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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF ECO-FRIENDLY BIO LUBRICANTS FROM PLANT-BASED OILS

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ABSTRACT

Nowadays petroleum oil lubricants are most commonly use lubricant in motor vehicles and industrial machines. But those petroleum base lubricants create major problems to the marine and terrestrial environment. Researchers are trying to find new substances which are chemically modified for the substitution for petroleum base lubricant. Therefore, in this research four different types of bio lubricants were prepared by chemical modification of plant base oils such as Coconut oil, Palm oil, Neem oil and Waste palm oil. The bio lubricant was characterized using GC-MS analysis. And also Flash point, density at 15 °C, 40 °C and 100 °C, viscosity at 40°C and 100°C, viscosity index, acid value, yield percentage and cost of product of samples were analyzed.

Keywords: *Chemical modification, Mineral oil lubricants, transesterification, GC-MS analysis*

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1. INTRODUCTION

Present day researchers are most commonly tending to do the research to find solution for the energy crisis while avoiding environmental pollution. Environmental issues caused by the petroleum products are the main reason for finding alternative fuels and bio-based lubricants from renewable raw materials. Petroleum oil based lubricants are commonly used in the automobile industry and machinery. In 2008 the usage of oils on the planet was 46 million kiloliters. Since then, it has expanded by 2 % consistently each year [1]. As a result of using the petroleum-based lubricants can create major problems to the marine and terrestrial eco systems [2]-[3]. Therefore, it is very important to identify environmentally friendly bio lubricant to replace Petroleum oil lubricant for reducing the use of fossil fuels. Bio lubricant can be produced from plant based oils, using chemical

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modifications on it. Its characteristics can be improved by adding additives to the base oil. Plant based oils have long chain hydrocarbons and they are structurally similar to the mineral oils. Hence use of plant based oils are more interested for synthesize of bio Lubricant. In addition to that because of its non-hazardous nature it is very easy for the disposal.

Lubricants are being used to minimize frictional resistance between moving surfaces in relative motions. It is being done by making a replacement of fluid friction for mechanical friction. The functions of the lubricant are expanding the life expectancy and proficiency of the vehicles and machines by decreasing wear and tear of machine parts. Liquid sealing, heat transfer, contaminant suspension, and corrosion protection are important advantages of lubricants [4].

This research was done with the investigate of the possibility of creating bio lubricant from series of non-traditional and traditional vegetable oils namely Neem oil, Coconut oil, Palm oil and Waste palm oil. They were chemically modified to bio lubricant and were evaluated for its physiochemical characteristic and compared those properties against standard commercially available lubricating oil.

2. MATERIAL AND METHODS

2.1 Chemicals required

Methanol (20%), Sulphuric acid (5%), Potassium hydroxide, Mono ethylene glycol, Sodium methoxide.

2.2 Oilesterification

Methanol and Sulphuric acid were mixed in a beaker. Then oil was weighted into another beaker. Then two beakers were put into a water bath and heat up to a temperature of 60 °C [5].

2.3 Methyl ester synthesis

Potassium hydroxide (1.0g), required amount of Methanol were weighted and mixed in conical flask for complete dissolves. Then esterified oil (100g) was put into 250 ml three neck flask. And then it was heated 55°C - 60°C. Then alcohol catalyst mixture added into three necks round bottom flask. Then three necks round bottom flask was placed in a Heating mantle for two hours. After that using the separator funnel, mixture was permitted to settle down for 15 - 20 minutes. Then the methyl ester phase can get from the upper layer. Methyl ester phase can be wash with de-ionized water slowly to remove impurities [5].

2.4 Biolubricant synthesis

Methyl ester and mono ethylene glycol were added into the three necks round bottom flask. Then 0.8% (w/w) of catalyst Sodium methoxide was added to the total reactant. Then three necks round bottom flask were placed in a heating mantle for two hours. After that using the separator funnel, mixture was allowed to settle down. Bio lubricant can be separate as a lower layer [5].

2.5 Gas Chromatography-Mass Spectrometry analysis

All the methyl esters synthesized were analyzed using GC - MS. DB-35MS capillary column with 30 meters in length and 0.25 in diameter of the column was used. Head pressure of 13.332 psi Helium gas was used as the carrier gas in split injection system. The initial temperature of the column was kept at 100ºC for 5 min and increased the temperature to reach a temperature of 240ºC for 15min for 4°C/min rate. The injection volume is 2µl (Personal Communication [Lab analysts, SGS Lanka (Pvt) Limited] 2 September 2020).

2.6 Flash point

Flash point is the least temperature at which a fluid will make a fume noticeable all around close to its surface that will streak or quickly light, on introduction to open fire. Flash point of bio lubricants were measured using closed cup flash point tester [6].

2.7 Kinematic Viscosity and Viscosity index

Brookfield viscometer RV model was used to measure absolute viscosity. The temperature of water bath was set at 40°C and 100°C separately and the measurements of all the samples were taken by Brookfield viscometer. Kinematic viscosity of each sample was measured at 40 °C and 100 °C and the viscosity index was calculated.

2.8 Density

Using Density bottle, specific gravity of each sample at different temperature was obtained and the density was calculated.

2. 9 Acid value

Acid value is the number of milligrams of KOH required to neutralize the free fatty acid in 1 g of the sample. The acid value of each sample was calculated using titration method [7].

3. RESULTS AND DISCUSSION

3.1 Characterization of the bio lubricant synthesized

Characterization of different bio lubricants was done using GC-MS. GC-MS gives data of the composition of bio lubricant. Composition was identified by using CRM (Saturated and Unsaturated bonds)

3.1.1 Gas Chromatography-Mass Spectrometer analysis

Characterization of the bio lubricants was done using GC-MS. The results are shown below and discussed accordingly.

Many minor and major peaks were observed between retention times 4 minutes to 19 minutes. Five major peaks are obtained at 3.60, 5.50, 5.70, 6.70, 7.00, 7.90, 8.25, 9.01, 9.50, 10.90, 12.90, 15.70 min. The peak was identified as Methyltetradecanoate as a long chain saturated fatty-acid ester and Dodecanoic acid, 2,3-dihydroxy propyl ester, Hexadecanoic acid, 11-Octadecaenoic acid, Myristic acid Hexadecanoic acid, Tetradecanoic acid were identified (Table 1 and Figure 1).

Table 1 Fatty acid composition of bio lubricant prepared from the coconut oil

Retention (min)	Name of fatty acids	Area (%)
3.60	Methyl tetradecanoate	6.40
5.50	Dodecanoic acid	5.70
5.70	2, 3-dihydroxy propyl ester	21.10
6.70	Hexadecanoic acid	18.40
7.00	11-Octadecaenoic acid	18.50
7.90	Myristic acid	5.40
8.25	Hexadecanoic acid	14.70
9.01	Tetradecanoic acid	16.80

In the chromatogram many peaks are observed in which two of them are observed at retention time of 5.60 and 6.70 minutes. Other small peaks are observed at retention time of 3.50, 4.55 minutes. Dodecanoic acid, methyl ester is saturated fatty acid ester consist long chain, 9, 12-Octadecadienoic acid (Z, Z) - methyl ester is unsaturated fatty acid ester and its long chain consist two double bonds, Methyl tetradecanoate is saturated fatty acid ester consist long chain, 9-Octadecenoic acid, methyl ester is unsaturated fatty acid ester its long chain consists one double bond (Table 2 and Figure 2)

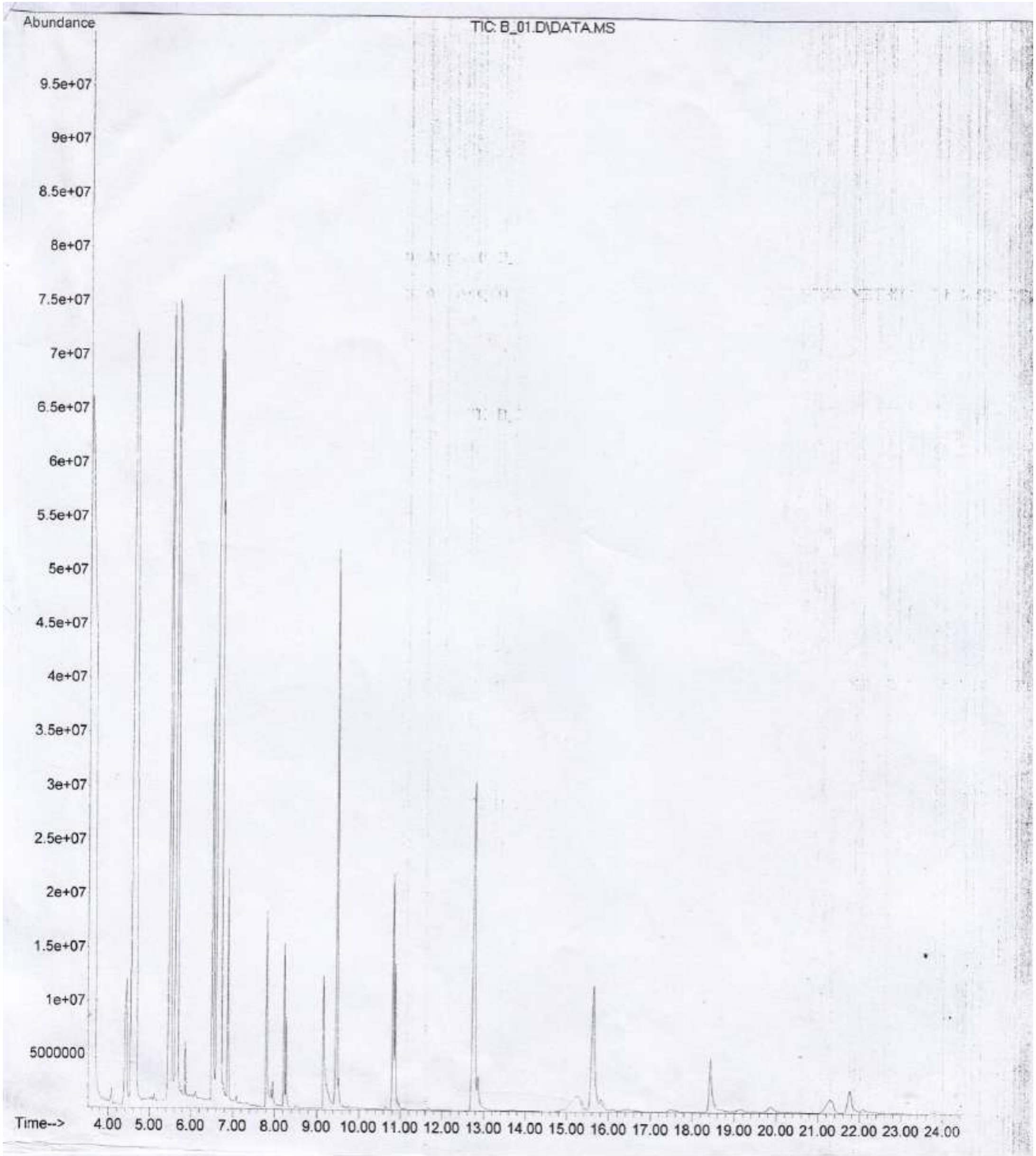

Figure 1 *GC-MS Chromatogram of bio lubricant prepared from the coconut oil*

Table 2 GC-MS Chromatogram of the bio lubricant prepared from the Neem oil

Retention (min)	Name of fatty acids	Area (%)
3.60	Methyl tetradecanoate	17.10
4.55	Dodecanoic acid	26.50
5.60	9, 12-Octadecadienoic acid (Z, Z)	28.70
6.70	9-Octadecenoic acid	21.70

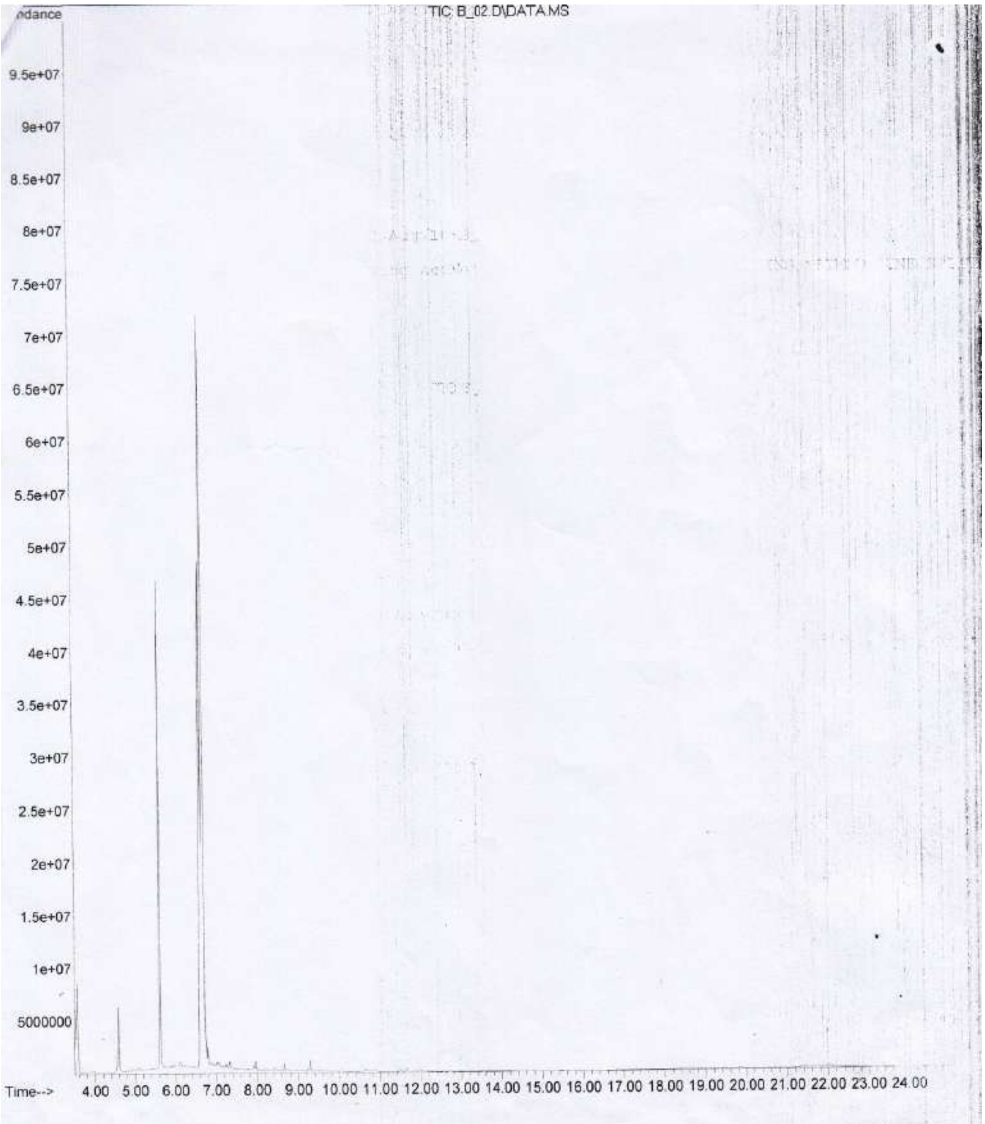

Figure 2 *GC-MS Chromatogram of the bio lubricant prepared from the Neem oil*

The above chromatogram is obtained from palm oil bio lubricant. The chromatogram shows four major considerable peaks at 4.60, 5.70, 6.80, 7.90, 9.30, minutes. Methyl tetradecanoate that is saturated fatty acid ester consist long chain, Hexadecanoic acid, methyl ester that is also saturated fatty acid with long chain, 11-Octadecenoic acid, methyl ester that is unsaturated fatty acid ester and its long chain consist one double bond, Hexadecanoic acid,2-hydroxyethyl ester that is saturated fatty acid ester with long chain contain one hydroxyl group, 9-Octadecenoic acid (z)-, 2-hydroxyethyl ester that is unsaturated fatty acid ester with long chain one double bond and one hydroxyl bond (Table 3 and Figure 3).

Table 3 GC-MS Chromatogram of the bio lubricant prepared from the Palm oil

Retention (min)	Name of fatty acids	Area (%)
4.60	Methyl tetradecanoate	16.50
5.70	Hexadecanoic acid	15.70
6.80	11-Octadecenoic acid	21.70
7.90	Hexadecanoic acid	12.30
9.30	9-Octadecenoic acid (z)	19.70

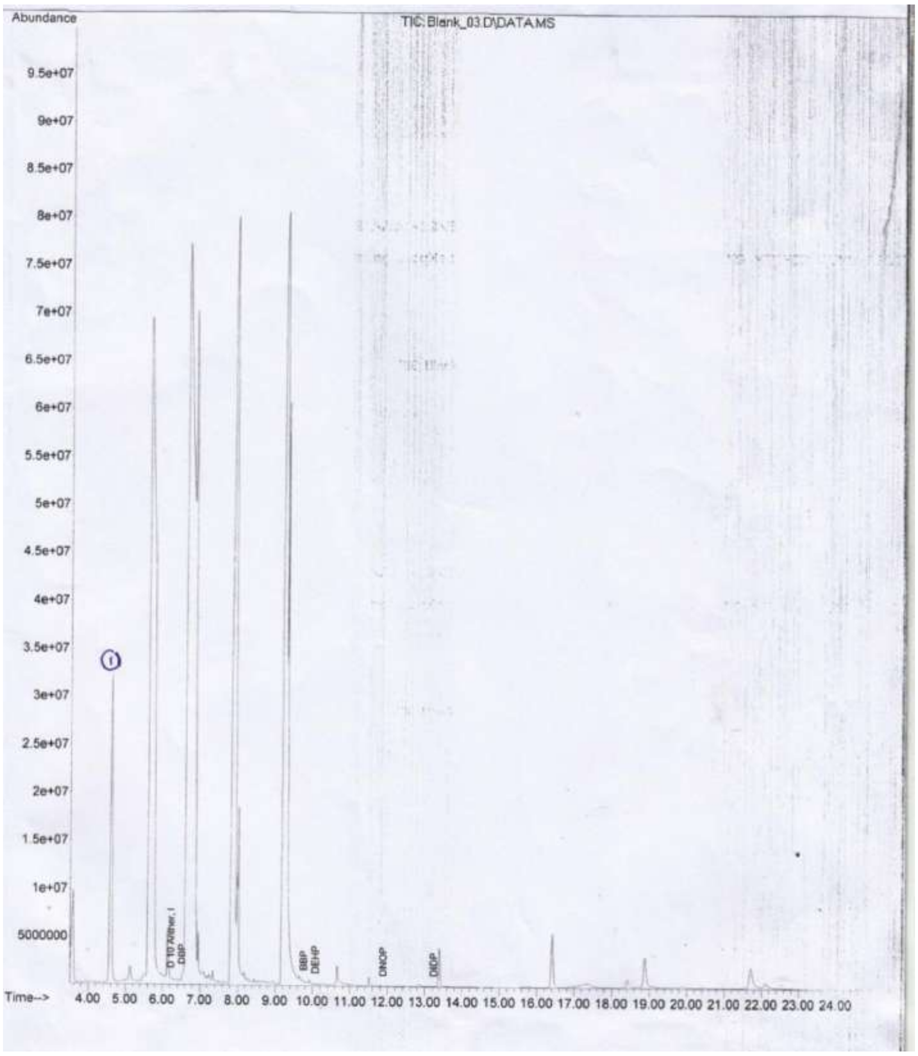

Figure 3 *GC-MS Chromatogram of bio lubricant prepared from Palm oil*

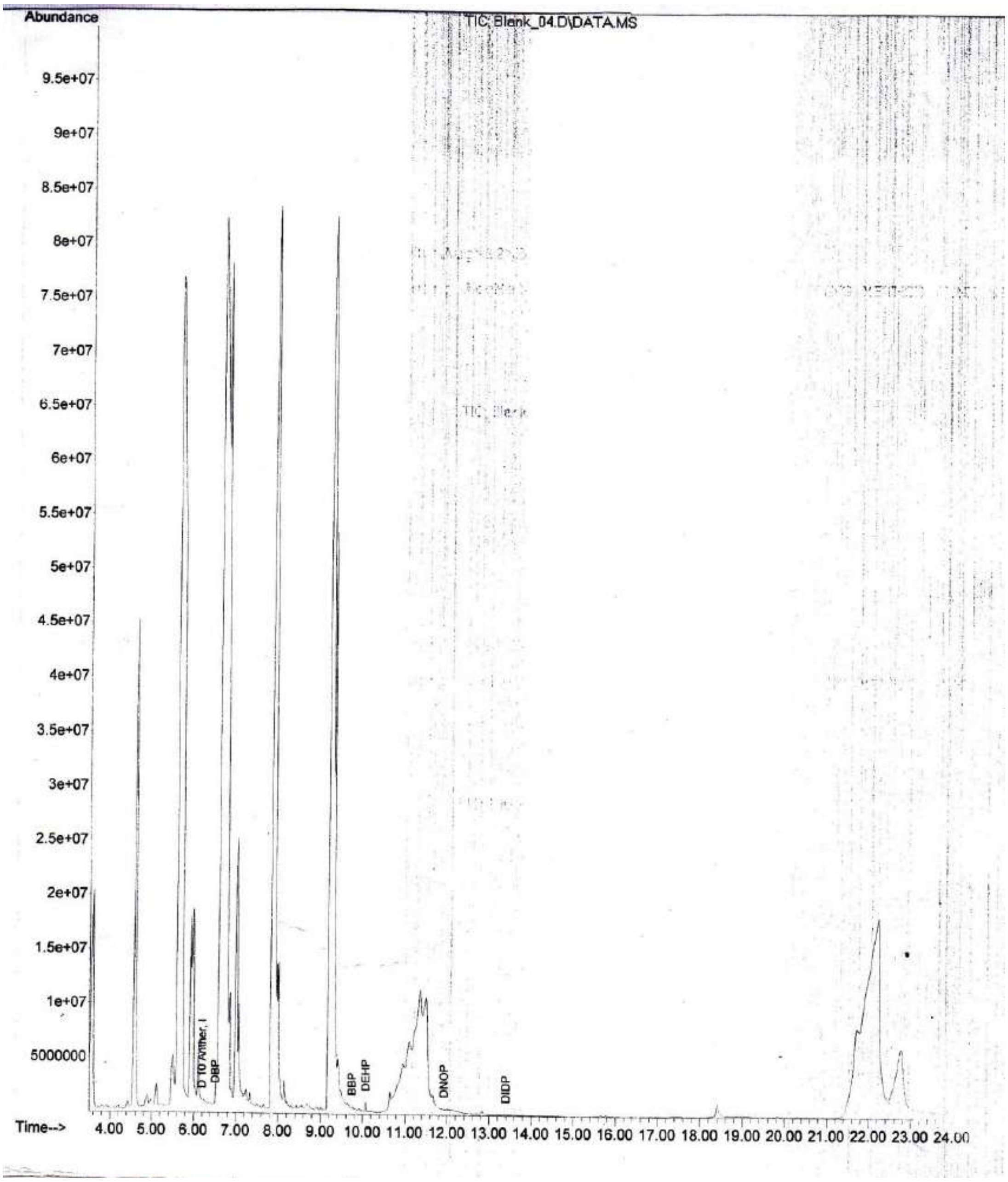

Figure 4 GC-MS Chromatogram of waste palm oil bio lubricant

From the chromatogram it is observed that there are five major peaks observed at retention time of 4.60, 5.70, 6.65, 7.90, 9.30 minutes. Methyl tetradecanoate that is saturated fatty acid esters containing long chain, Hexadecanoic acid, methyl ester that is saturated fatty acid ester with long chain, Next peak 11-Octadecenoic acid, methyl ester that is unsaturated fatty acid ester with long chain consist one double bond, Hexadecanoic acid,2-hydroxyethyl ester that is saturated fatty acid ester with long chain consist one hydroxyl group, 9-Octadecenoic acid (z)-,2-hydroxyethyl ester that is unsaturated fatty acid ester with long chain consist one double bond and one hydroxyl bond. Higher protections from oxidative thermal treatment obtain the presence of a bigger measure of the saturate content (Figure 4 and Table 4).

Table 4 GC-MS Chromatogram of the bio lubricant prepared from the waste palm oil bio lubricant

Retention (min)	Name of fatty acids	Area (%)
4.60	Methyl tetradecanoate	13.70
5.70	Hexadecanoic acid	14.40
6.65	11-Octadecenoic acid	19.60
7.90	Hexadecanoic acid	14.50
9.30	9-Octadecenoic acid (z)	16.70

Table 5 Identified compounds in each bio lubricant type

Type of bio lubricant	Identified compounds
Coconut oil	Methyl tetradecanoate and Dodecanoic acid, 2,3-dihydroxy propyl ester, Hexadecanoic acid, 11-Octadecaenoic acid, Myristic acid, Hexadecanoic acid, Tetradecanoic acid.
Neem oil	Dodecanoic acid, 12-Octadecadienoic acid (Z, Z), Methyl tetradecanoate, 9-Octadecenoic acid.
Palm oil	Methyltetradecanoate ,Hexadecanoic acid, 11-Octadecenoic acid, Hexadecanoic acid,2-hydroxyethyl, 9-Octadecenoic acid (z), 2-hydroxyethyl ester.
Waste Palm oil	Methyl tetradecanoate, Hexadecanoic acid, 11-Octadecenoic acid, methyl ester, Hexadecanoic acid,2-hydroxyethyl ester, 9-Octadecenoic acid (z),2-hydroxyethyl ester.

3.2 Analysis of produced the bio lubricants

The synthesized bio lubricants were exposed to certain property tests to study their pertinence as lubricating oil. Acid value, Density at 15°C, viscosities at 40 and 100 °C, Flash point and Viscosity index are the properties used to analyze. Then these properties were compared with the ISO VG 46 lubricant and mineral oil lubricant (Havoline Super 2T).

Density is the proportion of the mass of a substance corresponding to a known volume. Density is a key property in lubricants. In this study the lowest density can be observed in POBL. When compared with the ISO VG 46 and mineral oil lubricant, POBL density value (870.90Kgm^{-3}) is very closer to ISO VG 46 density value (875.3 Kgm^{-3}) and higher than mineral oil lubricant density value (857 Kgm^{-3}). And also, the other BL such as

COBL, NOBL, and WPOBL the density values are higher than the ISO VG 46 and mineral oil lubricant density value.

The density and lubricity are inversely proportional. Therefore, when the density is increasing the lubricity is decreasing. The density of POBL is in range of ISO VG 46 and mineral oil lubricant. This may attribute to the series chemical modifications it passed through. According to Density, Palm oil bio lubricant more effect as replace the mineral oil lubricant. Viscosity is a proportion of an oil thickness and capacity to stream at specific temperatures. Viscosity is the main consideration that decides bio lubricants application.

Table 6 Comparing properties of synthesized bio lubricant, ISO VG-46 and Mineral oil lubricant.

Property		Coconut oil biolubricant	Neem oil biolubricant	Palm oil bio lubricant	Waste palm oil bio lubricant	ISO VG 46[8]	Mineral oil lubricant [9]
Viscosity index		192	189	174	176	>90.00	141
Kinematic Viscosity (cSt or mm2/s)	40 °C	45.10	41.90	79.85	31.02	>41.40	59.2
	100°C	9.20	8.6	13.57	6.6	>4.1	9.4
Density (15°C) (Kgm^{-3})		1084.99	955.41	870.90	1097.58	875.3	857
Flash point(°C)		58.0	68.0	71.0	59.0	220	93
Yield percentage		50.62	53.88	74.93	58.52	-	-
Cost for 50ml lubricant. (SLRs.)		177.00	201.40	99.60	102.70	-	22.50 – 36.50

Hint, Coconut oil bio lubricant (COBL), Neem oil bio lubricant (NOBL), Palm oil bio lubricant (POBL), Waste palm oil bio lubricant (WPOBL), Mineral oil lubricant (MOL)

When the BL viscosities at 40°C and 100°C values were compared with the ISO VG 46, According to the Table 6 Palm oil BL viscosity at 40°C and 100°C (79.85cSt, 13.57cSt), Coconut oil BL viscosity at 40°C and 100°C (45.10cSt, 9.20cSt), Neem oil BL viscosity at 40°C and 100°C (41.90cSt, 8.6cSt) are in the range of ISO VG 46 viscosity at 40°C and 100°C (>41.40cSt, >4.1cSt). But Waste palm oil bio lubricant (31.02cSt, 6.6cSt) shows some deviation according to ISO VG 46. And the BL viscosities at 40°C and 100°C values were compared with the mineral oil lubricant and they show values in range of the mineral oil lubricant viscosity value at 40°C and 100°C (59.2cSt, 9.4cSt). But some deviation shows Waste palm oil lubricant and Palm oil lubricant.

Low viscosity stocks like WPOBL can be used as industrial oils. POBL, COBL, NOBL like higher viscosity lubricants can be used as diesel engine oils. The outcomes show that POBL is heavier and more viscous than the MOL. The viscosity index gives idea of how change of kinematic viscosity corresponding to temperature. A high viscosity index signifies a relatively small if change of kinematic viscosity low with temperature show high viscosity index value. Because of that high index value bio lubricants are more important than low viscosity index value bio lubricant [5]. The viscosity index values for BL were compared with the ISO VG 46 and mineral oil lubricant viscosity index values. According to the Table 6 all the BL viscosity index values are in the range of viscosity index of ISO VG 46 value (>90). And also, when compared with the mineral oil lubricant the viscosity index of all BL products is higher than the mineral oil lubricant viscosity index value (146) (Figure 4). According to these results, synthesize bio lubricant (Table 5) closely similar to lubricant of mineral oil source especially with the extra advantage of biodegradability. Higher viscosity index lubricants are more important for that machines work over a wide temperature range [3]. Bio lubricant’s volatility, fire resistance, flammability hazard of lubricating oil, transportation and storage requirements can be determined using flash point value.

The BL flash point compared with the ISO VG 46 flash point value, according to the Table 6, The ISO VG 46 flash point (240 °C) is higher than the all the prepared BL flash point values. And also, for the mineral oil lubricant flash point value also higher than the all the prepared BL flash point values but somewhat surround it value (Figure 4). Mixing unreacted reagents and impurities give early flash before bio lubricant. Used purification method was not enough and more method should be added.

According to the analysis of yield percentage of the bio lubricants, the POBL has the maximum yield percentage value (74.93%). The WPOBL has the next highest yield percentage (58.52%). And the third highest yield percentage is in the NOBL (53.88%). The lowest yield percentage is in the COBL (50.62%). This implies that the POBL is more effective than other bio lubricant. And also yield percentage is high means minimizes production cost. In here yield percentage of products are more important for cost analysis. Decreasing acid number as much as possible is better for increase yield percentage (Table 7).

According to the bio lubricant cost is higher than the mineral oil lubricant cost for 50ml. The Neem oil bio lubricant has the highest cost because Neem raw oil is more expensive than other raw oils. The Coconut oil bio lubricant has the second highest cost because its raw oil is not much expensive but its yield is very much low when compared with the other bio lubricants. The palm oil has the lowest cost because palm oil has the highest yield. In the case of waste palm oil, the waste palm oil can get free of charge but its yield is very low therefore the waste palm oil bio lubricant cost for production of 50ml is high compared with palm oil bio lubricant. But consider the depletion of mineral oil and environmental pollution can be extra cost advantage of using bio lubricant producing from natural oils than petroleum oil lubricant.

Table 7 Comparing properties of synthesized bio lubricant, ISO VG-46 and Mineral oil lubricant

Property	Coconut oil	Coconut oil bio-lubricant	Neem oil	Neem oil biolubricant	Palm oil	Palm oil biolubricant	Waste palm oil	Waste palm oil bio lubricant
Acid number (mg KOH/g)	12.79	9.08	7.85	5.05	10.43	16.71	28.49	6.17

High acid value in a bio lubricant cause erosion of machine parts and blocked oil filters. Number of additives and oxidation of bio lubricants are the factors which are depend on acid concentration of any bio lubricant [10]. According to the comparison of the acid value of raw oil and bio lubricant, the raw oil acid value is reduced after doing oil esterification. This is because of the free fatty acids, which mainly affect the acidity-converted into glycerol ester. That high value of acid number means high FFA in the oil which produced soap (saponification) reacts with the alkali catalyst. That usually causes in low yield and affects the purification process and the extraction of bio lubricant from reaction mixture.

CONCLUSION

According to lubricating property analysis shows chemical modification of natural plant base oil can be good replacement for mineral oil lubricant. These plant oil ester base lubricants are solutions for various environmental problems because of its biodegradability and also the solution for depletion of finite crude oil resources as bio lubricant can produce from renewable resources like plant base oils. In this research except their high flash point, other lubricating properties such as Density, Viscosity and viscosity index are in similar range to commercial industrial oil ISO VG46 required. However, this research must be forwarded to improve purity level of bio lubricant, improve on the yield of the bio lubricant and most important property is making bio lubricant for longer shelf life since bio lubricant properties can be easily damaged.

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