pollution and overall addition of carbon to the atmosphere. Machine oil-spill is one of the sources of land and water contamination while open burning of oil leads to atmospheric pollution. It has been shown that about 15 million tons of petroleum based oleo chemicals contaminate the biosphere yearly and 40% of this come from oil spillage, industrial/refinery processes, municipal waste/runoff, and condensation from marine engine exhaust (Salih, et al., 2013). The finite nature of petroleum deposit makes it difficult to solely rely on it for lubrication production and hence poses some threats on lubricant security. Alternative source of lubricant is imperative to ensure continual availability of the product even when the conventional base stock is no more. Considering the impact of petroleum based products on the environment and climate, the alternative base stock should be socially and environmentally suitable to replace the present material while its renewability is an added advantage.

The parent stock of lubricants play vital role in the lubricant's overall characteristics. Hence, base feedstock is the main constituent of a lubricant and it is usually combined with suitable additives to improve and/or impart its performance characteristics to the blend (Darfizzi & Jumat, 2013). The use of petroleum based oils in various applications such as forestry, farming, mining and marine have increased the search for environmental friendly oils (Salih, et al., 2013). Bio lubricants are pure and natural lubricants manufactured by environmental-safe processes. They do not contain toxic compounds and are biologically degradable (D¨orm˝o, et al., 2004) and renewable. It has been shown by Asadauskas, et al., 1997; Erhan & Asaduaskas, 2000; Jayadas, et al., 2007, that a bio-lubricant exhibits better lubricate, higher viscosity index, higher flash point and low evaporative loses than mineral oils.

A number of bio-materials have been investigated for their potential as sources of base oil for bio-lubricant production. These feedstock comprise edible and non-edible vegetable oils. For instance, Honary, (2010); Erhan & Adhvaryu, (2002); Salunkhe, et al., (1992); Doll & Sharma, (2012) have investigated bio lubricant production from soybean oil constituents in oxidation stability. Coconut oil has been studied by Jayadas& Nair, (2006a); Mannekote & Kailas, (2011),while rapeseed oil was studied by Arumugam et al., (2012; Zhang et al., (2000), pongamia oil by Bhat&Bekal, (2012) and sunflower oil by Quinchia et al., (2009); Quinchia et al., (2010) and Campanella et al., (2010). Quinchia et al., (2009), used ethylene–vinyl acetate (EVA) and styrene–butadiene–styrene copolymers to improve the kinematic viscosities of sunflower oleic oils from 150 to 250 cSt and 26 to 36 cSt at 40 ◦C and 100 ◦C respectively. It is in this vein that their further research showed that blending of EVA with soybean oil, sunflower oil and high oleic sunflower oils improved viscosities of these vegetable oils to 330 to 420% at low temperatures. The studies show that biomaterials possess qualities to make them suitable for bio-lubricant production in addition to showing that they have great prospects for bio-lubrication in different application (Quinchia, et al., 2010). Though these studies have been taken, bio-based oils have not found wide application in practical operational machines owning to insufficient research in bio-oil integration technology. The objective of this paper is to characterize palm oil (from oil palm tree) as more bio-feedstock and base oil for lubricant production. Pure palm oil has not been adequately considered for Bio-lubricant production other than its application in the manufacture of consumer products such as soap, detergents, vegetable (cooking) oil.

Vegetable oils (including those(from other oil producing plants)have not gained wide industrial usage as bio-lubricants because they possess some undesirable characteristics such as low thermal and oxidation stabilities, higher pour point, lower viscosity range than synthetic and mineral oils (Duangkaewmanee &Petsom, 2011; Sharma &Stipanovic, 2003; Quinchiac, et al., 2012).

Although, the use of bio-lubricants from rapeseed is going on in Western Europe and USA, it is however at its infancy, constituting only about 3.5% and 1.6% respectively of lubricants in those countries' lubricant marketers (Yong et al, 2014). It has been shown that about 200 companies have registered in the US to develop bio-lubricants for various applications (Rani, et al., 2015). As bio-lubricants are from renewable sources, they are believed to be potential sources of energy in future, especially for developing countries. Due to increased world industrialization and economic growth, there will be an increase in automobile ownership and subsequent increase in lubricants demand in most developing countries (Honary, 2010). This shows there are future prospects for bio-lubricant production in developing countries.

2. MATERIALS AND METHODS

2.1 Materials

The main materials used in this research include palm oil, Kaolin clay, laboratory reagents, petroleum based lubricants (for comparison) and some major laboratory equipment (such as atomic adsorption spectrophotometer, elemental analyser, Noack volatility test meter. Three samples of palm oil were purchased from open markets in South East (SE), South West (SW) and South (SS) zones of Nigeria and therefore, their fruits nature and processing methods could not be ascertained. Kaolin clay was sourced from Kakau village in Chikun Local Government Area (LGA) of Kaduna state, Nigeria. Its excellent adsorptive ability and available large deposits in all parts of Nigeria favored its choice to be used to produce the bleaching agent. Three commercial and industrial petroleum based lubricants were used as control lubricants. Mobil Super SAE20W40, Mobil gear oil – SAE75W90 and UFA hydraulic XL were the commercial oils used. These are industrial conventional light oil, heavy lubricants and a hydraulic fluid and are labeled C1, C2 and C3 respectively in this work. There were purchased from a local auto shop in Kaduna and were subjected to the same analysis as the raw and bleached palm oil samples. The third oil used as reference oil, UFA hydraulic XL (C3) is a hydraulic fluid produced by Chevron, it did not undergo the same laboratory analysis like the bio based and refined mineral oils, but its data was adapted from literature. Some major equipment used for analysis in this work include an Atomic Absorption Spectrometer (AAS) analyser-thermo scientific iCE3000 series, 200 RPM B. Bran Centrifuge machine, a viscometer and a Noak Volatility tester. Hydrochloric acid, Nitric acid and Acetic acid were the laboratory reagents used and were of analytical grade.

The elemental analysis of all the samples was carried out at the National Geosciences Research Laboratories Kaduna, Nigeria. Other tests were carried out at the Chemical Engineering laboratory, Federal University of Technology, Minna, Nigeria. The properties tested include; viscosity, viscosity index, flash point, pour point, cloud point, density @ 25°c, noack volatility, aniline point and total acid number. Specific ASTM standard methods were used to test for the properties.

2.2 Degumming and neutralization of palm oil

1000ml of the oil sample was measured in a beaker and heated to a temperature of 80°C. 50ml of 5% wt/wt of acetic acid was added to the oil sample while heating and stirring for 15 minutes. The resulting mixture was centrifuged to form two layers of the oil and aqueous solution containing phosphatides. The degummed oil was neutralised by adding 4 molar caustic soda solution and heated to 110°C for 20 minutes.

2.3 Procedure for Production of Acid Activated Clay (Kaolin)

The paste of the bleaching agent was formed by mixing 200g of powdered kaolin and 200ml of distilled water. 100ml of 20% Hydrochloric acid was added to the paste and heated at 110^{o}C on gallen kamp thermostatic control temperature hot plate for 60 minutes. A125mmsize What man filter paper was used to filter the warm mixture and the residue on the paper was dried at 105°C. The dried residue was ground into fine powder of acid activated clay for use in the bleaching of palm oil.

2.4 Procedure for bleaching of palm oil

5g of the acid activated clay was mixed with 100ml of the degummed oil sample. The mixture was heated to a temperature of 110°C for 1 hour with continuous stirring. The bleached sample was cooled and then filtered.

2.5 Digestion Technique for Elemental Analysis of Palm Oil

20ml of the raw and bleached palm oil were steamed by heating at 200°C and allowed to cool and solidify. 20ml each of concentrated Hydrochloric acid (HCl) and Nitric acid (HNO_3) were added and heated on the hot plate with close monitoring to avoid splattering. 20ml of distilled water was added and the mixture was heated and filtered warm into a 100ml bottle for atomic absorption spectrometry (AAS) analysis for sodium (Na), potassium (K), cupper (Cu), magnesium (Mg), iron (Fe) and lead (Pb). The oil sample was characterised using Atomic Absorption spectrophotometer (AAS), thermo scientific iCE3000 series.

3. RESULTS AND DISCUSSION

3.1 Viscosity

Table 1: Viscosities of samples at 40°C and 100°C

Temperature	Raw Samples			Bleached Samples			Control		
^{O}C	SW	SE	SS	SW	SE	SS	C1	C2	C3
40	34.71	33.65	35.77	8.21	7.92	8.39	89.10	116.20	32.6
100	7.12	6.21	7.87	1.92	1.57	1.92	14.20	16.80	5.4

Note: *C1 = SAE20W40, C2 = SAE75W90, C3 = Hydraulic XL* (UFA, 2008)

Viscosity is the measure of resistance to flow of a fluid (Shahabuddin, et al., 2013). The viscosities of the palm oil samples at 40 ^{O}C and 100 ^{O}C are presented in Table 1 and graphically in figure 1. Both Table 1 and Figure 1 show how the viscosities of the raw and bleached samples compare with the viscosities of the three reference oils C1, C2 and C3. The results show that viscosities of the raw oil samples conform to that of C3 at 40 ^{O}C as shown in figure 1. While viscosities of the raw oil samples are slightly higher than that of C3 at 100 ^{O}C. Conversely, the viscosity of both raw and bleached samples in this work do not compare favourably with C1 and C2 at 40 ^{O}C and 100 ^{O}C. This implies that both the raw and bleached samples cannot be used based only on viscosity in applications where C1 and C2 oils are used without improvement. Oils with low viscosities such as the bleached oil samples can be used for light duty applications, otherwise, they can have their viscosities improved by adding viscosity enhancers so that they can be suitable for heavy duty engineering applications. As also noted in Table 1, viscosity reduced as the samples are bleached. This could be as a result of removal of the gummy materials and other impurities via bleaching which

DOI: 10.31695/IJASRE.2021.33932

subsequently destroyed the dense chemical structure (saturated fatty acids content) of the samples. As the temperature of the oil increased, the particles making up the oil gains more energy and vibrates faster. Increase in temperature weakens the force of attraction between the particles, leaving larger spaces between them. This decreases the resistance of the oil to flow, resulting in a decreased viscosity. Marotrao, (2012) and Honary& Richter, (2011) also show that the viscosity of fluids tends to decrease as temperature is increased.

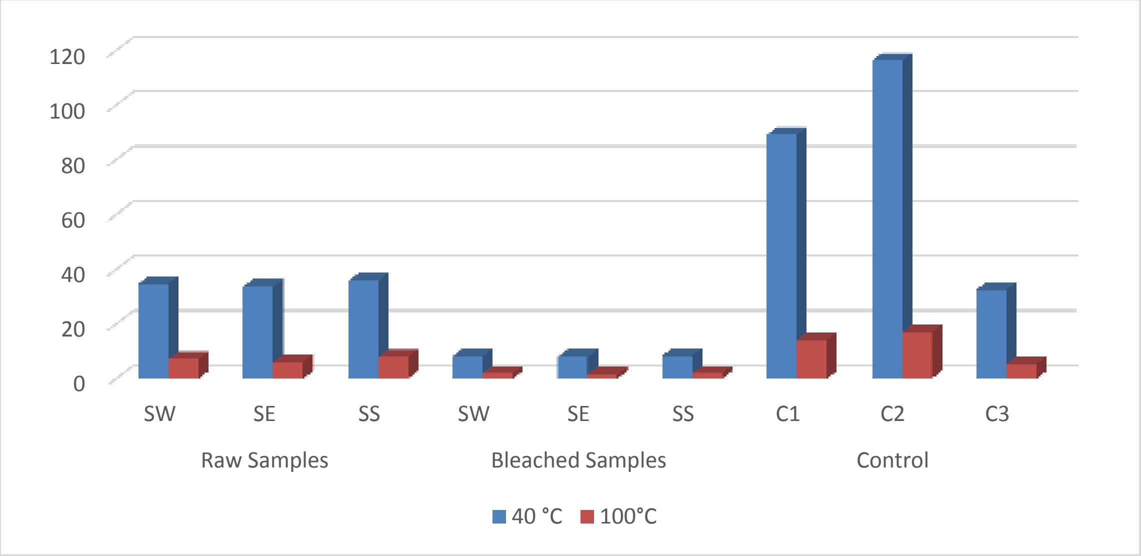

Figure 1: Viscosities of samples at 40°C and 100°C (Data for C3 is adapted from* (UFA, 2008).*3.2 Physicochemical properties of raw and bleached oils

Table 2: Physicochemical properties of raw oils

Characteristic	Unit	Raw Samples			Control oil samples	
		SW	SE	SS	C1	C2
Viscosity Index		149	131	157	165	146
Flash Point	^{O}C	252	251	257	226	212
Pour Point	^{O}C	12	10	13	-32	-41
Cloud point	^{O}C	16	14	17	8	10.2
Noack Volatility	wt. %	22.20	24.10	21.50	11.9	12.8
Aniline Point	^{O}F (^{O}C)	107.96 (42.2)	105.08 (40.6)	112.64 (44.8)	131	40
TAN	(mg kOH/g)	2.82	4.24	1.02	1.6	0.08
Density @ 15^{O}C	kg/m^3	900.25	904.03	916.47	870	889

The physical and chemical properties of raw and bleached samples are presented in tables 2 and 3 respectively and compared to those of the control oils. The raw and bleached samples from the three regions have shown high viscosity indices and are in the same range with the control oils. This implies that an increase in temperature of these oils will have little effect on their viscosities and as such if these oils are used as base oil in the formulation of lubricant, they may not thin out easily at reasonable temperature range especially when used where temperature of the machines (or engines) vary with time. Ideally, VI of oils should be positive but oils of negative VIs down to minus 60 are in commercial oil market (Fitch 2012). Negative VI implies that the oil is not stable at varying temperature. However, the flashpoints of both raw and bleached palm oil samples are higher than those of the control oils, showing the higher flammability stability in vegetable oils than mineral based oils (Honary & Richter, 2011). This also agrees with the result of flash points of other plant oils in literature. For instance Salih, et al., (2011).reported flash point of soybean oil, sunflower oil, rapeseed oil, jatropha oil and Castor oil as 240 ^{O}C, 252 ^{O}C, 240 ^{O}C, 240 ^{O}C and 250 ^{O}C respectively.

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The cloud points of the control oils C1 and C2 are 8 ^{O}C and 10.2 ^{O}C respectively (table), which are similar to 8.6 ^{O}C, 9 ^{O}C and 10.2 ^{O}C values obtained for the bleached oil samples from SW, SE and SS regions respectively. There is an improvement in the pour and cloud points as the samples transit from the raw sample state to the bleached sample state as shown in tables 2 and 3. However, the low temperature properties, such as pour point, of the raw and bleached oils from all the three regions are high compared to that obtained from the control oils C1 and C2. The inferior flow characteristics exhibited by palm oil samples which make it undesirable for use as bio-lubricants base oil in regions with extreme cold climates (Honary & Richter, 2011), could be improved upon. This flow difficulty could be attributed to the level of unsaturation nature of the fatty acid content of palm oil (EPOA, 2015). Moreover, the inferior flow characteristics do not affect the use of these samples as lubricant bases so much in tropical countries.

Table 3: Physicochemical properties of bleached oils

Characteristic	Unit	Bleached Samples			Control oil sample	
		SW	SE	SS	C1	C2
Viscosity Index		-13.5	4.6	-124.8	165	146
Flash Point	^{O}C	221	219	232	226	212
Pour Point	^{O}C	6	5.80	4	-32	-41
Cloud point	^{O}C	8.60	9	10.20	8	10.2
Noack Volatility	wt. %	17.05	19.20	15.50	11.9	12.8
Aniline Point	^{O}F (^{O}C)	92.48 (33.6)	89.24 (31.80)	97.7 (36.5)	131	40
TAN	(mg kOH/g)	0.84	0.98	0.70	1.6	0.08
Density @ 15^{O}C	kg/m^{3}	905.42	907.71	913.0	870	889

The bleached samples how less volatility values than the raw samples as shown in Tables 2 and 3 which signifies reduced loss of oils due to evaporation. Similarly, the reduction in the acid content of the raw samples show that treating the raw oil with acid activated clay has positively enhanced the samples, hence, the low acidity content of the bleached samples. The little variation in the total acid number could be due to production process discrepancies. These production discrepancies may result from the use of fermented palm fruits, mixing oil from fermented fiber with that from fresh palm oil press, boiling palm fruits in drums other than in steam boilers etc. Aniline point shows an indication of solubility of oil, i.e., ability of an oil to dissolve polymers, additives and oxidation products (Nynas Corporation, 1997). As shown in tables 2 and 3, aniline points of all the samples are lower than that of C1 but higher than that of C2. This implies that all the samples (raw or bleached) will be more soluble than the C1 oil but will be less soluble than the C2 oil, based on the assertion by Nynas Corporation, (1997), that the lower the aniline point of an oil, the more soluble it is. Therefore, the bleached samples from the three regions which have lower values of aniline points could be more soluble and suitable to be used as base oils for the formulation of lubricating fluids and oils than the raw samples. shown in Table 3, the raw and bleached oil samples show good density values in that they are relatively less than the density of water. This indicates less energy to carry the samples from one point to the other as against equal volumes of water. These values are in agreement with Ing, et al., (2012), Musa, (2010) and Okolo &Adejumo, (2014) in evaluation of palm oil lubrication properties.

Table 4: Elemental analysis of the raw samples

Element	Unit	Raw		
	ppm	SW	SE	SS
Iron (Fe)		93.8614	93.8920	93.8546
Copper(Cu)		0.0948	0.0962	0.0901
Lead (Pb)		nil	nil	nil
Sodium(Na)		8.7358	8.730	8.7395
Magnesium(Mg)		21.575	21.2890	21.5669
Potassium(K)		8.0781	7.9856	8.0123

The element analysis of lubricants carried out to ascertain the type and amount of metals present in it. Tables 4 and 5 present the results of the elemental analysis of raw and bleached oil samples respectively. It is observed that Lead (Pb) is non-reactive in both

DOI: 10.31695/IJASRE.2021.33932

raw and bleached samples as shown in Tables 4 and 5. Except for Iron (Fe), all other metal contents reduced after the oils were bleached as shown in table 5. Tables 4 and 5 have also shown that Fe is the major metal content in the samples and its content increased after oil was bleached. This increment may be due to reaction with the Fe deposits in the kaolin used for bleaching. It is also noted that the contents of potassium (K), magnesium (Mg), sodium (Na) and copper (Cu) in the bleached samples are negligible. This is because SAIT (2015) has shown that crude petroleum oil used for production of lubricants contain <1000 ppm metal. Therefore, if this crude petroleum oil has been used at this level of metal content to produce commercial lubricants, then these bio-base palm oils can be used to produce safe bio-lubricants.

Table 5: Elemental analysis of the bleached samples

Element	Unit	Bleached		
	ppm	SW	SE	SS
Iron (Fe)		140.7963	140.8101	140.7885
Copper(Cu)		0.0968	0.0874	0.0993
Lead (Pb)		nil	nil	nil
Sodium(Na)		8.3701	8.3584	8.3647
Magnesium(Mg)		3.0987	3.1248	3.1939
Potassium(K)		1.693	1.7100	1.7052

Some specifications for lubricants formation may not allow the use of certain metals while some others can be used to enhance the quality of the product. For example, as oil that contains sodium is not desirable for furnace application (Bolt & Hill 1977), sulphur and zinc are used as anti-wear and extreme pressure property enhancers in lubricating fluids (Honary & Richter, 2011) even though they are not also desirable in some applications.

The technical feasibility of palm oil has been undertaken in this study through experimental determination of palm oil samples from three locations in Nigeria. The quality of the samples were modified by bleaching them using self-produced chemical activated clay from kaolin. There are little variations between the properties of raw oils from different zones. This could imply that there is no location effect on the samples. This is also applicable to the samples under bleached condition. This also means that no matter where you pick palm oil from Nigeria, the oil can be suitable for bio-lubricant production. From the research results, palm oil, in raw and bleached state possess some of the qualities such as high viscosity indices and low volatility, required for lubricant base oil. This agrees with the results of experimental work carried out by Salih, et al., (2013) that revealed that vegetable oils have better viscosity indices, low volatility and high lubricity than mineral oils. These qualities are acquired due to their inherent high molecular weight and ester bonds which enable the oil molecules to cling to metal surfaces through physical bonding for better boundary lubricity.

The poor low temperature behavior and thermal instability characteristics of palm oil as shown in the results of this work have also agreed with Shahabudd in, et al., (2013) and Ponnekanti & Kaul, (2012) that vegetable oils have these limitations but could be improved.

Despite its high pour points, other lubrication properties such as viscosity, high viscosity index, high flash point, high solubility, low volatility and acidity properties are comparable to commercial hydraulic fluids and lubricants. The pour point problem associated with the saturation level in palm oil could be improved with proper additives. It is believed that palm oil could be used in its raw and treated state as a good base oil to formulate a wide variety of fluids with diverse applications: hydraulic fluids, fire resistant fluids, and general lubricating oils.

Commercial production of bio-lubricant from palm oil in Nigeria could face serious challenges which range from technical to economic issues. Technologically, bio-lubricant production from palm oil is a technology that is about to ‘wake’ in that there is no existing infrastructure in place for it globally. The technique is one that should stem out from the first principles with robust research. Since the technology is not yet mature, it will take but a while before the first commercial industry certified palm oil based bio-lubricant can hit the market.

Economically, a market has already been established for petroleum based lubricant with its overarching mature technology and investment benefits to the Nigerian nation. Hence, implementation of the proposal might suffer setbacks due to the presence of abundance crude oil from petroleum.

4. CONCLUSION

Based on the properties tested and the subsequent results, the palm oil samples exhibited diverse properties. It might not be easy to conclude on the feasibility of the samples for bio-lubricant production based on a particular property. This is also applicable to other base materials from petroleum. Therefore, palm oil samples can form a good base for lubricant production as petroleum base oils have been used. Further research needs to be carried out towards production of lubricant from them. Therefore the following conclusions can be made:

1. It is observed that viscosities of all the samples decreased with increase in temperature. This decrease was more with bleached palm oil in which gave 3.84, 3.22 and 3.91cSt at 100°C for oils from South West (SW), South East (SE) and South (SS) respectively and less with Mobil gear oil SAE75W90(C2) with 16.80 cSt. Hence, the oils may not be used to produce heavy lubricants without industrial treatment
2. At 40 °C, the viscosity of all bleached samples are identical with ISO VG 15. Therefore, bleached palm oil can be used as light lubricant without much industrial treatment especially where environmental temperature is favourable.
3. Bleaching of crude palm oil helped in removing the gummy elements and destroyed the carotene (red colour) of palm oil thereby reducing its volatile elements, hence the reduction in the Noack volatility level in the bleached samples.
4. The raw samples show similar physical properties. Therefore location does not have much effect on the properties of the raw palm oil. However, this can be further investigated on a broader perspective.
5. The poor low temperature behavior (pours and cloud points) of palm oil as shown in the results of this work have also agreed that vegetable oils have temperature limitations.

Therefore, the lubrication properties of palm oil in its raw and bleached state indicated good potential as base stock in biodegradable lubricant formulation. However, it is recommended in order to ensure smooth take off and implementation of the research objectives that;

- There should promulgate policies and enabling framework to implement bio lubricant programme.
- There should ensure adequate and sustainable feedstock supply. This could be done by focusing on oil palm agronomy (improved and high yield species), improved varieties by genetic modification of oil palm for high oil content yield, early fruiting and easy commercial processing viability and introduction of financial incentives to oil palm farmers to diversify palm oil production.
- Infrastructure development - Local non-mechanised palm oil processing units should be encouraged through community participation programmes that will operate on build operate and transfer basis and federal government should enter into public-private partnerships (PPPs) with stakeholders.
- Further research and development (R&D) is recommended on the oil properties and also into the (economic) feasibility and viability of using palm oil as bio-based oil for formulation of bio-lubricants.

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DOI: 10.31695/IJASRE.2021.33932