CHEMICAL MODIFICATION OF PALM OIL AS A BIO-BASED LUBRICANT: A REVIEW

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ABSTRACT

Mineral oil is commonly used in automotive applications or other industrial equipment due to its vast advantages. However, it is a non-renewable resource, and the pollution generated from the emission during its use has become a massive issue for the environment; hence the substitution of mineral oil with vegetable oil as a base stock has overcome these issues. Palm oil is used as a case study because of its advantages over mineral oil. Palm oil is recognized for its good lubrication performance and the possibility of reducing reliance on mineral-based oil lubricants. This study aims at the development of palm oil as a lubricant via a chemical modification method. Palm oil is used as a case study because of its advantages over mineral oil. Many researchers present convincing results on the ability of palm oil have been widely used as a lubricant in engineering applications. Palm oil is recognized for its good lubrication performance and the possibility of reducing reliance on mineral-based oil lubricants.

Keywords: Palm oil, Vegetable oil, Chemical Modification, Bio-Lubricant

1. INTRODUCTION

The palm oil sector is one of the decisive revenue earners for Malaysia's economy after the electrical, electronic, petroleum, and chemicals industries. According to the Department of Statistics Malaysia, 457 oil palm mills in Malaysia are in operation in 2020, with a total processing capacity of 116.81 million tonnes of fresh fruit bunches yearly. Over the years, demand for palm oil has been steadily increasing. To meet this demand, the planted area of oil palms reached 5.87 million hectares in 2020. Vegetable oil-based lubricants are eco-friendly and have been extensively studied as a viable alternative to conventional petroleum-based lubricants due to their non-renewable resource and impact on environmental pollution. Palm oil can be used as a substitute for bio-lubricant due to its high production rate. Recently, mineral oil has been widely used as a lubricant in many sectors, namely automotive, metalwork, electronic and electrical, food and many more.

There is an attempt to study the potential of vegetable oils to be used as bio-diesel and bio-lubricant. Malaysia and Indonesia are the tropical countries with the largest palm oil producers globally that are virtuous for agricultural activities. Malaysia generates RM 64.84 billion with approximately 5.9 million hectares in the year 2019 [1]. However, according to the Department of Statistics Malaysia, the COVID-19 pandemic has affected Malaysia's economy in the first quarter of the year 2020 as it presents a decrement in Gross Domestic Product (GDP) in the palm oil sector [2]. In addition, Ghulam et al. [3] reported that Malaysia is among the countries in Asia that dominates the international trade with about 80% of palm oil supply.

In this study, palm oil is used as a case study because of its advantages over mineral oil. Many researchers present convincing results on the ability of palm oil have been widely used as a lubricant in engineering applications. Palm oil is recognized for its good lubrication performance and the possibility of reducing reliance on mineral-based oil lubricants.

Bio-lubricant or bio-based lubricant is known for its eco-friendly biodegradable and eco-toxicity to the environment. Bio-lubricant has been synthesized as a lubricant extracted from raw materials of vegetable and animal oils, renewable sources, and non-toxic to humans or environmentally living things [4][5]. The bio-lubricant is generally used to replace conventional entirely or partially mineral-based lubricants, for example, petroleum-based mineral oils. Statistics in Figure 1 presented by Salih et al. [6] show that Grand View Research published the increasing number of expected lubricants in the global market by the year 2021. This happened due to the high demand in oilfield activities and the high sales in the automotive sector. Over the year, the high market demand for lubricants has caused a detrimental effect on human health, increased toxicity, mess up with marine ecosystems, air pollution, and soil contamination, thus leading to a mineral-based lubricant replacement the bio-lubricant based.

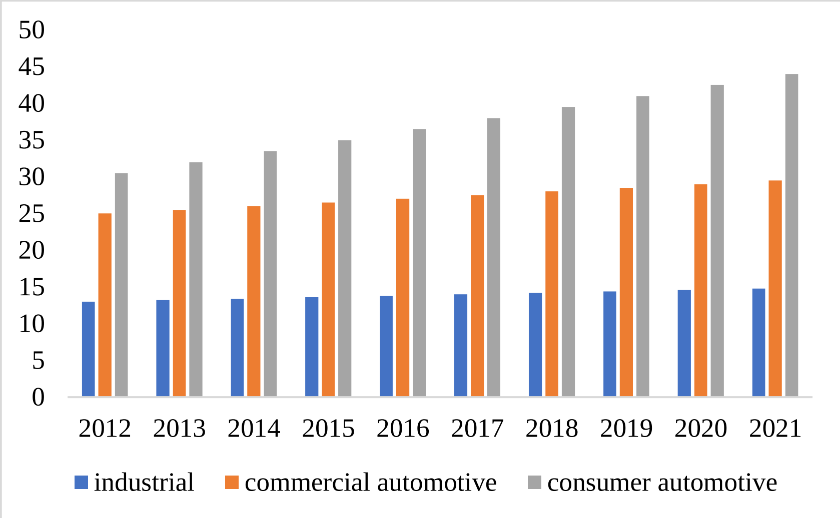
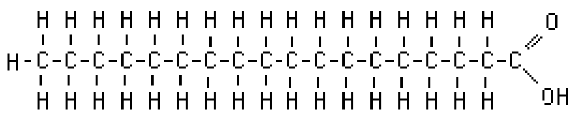
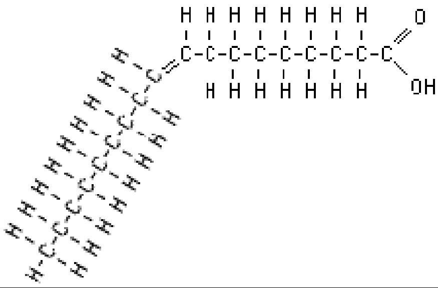
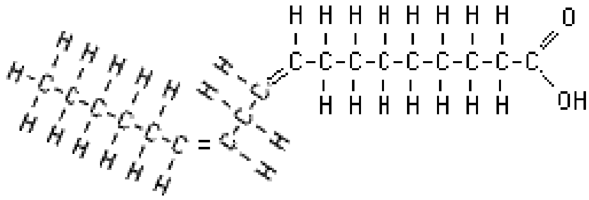


Figure 1: Global Lubricants Market Volume by Product, 2012 – 2021 (Million Tons) [6]

Vegetable oil is composed of glycerol and fatty acids known as triglycerides. These fatty acids can be categorized according to the number of double bonds in their carbon chains; saturated and unsaturated. Saturated acids contain no double bonds in their carbon chains, whereas unsaturated acids contain double bonds and are referred to as mono-unsaturated and poly-unsaturated, as shown in Table 1.

Table 1. Classification of Fatty Acids [7]

Fatty acids group	**No. of Double bonds**	**Example**	**Molecular structure**
Saturated	0	Stearic acid	

Mono-unsaturated	1	Oleic acid	
Poly-unsaturated	2	Linoleic acid	

Most vegetable oils are less suitable for lubricants due to their more significant percentage of unsaturated oil with oxidation active sites β-hydrogen. The chemical structure of the glycerol backbone and double bonds in the fatty acids produce a high temperature, which then causes the vegetable oil to become unstable. These fatty acids composition in vegetable oil triglycerides is identified by ratio and carbon bonds as most plant-based oils are between 14 and 22 carbons long. The greater amount of double bond in plant-based oil contributes to the higher level of the unsaturated value, leading the oil to become oxidized [8][9]. This oxidation causes the oil to polymerize, reducing lubricity capability and increasing viscosity.

Vegetable oil generally has high viscosity index, low friction and wear, good flash point, low volatility, and high biodegradability [10][11]. It is because of the structure molecule. Vegetable oils are suggested to be an alternative to mineral oils due to their long-chain fatty acid and polar groups of the molecule structure. However, even though vegetable oils have numerous advantages in their lubricating properties, it is not able to replace the mineral oils entirely due to its limitation on oxidative stability, poor thermal and higher pour point. This issue can be resolved by implementing the proper additives. Vegetable oils can be classified into two groups: edible oils and non-edible oils. Non-edible oils are environmentally friendly hence have been widely used as bio-lubricants in engine fuels and automotive applications. Typical vegetable oils used as a bio-lubricant are sunflower, jatropha, castor oil, palm oil, etc.

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1.1 Palm Oil as a Bio-Lubricant

Palm oil is one of the vegetable oils characteristically extracted from the oil palm tree. According to Soh et al.[12], there are two types of palm oil produced: crude palm oil (CPO) and palm kernel oil (PKO). Palm oil has a wide range of applications, 80% of the palm oil is used in food industries, mainly as cooking oils, and 20% is used as an oleochemicals product in lubricant industries. Palm oil has been tested widely compared to mineral oil in the lubricant industry due to its numerous advantages: inexpensive, readily available, biodegradable, environmental-friendly, and renewable [13]. Palm oil has a unique balance of saturated and unsaturated fatty acid composition, suitable for many applications. There are two ways to use palm oil as a bio-lubricant; converting the oil into fatty acid methyl ester

(FAME) or blending the oil with commercial lubricant and using it as a lubricant additive in internal combustion engines [14]. Palm oil can be used to produce the bio-lubricants and allow their direct use as lubricant-based stock through the right modification processes. The modification methods are viscosity modifiers, direct addition of anti-oxidants, genetic modification of fatty acid profile, pour point depressant, emulsification, and chemical modification of palm oils [10]. Hydrogenation [15], epoxidation [16], estolide formation [17], and esterification or transesterification are mainly processes that involve chemical modification. Cecilia et al. [17] have presented the difference between chemical modification of various vegetable oils with its advantages and disadvantages in Table 2.

Table 2: Vegetable Oils Chemical Modifications [17]

Chemical Modification	**Description**	**Advantages**	**Disadvantages**
Esterification/ transesterification	Transformation of an ester to another ester with higher thermal stability	Improves thermo-oxidative stability Improves low-temperature properties	Requires feedstock with high oleic acid content High reaction temperature
Selective hydrogenation	Hydrogenation of unsaturation and thermochemical cleavage of the ester	Reduces degree of unsaturation Improves oxidative stability	Isomerization reactions (cis-and trans-acids) High reaction temperature
Epoxidation	Unsaturated C-C bonds, which are interconnected by an oxygen atom	Improves lubricity Improve thermo-oxidative stability Low reaction temperature	Increase pour point value Decrease viscosity index
Estolide formation	The reaction between two identical or of different acidic molecules	Improves thermo-oxidative stability Low reaction temperature Allows the use of several vegetable oils	High production cost

The hydrogenation process is the liquid fraction of the semi-solid palm oil modified physically for a particular application. In this process, the unsaturation of triacylglycerol oil is reduced, thus increasing its putrefaction and oxidation stability. Epoxidation is similar to hydrogenation as it converts the double bond in an unsaturated fraction into the epoxide functional group. Palm oil contains unsaturated fatty acids such as oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3), as well as saturated fatty acids such as palmitic acid (C16:0) and stearic acid (C18:0). The unsaturated fatty acids in molecules cause an effect on palm oil oxidative stability. Therefore, chemical modification is a standard method to improve its unsaturated acids.

1.2 Chemical Modification of Palm Oil

Esterification is a chemical reaction process in combining an acid and alcohol to produce an ester. In contrast, transesterification converts triglyceride esters into triesters through the alkyl group modification with a catalyst [18][19]. Transesterification involves two-stage palm oil synthesized due to the high free fatty acid (FFA) content in the oil, as shown in Figure 3.

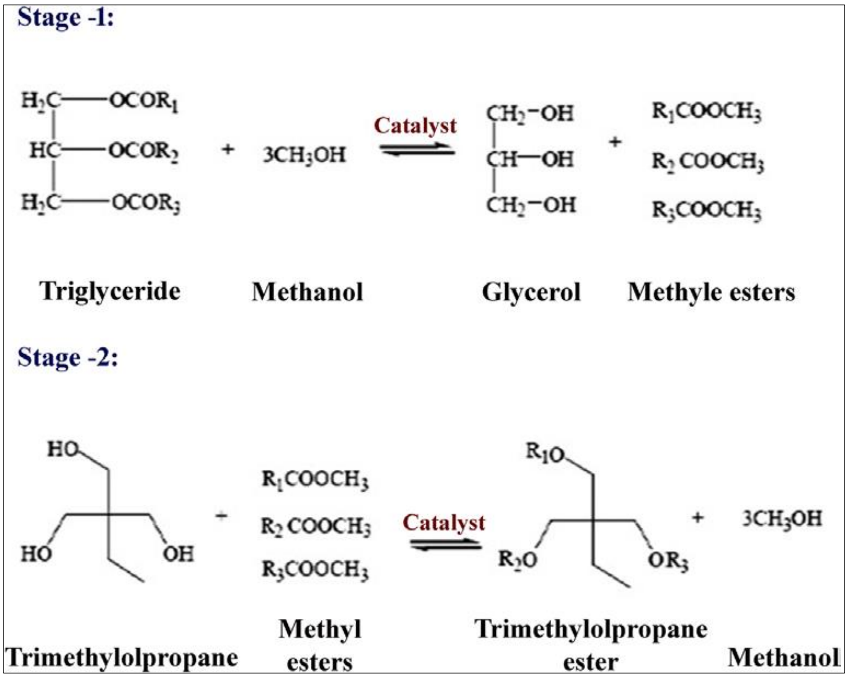

Figure 3: Synthesis of Palm Oil in the Transesterification Process[20]

The first stage is the process of converting palm oil using methanol into palm oil methyl ester (POME) with a presence of a base catalyst. Typical catalysts used are sodium methylate, sulphuric acid, p-toluene sulphonic acid, tetraalkyl titanate, anhydrous sodium hydrogen sulphate, phosphorous oxides, stannous octanoate, immobilized lipases, and mucor or rhizomucor miehei [21]. The second stage process involves the formation of palm oil-based polyol esters via the reaction of the POME with polyhydric alcohol. Glycerol, trimethylolpropane (TMP), neopentylglycol (NPG), and pentaerythritol (PE) are the common types of polyhydric alcohol [22][20]. These palm oil-based polyol esters show potential as an alternative to bio-lubricants. According to Raof et al.[22], TMP ester and PE ester are common palm oil-based polyol esters.

Polyhydric alcohol has a significant influence on the thermo-oxidative stability of the ester synthesized. Therefore, TMP is chosen in this study compared to other alcohol due to its relatively low melting point, moderate price, environmentally friendly, and good friction-reducing characteristics that are important as bio-lubricants base oil [23] –[25]. According to Mahmud et al.[26], TMP and PE ester have shown a high yield percentage from the synthesized process and present a good lubricity performance; nonetheless, TMP ester has tremendous potential and quality as a lubricant compared to PE ester.

Table 3: Transesterification Process Methods for Palm Oil Bio-Lubricants

Reactant	**Alcohol**	**Catalyst**	**Reaction conditions**	**Yield**	**Reference**
Palm Oil Methyl Ester (POME)	Trimethylolpropane (TMP)	Sodium methoxide	Temperature: 110°C Vacuum pressure: 1 to 1.5 mbar	98%	Abd Hamid et al.[27]
Palm Oil Methyl Ester (POME)	Trimethylolpropane (TMP)	Sodium methoxide	Temperature: 130°C Vacuum pressure: 20 mbar Time: 1h	98%	Yunus et al.[21]
Palm Oil Methyl Ester (POME)	Trimethylolpropane (TMP)	Calcium carbonate	Temperature: 180°C Vacuum pressure: 50 mbar Time: 8h	92.38 %	Masood et al.[29]
Palm Methyl Ester (PME)	Trimethylolpropane (TMP)	Sodium methoxide	Temperature: 140°C Vacuum pressure: 25 mbar Time: 25min	94.6 %	Ying Koh et al.[31]
Palm Fatty-Acid Distillate (PFAD)	Trimethylolpropane (TMP) Neopentylglycol (NPG)	Acetyl Chloride	Temperature: 40°C to 50 °C Time:10 and 8 h	94% 87%	Fernandes et al.[30]

Numerous studies have been conducted previously on the transesterification process used to create palm oil bio-lubricants. Table 3 presents the methods of palm oil bio-lubricants by transesterification process. It showed that the highest conversions are 98% Abd Hamid et al.[27] and Yunus et al.[21] Both had produced palm oil bio-lubricants on Palm Oil Methyl Ester (POME) and Trimethylolpropane (TMP) alcohol using sodium methoxide as a catalyst. The process was conducted at a reaction temperature of 110°C and 130°C with a vacuum pressure of 1 to 1.5 mbar and 20 mbar. The same method was also done by Ying Koh et al.[28] on the synthesis process of palm oil-based trimethylolpropane esters. However, the fractionated palm oil TMP esters by Ying Koh decreased to 94.6 % compared to the 98% by Abd Hamid et al. and Yunus et al. Masood et al.[29] and Fernandes et al.[30] conduct a study on a transesterification reaction apart from sodium methoxide catalyst, calcium carbonate and acetyl chloride. Based on research by Masood et al., the product yield 92.38% with a temperature of 180°C and a pressure 50 mbar within 8 hours. As for Fernandes et al., NPG and TMP were used as polyhydric alcohol in order to produce polyol esters. The product yield 94% and 87% of palm-based polyol triesters, respectively.

2. CONCLUSION

At present, most commercial engine oil is mainly mineral oil-based due to its readiness, cost rate, and performance. However, these factors cannot be sustained in the future because petroleum is a non-renewable resource, and pollution has become a great deal of environmental impact. Hence, palm oil is used as a case study in this study because of its advantages over mineral oil.

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