

HALAL GREEN FROM PLANT-BASED PRODUCT PERSPECTIVE: PALM OIL AS A POTENTIAL SOURCE FOR MARINE ENGINE LUBRICANT

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ABSTRACT

The green concept is the idea or the theory that harmony with the demand of Shariah, and therefore, it needs to be put into practice in the daily lives of every inhabitant on earth, including Muslims. Everyone can contribute and create impacts with their actions towards the environment; it may be good but also bad. As Muslims, it is part of their religious duties to make a good impact on the environment in general and the earth in particular. This research project is an attempt towards a halal green perspective of palm oil as a potential source of marine engine lubricant. This is because the Synthetization of Trimethylolpropane (TMP) esters derived from palm oil through transesterification has proven to be a suitable lubricant for industrial purposes. The lubricant displays good thermal and oxidative stability, a high viscosity index and, most importantly, good biodegradability. Thus, they are suitable for marine applications where environmental concerns are paramount due to oil spillage. However, the high requirement of lubricant properties due to extreme conditions for marine vehicles prevents the lubricant from being used for marine applications. Thus, this work aims to improve the important properties of TMP esters by blending them with synthetic marine engine oil. This will allow the TMP ester to achieve a higher kinematic viscosity, lower pour point and stronger wear prevention properties that are critical for applications in marine four-stroke engines while still retaining the biodegradability of the lubricant to some degree. The result obtained was a 40% TMP to 60% Synthetic Oil blend ratio that is most suitable to ensure maximised biodegradability potential without sacrificing engine performance.

Keywords: *Halal Green, Palm Oil, Marine Engine Lubricant*

1. Introduction

It is not exaggerated to say that the Halal green concept has long existed in Islamic teachings, although the term green concept is not being used. This indicates that the roots of halal green may reflect Islam's teachings that encourage Muslims to protect the earth and its surroundings. For example, 'Green Deen', 'Halal Green', may understand and reflect from a hadith of Prophet Muhammad, peace be upon him, in which he said: 'Wherever you may be at the time of prayer, you may pray, for it (the Earth) is all a mosque' (Sahih Muslim). This hadith indicates that the earth, like the mosque, is a sacred place that all must preserve and protect. From this understanding, it is discovered that the core message of Islam provides a helpful lens to Muslims and everyone else who is concerned with saving the earth to take the necessary actions. By protecting the earth and returning it to its original state, Muslims were educated as the way to understand the Oneness of Allah (s.w.t) (*tawhid*) so that humans may see and reflect the signs of God everywhere, being a steward (*Khalifah*) of the earth, honouring the covenant, or trust, we have with God (*Amanah*) to be protectors of the planet, moving toward justice (*adl*), and living in balance with nature (*mizan*) (Nurdeng Deuraseh, 2003). All these principles show that Islam teaches a deep love of the planet, and this is because to love the world is to love ourselves and to love the Creator (Nurdeng Deuraseh, 2010).

Regarding the above, developing the product from plants is essential to make halal green. Palm oil should be considered a potential halal green source in producing marine engine lubricants. Lubricants are being developed not only based on their properties but also require parameters such as load, temperature, and speeds for scientists to investigate the change in bulk material when the surfaces of material contact and move relative to each other. Lubrication is simply the use of material to improve the smoothness of movement of one surface over another, and the material which is used in this way is called a lubricant (Lansdown, 1982). Lubricants are also commonly used to reduce and minimise the friction and wear of interacting surfaces in mechanical systems so that the system can operate smoothly and run for an extended period.

Currently, mineral and synthetic oils are widely used in the lubrication industry. Because of the significant damage to the environment due to the toxicity and not readily biodegradable of this current lubricant (Castro et al., 2006; Zulkifli et al., 2013) increases worldwide health concerns. This issue is more problematic for marine applications since oil spillage, a common occurrence, will disrupt the marine ecosystem and suffocate living organisms. An alternative lubricant, such as vegetable oils, may solve the problem since it is non-toxic, biodegradable, and renewable. Additional beneficial properties of vegetable oil, such as a high viscosity index, good lubricity, high flash point and low evaporative loss, have also made it preferable for use instead of mineral oil-based lubricants (Syahrullail et al., 2013; Ghani et al., 2015; Zulkifli et al., 2014). However, vegetable oil has poor low-temperature behaviour, low oxidative stability, and poor thermal stability, which limit its potential application in industrial lubricants.

Palm oil is a vegetable oil-based that has been tested widely in the lubrication industry because of its advantages over mineral oil, which are inexpensive, readily available, biodegradable, environmental-friendly and renewable (Lewate, 2002; Battersby, 2000). Malaysia is now the second largest country as a palm oil producer after Indonesia. Much research is being done on testing the performance of palm oil as a lubricant, and it reports that it can be a good lubricant since it gives a low coefficient of friction (Jabal et al., 2014).

Thus, to improve these properties, one approach is to convert the oils to natural synthetic esters through various structural modifications. The new ester may have better pour point (PP) and thermal and oxidative stability properties but could also exhibit negative traits such as inferior viscosity, viscosity index (VI), and biodegradability.

Yunus et al. (2003) have described a method known as transesterification of palm oil to modify the structures of palm oil to form new natural, synthetic esters. This newly revised palm oil structure has been proven to be a very effective lubricant for industrial applications.

2. Research Background

2.1 Problem Statement

Various severe environmental problems threaten the planet's future, including global warming or climate change, pollution problems, over-consumption and increased waste. From this phenomenon, the world today is concerned with tackling this environmental crisis, most notably via the implementation of "Go for Green" or, in an Islamic context, "Go For Halal Green" in today's life, mainly to deal with the challenge of global warming that the world is facing today. It is the gradual rise of the earth's temperature. In some areas, the

temperature has increased by as much as 7 degrees Fahrenheit (or 3.8 degrees Celsius) over the past 50 years. This rapid rise has been linked to the way humans live today. Many scientists believe the Earth will continue to become warmer and endanger lives by changing environments and animal habitats if human lifestyles do not change. Without the proper intervention, this will have devastating consequences, including affecting the state of the global economic system.

In marine lubrication, the concern is to focus on the issues related to many lubricants lost in the environment due to spillage. This concern was greatly shown when the US Environmental Protection Agency (EPA) published the Vessel General Permit (VGP), which came into force in Dec 2013. The VGP demanded that an environmentally acceptable lubricant (EAL) must be used for all ship equipment having an interface with seawater and applies to all vessels (>79 feet in length) entering US waters unless technically infeasible. The EAL mainly focuses on biodegradability and low toxicity, where a lubricant must be at least 20% biodegradable and 60% biodegradable in 28 days. This enforcement law has spread to parts of Europe and will soon be established worldwide when the environmental concern has peaked.

Therefore, manufacturers have been exploring using vegetable oils and biodegradable synthetic lubricants. However, vegetable oils such as palm oil, though they have been improved using various methods such as transesterification (Yunus et al., 2003), still need to compete with cheap mineral oils and high-performance synthetic lubricants. This is especially true due to their inferior viscosity and pour point compared to synthetic lubricants.

Thus, one such method of producing biodegradable synthetic lubricants is through a mixture of palm oil and synthetic oil to achieve biodegradable lubricant properties without sacrificing performance. Therefore, this study will be conducted where the modified palm oil, TMP ester, blends with the current synthetic lubricant. Using TMP ester in present synthetic lubricant will increase the biodegradability of the lubricant which allows the lubricant to be considered as an Environmentally Acceptable Lubricant (EAL). Thus, this study aims to investigate the important lubricant properties of said mixtures or blends, such as anti-wear, kinematic viscosity and pour point of TMP ester with synthetic oil in different blending volume ratios to allow the lubricant to obtain a biodegradable property without sacrificing performance.

2.2 Research Objective

This study was carried out to investigate the possibilities of applying TMP esters derived from palm oil for marine application through the blending method with current synthetic lubricants. The objectives of this study are:

1. To investigate the effect of blending Synthetization of Trimethylolpropane (TMP) ester with Synthetic Oil on the kinematic viscosity of the lubricant.
2. To analyse the performance of the Synthetization of Trimethylolpropane (TMP) esters blended with Synthetic Oils on the lubricant's pour point.
3. To study the effect of the Synthetization of Trimethylolpropane (TMP) esters blended with Synthetic Oils on the wear-preventive characteristics of the lubricant.
4. To develop a product from a plant-based perspective, palm oil is a potential source of marine engine lubricant.

2.3 Scope of Work

This study aims to identify the feasibility of TMP esters as biolubricants for marine applications and how it can achieve the minimum requirement to be used as lubricants for a four stroke Marine Engine. Tests will be done on the blends of TMP esters with Synthetic Oils to analyse their quality and characteristics. However, due to the limited resources and time to investigate every qualification required to be acceptable as a marine lubricant, the test is limited to three different types, mainly viscosity, pour point, and wear prevention tests.

3. Literature Review

The term “Green” has become popular in modern literature, especially after many environmental crises, i.e., in-normal floods, earthquakes, and tsunamis, have had outbreaks in several countries. Apparently, ‘Green’ refers to the colour green, which is a result of combining yellow and blue. It has several signs representing or reflecting what human beings feel through expression and perception. However, green is generally one of the positive perceptions abundantly portrayed in foliage, alleviating tension and cooling the eyesight. For this reason, it can be expressed in application to the environment that green refers to something friendly and protects the environment, in line with the green concept that green relates to something that reduces the negative effect on the environment. Hence, this special feature of green was universally adopted and accepted in various fields (Nurdeng Deuraseh, 2023).

About the above, Sajeewanie et al., 2019, provide a very relevant suggestion when he/she defines the Green concept as “a set of effective, thoughtful and preventive actions that lead to the conservation of natural resources, including the integrity of animal and plant life and the individual and social welfare of present and future generations of human beings” (Sajeewanie et al. (2019).

Regarding Islamic literature, the term “Halal Green” is not mentioned, especially in Islamic classical literature. However, few have been mentioned in modern Islamic literature since Halal-Green is a new term produced by combining the terms Halal and Green. Similarly, there is no doubt that the term ‘Halal Green’ does not exist in the Holy Book. However, it is to be understood that the concept of Halal Green is quite similar to the idea of Halalan Tayyiban, which is mentioned several times in Al-Qur’an and Sunnah of the Prophet (peace be upon him). The similarity can be seen in that both terms, Green and Tayyiban, aim to impact humans and nature positively. (Deuraseh, N. 2023).

“Halal” is mentioned several times in the Quran and the Sunnah. It comes from the Arabic word Halal, generally understood as “things or activities permitted by Islamic Law.” Since Islamic law is the law that governs, manages and maintains human life, the halal concept must not just be about the slaughter of animals, alcohol use, or the sources of food and beverages but also about management, services, standards and processes that contribute to becoming a guideline for safety, cleanliness, reliability, and quality assurance. For this reason, to form a comprehensive and realistic green concept in the light of Islam, it should be built, and the term Green with the term “Tayyiban” is closely related to the Halal Green concept found in al-Qur’an. From an etymological perspective, Tayyiban means clean, sacred, safe, possessing quality and not detrimental. Thus, when the green and Tayyiban concepts are merged or related, a relationship will exist between the two, pertaining to goodness towards humankind and the environment. In this regard, when we associate the word green with halal as “halal green”, the term Halal Green is produced from the combination of the words ‘Halal’ and ‘Green’, which may be understood as the way to produce green in according to shariah which is mainly based on the term concept “Halal”-

the term that is derived from Arabic word, which means permissible or allowed and term Tayyib which mean safety, clean and wholesome. To explain further, Halal is anything permissible according to Shariah Law and is not limited to the products for Muslims' consumption. In Islamic jurisprudence, there are two meanings of Halal, one of which is that Halal means everything that makes a person not to be punished if he makes use of it, while the other meaning is that Halal is the act that can be done according to Shariah Law (Deuraseh, N. 2009; Deuraseh, N. 2023).

For example, if we say that Muslims have to live a Halal-Green lifestyle., it may be understood that Muslims should live and promote environmentally friendly living. More than that, according to Hanapi and Wan Khairuldin, 2017, the concept of Halal and Green should not be separated; this is to build a management model that is complete and comprehensive to combine both the physical and spiritual qualities (Hanapi, M. S., & Wan Khairuldin, W. M. K. F. (2017).

According to Ibrahim Abdul-Matin in his book 'Green Deen', he gives the understanding from a hadith of Prophet Muhammad, peace be upon him, in which he said: "Wherever you may be at the time of prayer, you may pray, for it (the Earth) is all a mosque". (Sahih Muslim). From this, Ibrahim Abdul-Matin said that because of the parable between the earth and a mosque, he understood that the earth, like the mosque, is also a sacred place. From this understanding, he discovered the core message that Islam provides a helpful lens to Muslims and everyone else who is concerned with saving the planet to take the necessary actions. This lens carries various ethical principles, including understanding the Oneness of God and His creation (tawhid), Seeing signs of God everywhere, being a steward (*Khalifah*) of the earth, honouring the covenant or trust, we have with God (*Amanah*) to be protectors of the planet, moving toward justice (*adl*), and living in balance with nature (*Mizan*). All of these principles show that Islam teaches a deep love of the planet, and this is because to love the world is to love ourselves and to love the Creator.

Based on the above, Halal Green should be proposed as one important course that may educate students about green. In this regard, halal green discipline may, technically, be defined as a discipline of knowledge and practices about the reality of all aspects of preservation of the environment, such as cleanliness, sanctity, safety, quality and being not deleterious besides being 'environmentally friendly' by way of protecting and nurturing environmental sustainability as well as beneficial to humankind. To achieve the objective of Islamic law, as Muslims, we have to play a role in maintaining a healthy environment with a particular focus on the global warming crisis.

In light of the above concept, palm oil is a potential source of marine engine lubricants towards halal green. As we know, a lubricant is generally a liquid substance introduced between two moving surfaces to reduce friction, improve efficiency and reduce. Lubricants dissolve or transporting foreign particles and distribute heat. In addition to serving these primary purposes, lubricating oils are also required to perform various other functions, including removing heat, preventing corrosion, and transferring power. Lubricants must also provide a liquid seal at moving contacts and remove wear particles. The most important properties of lubricants which determine their applicability and efficiency are viscosity, viscosity index, oxidative stability, thermal stability, flash point, low-temperature fluidity, corrosivity, wear resistance, biodegradability and non-toxicity. The most fundamental requirement of lubricants is that the oil should remain liquid over a wide temperature range, which could be as much as 300°C for aviation lubricants. In commercial uses, the usable liquid range is limited by the pour point at low temperatures and the flash point at higher temperatures. The pour point of a fluid is defined as the lowest temperature below which it would cease to flow. Similarly, another property is cloud point, which is the temperature at

which the dissolved solids in the fluid are no longer wholly soluble and precipitate as a second phase, giving the fluid a cloudy appearance. The cloud point is generally higher than the pour point in most cases. The flash point is the lowest temperature at which a liquid can vaporise to form an ignitable mixture in air. This point marks the temperature beyond which lubricant loss to the surrounding environment is at risk. Thus, the more significant the difference between the pour and flash points, the broader the temperature range over which the lubricant could be used safely. The viscosity of the lubricating liquid is a critical factor in determining the temperature range over which the lubricant offers the best performance. If the lubricating fluid is very thick, it will lead to energy loss due to viscous forces and the heating up of the liquid. Similarly, if the fluid is very thin, it will not lubricate the machinery efficiently by allowing the metal surfaces to come in contact with each other, leading to excessive wearing. In the case of liquid lubricants, viscosity generally decreases as the temperature increases. The viscosity index (VI) measures the amount of change in the viscosity of a fluid with a temperature change. Fluids with high viscosity indices show a minimal change in viscosity with temperature. Oxidative stability is the property by which the lubricant can resist oxidation and is necessary for satisfactory performance in various environmental conditions. Thermal stability becomes essential when the lubricant is intended to be used at high temperatures, during which its lubricating properties may be degraded by polymerisation or by forming undesirable compounds. Croda Lubricants, Chevron Corporation, Exxon Mobil, and Shell are leading lubricant manufacturing companies. Croda Lubricants is the leading global supplier of lubricant base fluids and additives. Chevron Corporation is one of the world's six major oil companies. Shell, another member of the elite club of major oil companies, is a world leader in producing aviation lubricants that have applications in aeroplanes and flight equipment and demand the most stringent requirements.

Conventional lubricants driving the markets are significant mineral oil or synthetic oil-based. However, vegetable oils are experiencing a comeback due to environmental concerns as their chemical derivatives are rapidly bio-degradable. Vegetable oils have several inherent qualities that give them advantages over petroleum oils as the feedstock for lubricants. Unlike mineral oils, which can persist in the environment for years, vegetable oils are readily biodegradable. Vegetable-based lubricants can be derived from various vegetable oils, are inherently biodegradable, are low in toxicity, and do not harm aquatic organisms. These qualities are essential for lubricants used in environmentally sensitive areas such as marine ecosystems and those with a high potential of being lost to the surrounding environment.

3.1 Vegetable oils as biolubricants

Since every technology upgrade affects people and the environment, commercial petroleum-based lubricants aided with chemical additives used in transportation, agriculture, mining, and manufacturing are no exception. Moreover, depleting mineral oil resources with increasing crude oil prices has highlighted the urgent need to manufacture non-mineral oil-based lubricants. Vegetable oils provide an excellent lubricant base stock, mainly imputable to their environmentally compatible nature. Conventional mineral oil-based lubricants gained primacy over bio-lubricants due to their low cost and efficacy. Although the petro-based lubricants met most of the demands to be an adequate lubricant base stock, their main disadvantages lie in being non-renewable and toxic to the environment with poor biodegradability. The advantages associated with vegetable oils are their high viscosity indices, good anti-corrosion properties, high flash and fire points, low volatility, good additive compatibility, high affinity to metal surfaces and low eco-toxicity owing to rapid

biodegradability (Bart et al., 2013). All these significant attributes present them as an ideal alternative for lubricant formulations. In contrast to mineral oil and synthetic oils, vegetable oils exhibit few shortcomings like sensitivity towards hydrolysis, low thermo-oxidative stability and poor low-temperature behaviour. However, these drawbacks can be successfully improvised to produce feasible lubricant components by adding chemical additives, biotechnological interventions, or chemically modifying vegetable oils.

The main components of vegetable oils are triglycerides (natural esters), and the precise chemical nature depends on the plant species and strain from which the oil is obtained (Haberader et al., 2008; Nelson, 2000). Pure vegetable oil-based lubricants comprise a relatively small fraction of the biolubricant market mainly because of performance issues related to low thermo-oxidative stability and poor cold flow behaviour. Another reason is that vegetable oil-based lubricants are much less available than synthetic esters (Bremmer & Plonsker, 2008). To date, their most common commercial applications include hydraulic fluid and wire rope grease.

The poor oxidative stability is mainly attributed to the presence of double bonds in the fatty acid chains of triglyceride molecules. The presence of α -hydrogens (bis-allylic protons) in the triglyceride molecule makes the vegetable oils highly susceptible to radical attack and subsequent oxidative degradation, which results in polar oxy compounds (Erhan et al., 2008). This oxy-polymerization process ultimately forms insoluble deposits and increases oil acidity and viscosity. Vegetable oils also cause the corrosion of metals. The presence of ester functionalities renders these oils susceptible to hydrolytic breakdown. Low-temperature studies have also shown that most vegetable oils undergo cloudiness, precipitation and solidification at cold temperatures, thus giving rise to poor low-temperature properties.

A review by Fox et al. [2007] addresses oxidation as a limitation of vegetable oil-based lubricants. The oxidative stability of triglyceride-based vegetable oils is primarily limited by the degree of unsaturated double bonds. Unsaturated carbon-carbon bonds function as active sites for many reactions, primarily oxidation. Most triglyceride-based vegetable oils contain unsaturated fatty acids and are susceptible to oxidation. The greater the level of unsaturation, i.e., the more double bonds there are, the more susceptible the oil becomes to oxidation.

Furthermore, vegetable oil lubricants are also more expensive than comparable mineral oil lubricants as a function of both higher base oil costs and higher costs for the base oil-compatible additives (ACE, 1999). Although Miller (2008) stated that vegetable oil lubricants cost approximately double that of mineral base oils, more recent information obtained from a significant lubricant supplier suggests that the current cost premium for these biolubricants may be only 20% more. Changing from a mineral to a vegetable oil lubricant is relatively simple, as vegetable oils and mineral oils are compatible, and vegetable oil lubricants will perform adequately if some mineral oil residue remains. Because the overall formulations are less toxic, disposal costs are generally lower; however, this may only sometimes be the case, as fewer disposal stations can accept spent bio-based lubricants (ACE, 1999; Nelson, 2000; Bremmer & Plonsker, 2008)

3.2 Transmogrification of Palm Oils

In Malaysia, palm oil methyl esters (POMEs) and TMP are the building blocks for synthesising vegetable oil synthetic esters to produce lubricants. Malaysia is one of the world's major pioneers of oils and fats and has become the second largest palm oil producer, after Indonesia, since 2006. With this advantage of being at the highest position in the world in terms of oils and fats production, palm oil products such as POME have been utilised as

green biodiesel with positive results that are competitive with petroleum diesel. This would provide an additional advantage to the biolubricant industry, because the POME is readily available from the biodiesel industry. Furthermore, the TMP esters derived from palm oils have improved the lubrication properties compared to the original palm oil. A batch scale production of palm oil-based synthetic lubricant in a mini pilot reactor has been published and was successful to be used for the biolubricant production (Sulaiman et al., 2007).

The transesterification methods to produce palm oil-based lubricants are comparable to those of other vegetable oils to methyl esters. This is due to a similar reaction mechanism involving three consecutive competitive, reversible reaction steps. These transesterification reactions have been studied and used for other vegetable oils such as soybean, rapeseed, sunflower, palm and safflower seed and sesame oil.

Yunus et al. (2003) have described a method known as transesterification of palm oil to modify the structures of palm oil to form new natural, synthetic esters. This transesterification process involves the reaction between methyl esters in palm oils with trimethylolpropane [2-ethyl-2-(hydroxymethyl)-1,3-propanediol] (TMP) in the presence of an alkaline catalyst. They reported the optimal reaction conditions to be as follows: - duration: 1 h; temperature: 130°C; pressure: 20 mbar; catalyst: sodium methoxide at 0.8% w/w; and the molar ratio of POME: TMP at 3.9:1. TMP ester of palm oil containing 98% w/w TE was successfully synthesised in less than one hour. The transesterification process eliminates the hydrogen molecule on the beta-carbon position of the palm oil substrate. This improves the oxidative and thermal stability of the new TMP ester, a rare characteristic found in vegetable oils. Thus, it has been proven to be a very effective lubricant for industrial applications.

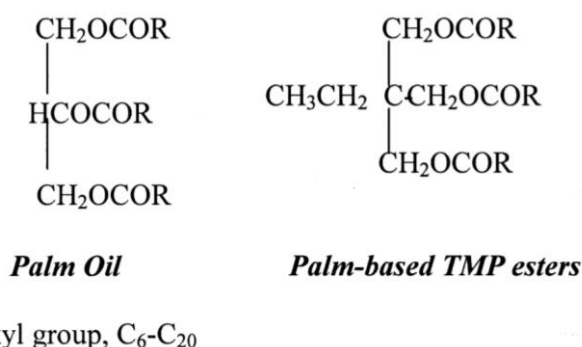


Figure 1 Molecular structures for palm oil and palm-based trimethylolpropane (TMP) ester

In comparison with other vegetable oils, researchers have reported the following kinematic viscosities at 40°C: 44.8-52.4 cSt for TMP esters of palm and palm kernel oils (Yunus et al., 2003), 43.9 cSt for TMP esters of jatropha curcas oil (Ghazi et al., 2009) and 11.2–36.1 cSt for TMP esters of 10-undecenoic acid (Rao et al., 2012) and 35.56 cSt for TMP esters of sesame oils. Thus, TMP esters of palm oil exhibit the best potential as lubricants viscosity-wise compared to other TMP esters.

3.3 Environmentally Acceptable Lubricants (EAL)

Environmentally acceptable lubricants are commonly classified according to the type of base oil used in their formulation. Lubricants generally consist of approximately 75 to 90 per cent base oil. Greases contain about 10 per cent thickening agent, usually soap (Gow, 2009) and base oil. The remaining fraction of a lubricant formulation consists of performance-

enhancing additives. A lubricant formulation can include hundreds of additives, which address performance issues specific to their application and performance shortcomings of the base oil. Additives are commonly used to manage oxidative ageing, corrosion, high-pressure, low or high-temperature conditions, phase transition, shear, foaming, and hydrolysis (particularly for vegetable and synthetic ester-based oils) (Habereeder et al., 2008).

The number of additives compatible with vegetable oils, synthetic esters, or polyalkylene glycols is small relative to the number of additives compatible with conventional (mineral) base oils. However, this is changing due to increased emphasis on EAL development. Additive manufacturers are working more closely with the lubricant industry to design more environmentally benign additives suitable for improving the performance of EALs (Aluyor et al., 2009). For some of the more stringent labelling programs, additives used in EAL must be ashless (i.e., containing no metals other than Ca, Na, K, Mg) and non-toxic (Habereeder et al., 2009). Calcium-based soaps are considered less toxic compared to different types (e.g., lithium-based), and soaps, in general, are considered less toxic than graphite thickeners (Gow, 2009).

Although EALs have been in commercial production for years, they comprise a small portion of the total lubricant market and are still considered niche products (Habereeder et al., 2008). The market for EALs continues to expand, particularly in Europe, where using such lubricants is encouraged through tax breaks, purchasing subsidies, and national and international labelling programs based on well-defined criteria. Many lubricants are advertised as being environmentally preferable; however, currently, there are no regulatory standards for EALs and no internationally accepted term by which they are defined. To distinguish lubricants which are both biodegradable and non-toxic according to acceptable test methods from those lubricants that are marketed as being “environmental” (or similar terminology), in their 1999 Lubricants and Hydraulic Fluids Manual, the US Army Corps of Engineers recommended the use of the term “environmentally acceptable” (a term commonly used by American Society for Testing and Materials (ASTM) committees) to address environmental lubricants. Bioaccumulation potential was not discussed within this definition of EALs.

While numerous terms are presently used to advertise lubricants as having desirable environmental properties, there is growing consensus to use the term “environmentally acceptable” to denote a biodegradable lubricant that exhibits low toxicity to aquatic organisms and has a low potential for bioaccumulation. Although many tests for these qualities exist, there is also harmonisation underway within the lubricant manufacturing community regarding the most appropriate standard testing methods for these and other attributes determined to be essential for an EAL, such as the proportion of renewable (recyclable) materials used in manufacturing. An environmentally acceptable lubricant should still perform well compared to the conventional lubricant it replaces. This harmonisation is driven by national and international labelling programs, particularly in European nations where the testing procedures and criteria have been codified (Habereeder et al., 2008 IENICA, 2004). While not regulated by law, these labelling requirements have helped clarify the difference between EAL and EFL products in the marketplace.

Because most lubricants are composed of base oil, the base oil used in an EAL must be biodegradable. The three most common categories of biodegradable base oils are 1) vegetable, 2) synthetic esters, and 3) polyalkylene glycols. Due to the low toxicities of these three types of base oils, aquatic toxicity exhibited by lubricants formulated from them is typically a consequence of the performance-enhancing additives or thickening agents (found in greases) used in the formulation, which can vary widely.

4. Materials and Methodology

For this study, the methodology can be divided into 3 parts which are:

1. Synthetization of Trimethylolpropane (TMP) ester.
2. Blend TMP ester with marine engine oil.
3. Characterization of Blends.

4.1 Materials

Palm oil methyl esters (POMEs) were obtained from Carotech (Malaysia) Sdn. Bhd. Trimethylolpropane, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol was purchased from Fluka Chemie GmbH (Switzerland) and alkaline catalyst, liquid sodium methoxide was obtained from Merck-Schuchardt (Germany). Other chemicals, such as ethyl acetate and N, O-Bis (trimethylsilyl) trifluoroacetamide (BSTFA), were purchased from Fluka Chemie GmbH.

4.2 Experimental Procedure

4.2.1 Synthetization of Trimethylolpropane (TMP) ester

TMP esters were synthesised by transesterification of methyl esters prepared from palm oils with trimethylolpropane [2-ethyl-2-(hydroxymethyl)-1,3-propanediol] (TMP). The reactions were performed in a pulse loop reactor. The reaction chamber comprises two stainless steel cylindrical columns interconnected via a U-shape configuration. This reactor is maintained at a temperature of 1300 C, pressure of 10 mbar and stirred at 60 rpm. Sodium methoxide is added as a catalyst, and the molar ratio of each component is as follows:

Table 1.1 Molar Ratio of TMP ester synthesis

Palm Oil	TMP	Catalyst
3	9	1

In this process, three alcohol groups in TMP were synthesised, and the process yielded reaction intermediates, namely monoesters (ME) and diesters (DE). The product is then filtered for 24 hours to remove impurities. The final product consisted mainly of triesters (TE) and a small fraction of DE. Unreacted POME was separated by vacuum distillation. POME, ME, DE, TE, and TMP samples were analysed by gas chromatography (GC).

4.2.2 Blending of TMP ester with Synthetic Oil

After synthesised TMP esters, the product was blended with a Marine Engine Oil, specifically a Synthetic Oil. The Synthetic Oil selected was a product named 'Marine 4T Motor Oil 10W-40' from LiquiMoly. 6 samples of the blend were synthesised between these two lubricants with the following volume ratio:

Table 1.2 Blending ratio of TMP esters with Synthetic Oil

Sample no.	TMP ester (%)	Marine Engine Oil (%)
1	100	0
2	80	20
3	60	40

4	40	60
5	20	80
6	0	100

400ml of sample was prepared for every oil composition. The equation used to obtain the oil composition was as follows:

$$\text{Oil composition} = Y \frac{X}{100} \quad (4.1)$$

Y is the total oil composition (ml), and X is the composition value for one oil. All the oil composition was mixed using a mixer. This mixer blade rotated at 200 rpm for 30 minutes. The samples were blended in terms of volume ratio due to the similarities of density between the TMP esters and Marine Engine Oil (0.05% difference).

4.2.3 Characterization of Blends

The blend has three important characteristics that must be tested according to the American Society for Testing and Materials (ASTM) methods to ensure the blends meet the standard criteria to be considered marine engine oil. The parameters are Kinematic Viscosity, Pour Point (PP), and Wear Preventive (PV) properties.

Viscosity and Viscosity Index (VI)

The experiment was carried out according to the ASTM D445, which described the measurement method for kinematic viscosities of a lubricant at 40 °C and 100 °C. This experiment used a constant temperature bath from Tamson, Model TV4000 (Zoetermeer, Holland) model TV4000, using an Ubbelohde capillary tube viscometer (Ubbelohde). The lubricants were tested for the time required to flow between two specific space intervals in the viscometer at the specified temperature. Furthermore, the Viscosity Index (VI) was calculated following the ASTM method D2270 based on kinematic viscosities at 40 °C and 100°C. The constants used in the viscosity calculations were acquired from measurements on calibration fluids provided by the manufacturer.

Pour point (PP) Test.

The test methods and apparatus for PP measurements follow the methods described in the ASTM D97. The pour points were measured using a low-temperature bath supplied by *Petrotest Instruments* (Dahlewitz, Germany). The sample was first preheated to a temperature of 45°C in a water bath maintained at 48°C, then cooled to 27°C in a second water bath set at 24°C. The sample was then transferred to the low-temperature bath kept at 0°C. The low-temperature bath is then placed at specific temperatures mentioned in the ASTM D97 to cool the samples at a specified rate. PP is the temperature at which no visible oil movement is observed when the test jar is held horizontally for 5 seconds. Thus, the sample flows were examined at a decrease of 3°C interval.

Wear Preventive Test

The test was run according to standard ASTM D4172, which is the standard test for Preventive Characteristics of Lubricating Fluid. Six different ratios of lubricant samples are being tested: the mixture of TMP ester and Synthetic Oil. The condition of the experiment is given below:

Speed	:	1200rpm
Temperature	:	75°C
Time	:	1 hour
Load	:	40kg

The sample volume used was approximately 10 ml per test, and the lubricants were compared using the average size of the scar diameters worn on the three lower-clamped balls.

5. Result and Discussion

5.1 TMP esters blend



Figure 2.1 Six samples of TMP blends with Synthetic Oil

In this study, TMP esters were blended with a 4-stroke marine engine synthetic oil(SO) at 100%, 80%, 60%, 40%, 20% and 0% volume ratio to produce 6 sample blends as shown in Figure 2.1(from left to right). Three tests were used to determine these blends' kinematic viscosity, pour point, and wear preventive characteristics. The results assess its potential to be used as a marine engine lubricant. It should be noted that the TMP esters were mixed quickly with Synthetic oil, indicating a good compatibility between the two lubricants.

5.2 Kinematic Viscosity Test

Kinematic viscosities of different blend ratios of TMP ester derived from palm oil and fully synthetic oil were measured at 40 °C and 100 °C in a temperature-controlled oil bath using Ubbelohde viscometers as described by ASTM method D445. The VI was determined according to ASTM method D2270. Figure 2.2 and 2.3 compares the results of kinematic viscosity measurements for all lubricant blends measured at 40 °C and 100 °C. The pure TMP ester derived from palm oil has a viscosity of 46.8 cSt, which is higher than other vegetable-based TMP esters such as TMP esters of jatropha oil (43.9 cSt), TMP of rapeseed oil (37.6 cSt) and TMP esters of sesame oils (35.56 cSt). Thus, TMP ester derived from palm oil are proven to be one step ahead of becoming the best possible biolubricant. Synthetic Oil are known for their superior performance for marine engine oil, especially in wear resistance over vegetable oils. However, they are relatively expensive compared to vegetable oils, even after consideration for the cost of modification of palm oil, such as the transesterification of TMP esters. This has led to some interest in understanding the tribological response after adding several vegetable oils, such as palm oil.

It was found that the lubricant viscosity increases as more synthetic oil is added to the TMP ester. The graph indicates that the lubricant increases its kinematic viscosity at 40 °C by approximately 10 cSt for every 20% increase in the ratio of synthetic oil. The linearity of the graph indicates a good compatibility and mixture between the two lubricants.

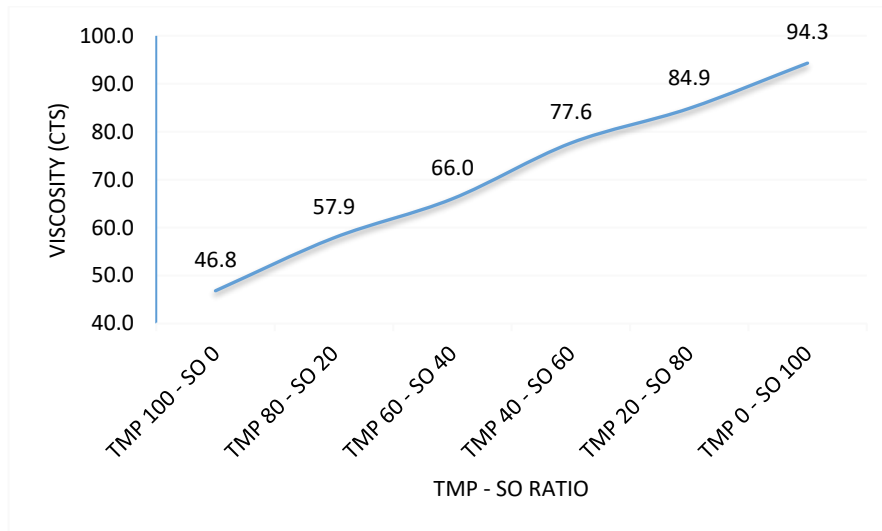


Figure 2.2 Kinematic Viscosity of blends at 40°C

For the kinematic viscosity of the lubricant blend at 100°C, the viscosity ranges from 9.4⁰C to 14.5⁰C. The increase is slight but linear as more synthetic oil is added with TMP ester. Although the rise is only 1⁰C for every 20% synthetic oil added, the value is more crucial due to the lubricants' function greatly diminishing at high temperatures as they become more fluid. This leads to lower lubricant efficiency of the 4-stroke engine as the viscosity decreases. Thus, the Society of Automotive Engineers (SAE) developed a specific scale to standardise the quality and requirement of an engine lubricant. For marine engine lubricants with SAE grade 10W-40, the minimum kinematic viscosity of a lubricant at temperature 100⁰C is 12.5 cSt. This implies that only a maximum blend of 40% TMP ester is allowed in the synthetic oil to ensure the standard criteria are met.

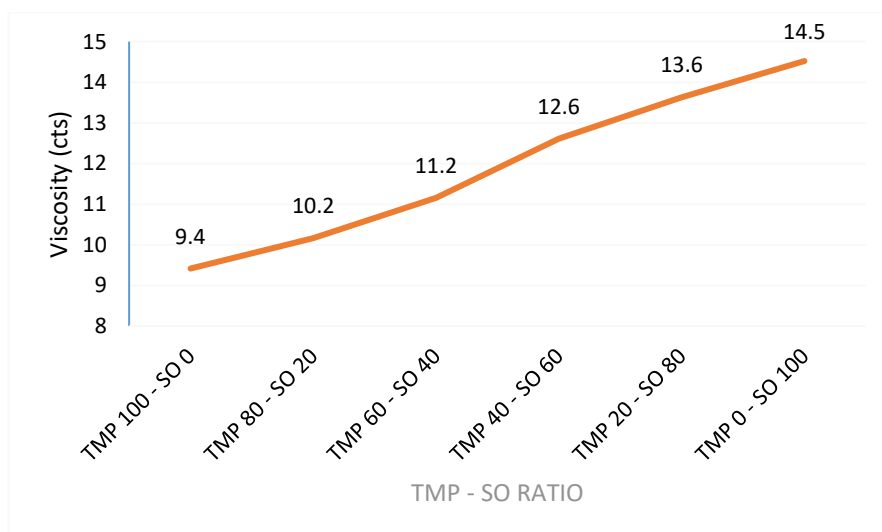


Figure 2.3 Kinematic Viscosity of blends at 100°C

The viscosity Index is the viscosity change rate between two temperatures measured to determine its ability to reduce friction in solid body contacts. If the lubricant is too viscous, it will require much energy to move, and if it is too thin, the surfaces will come in contact, and friction will increase. The best oils have the highest VI as they will remain stable and not very viscous over the temperature range. This allows for consistent engine performance within normal working conditions. The value of the blends is calculated according to the ASTM method D2270. Figure 2.4 shows that the difference of VI is relatively small except for the 100% TMP ester blend. 100% TMP ester has a higher VI, indicating a more reliable and stable viscosity rate.

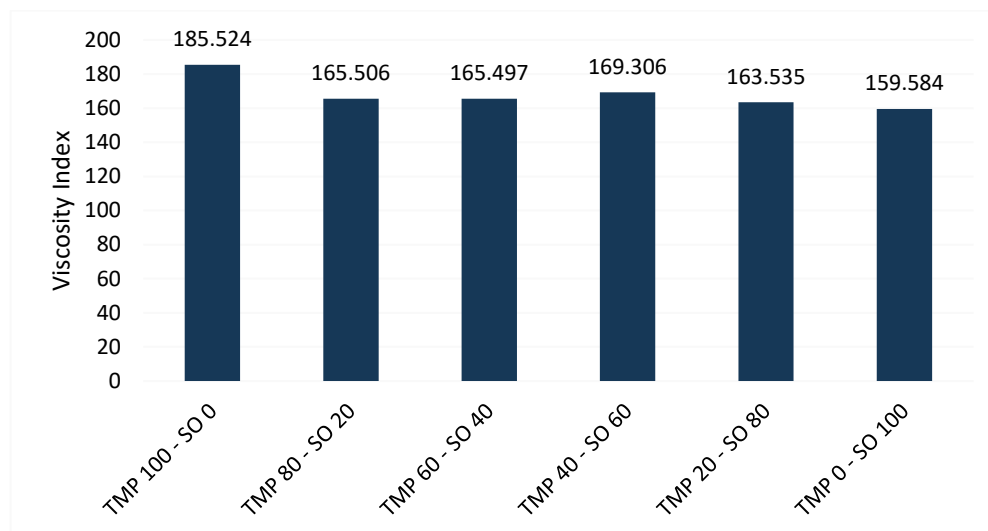


Figure 2.4 Viscosity Index of TMP ester blends.

5.3 Pour Point Test

The pour point (PP) is the temperature at which fluid movement is completely stopped. This test was done following the ASTM D97 method, and the results are displayed in Table 2.1. One of the most important reasons the current market does not use vegetable oils as biolubricants is their high pour point. Vegetable oils have poured point values of more than 0°C. This might not be an issue for lubricants that require operating in room condition. However, most applications, especially marine applications, require the capability of lubricants to act at very low temperatures. This is due to the long-term inactivity of typical marine engines, which usually run between seasons in most places worldwide. Seasons also play a vital aspect in the operation of lubricants. Winter seasons require marine engines to be able to start at conditions below freezing temperatures.

The TMP ester derived from palm oil has a pour point of -21°C. Although this value is higher than the desired pour point, it is similar to conventional mineral oil. It is also a large improvement compared to pure palm oil, which is 12°C. TMP ester derived from palm oil has also been shown to have a better pour point compared to other TMP esters of vegetable oil, such as TMP ester of jatropha oil and rapeseed oil, which are -6°C and -10.5°C respectively.

From the table, it can be observed that the pour point of TMP ester increases as synthetic oil is added. A standard 10W40 grade marine lubricant is expected to function at temperatures as low as -18°C. Therefore, it is ideally suitable for the lubricant's pour point to be more than 10°C below the engine's lowest operating temperature, around -28°C. Thus,

with the improvement of the pour point of TMP ester when synthetic oil is added, samples 4, 5, and 6 met the minimum criteria to allow the lubricant to function at operating temperatures as low as 18 °C.

Table 2.1: Pour point of 6 samples of TMP blends

Sample no.	TMP-SO ratio	Pour point [°C]
1	100-0	-21
2	80-20	-25
3	60-40	-28
4	40-60	-30
5	20-80	-33
6	0-100	-36

5.4 Wear Preventive Test

Wear Preventive lubricant characteristics are key to ensuring the engines last longer and do not lose excessive heat due to friction between two metals. Therefore, the four-ball wear test has been the base reference for all lubricant engineers to detect the degree of wear resistance for each lubricant. This test aims to determine the wear-preventive characteristics of a lubricant. In the four-ball wear test, a steel ball is rotated against three lubricated stationary steel balls under a specified load, speed, temperature and time, according to the ASTM D4172. This study tested the 6 blends of TMP esters produced under the four-ball wear test machine in the Faculty of Engineering, University of Malaya. After being tested, the three steel balls are chosen randomly to be placed under a microscope capable of measuring the diameter of the scars on the steel ball. Figure 2.5 shows the resultant diameter of the scar on the steel ball for all six of the TMP blends.

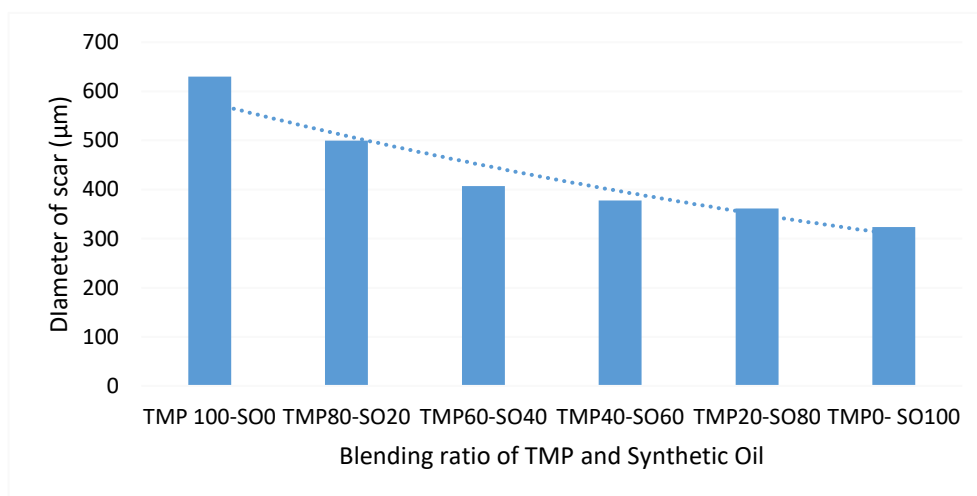


Figure 2.5 Diameter of scar on steel ball

Figure 2.5 shows that the scar diameter for TMP 100% is 629.9 µm, whereas a 100% Synthetic Oil has a scar diameter of 323.3 µm. As synthetic oil is added to TMP esters as blends, the scar diameter of the four-ball test has been reduced significantly. This allows marine engines to last longer as abrasive and adhesive wears are reduced as much as possible. It can also be observed that after 40% of synthetic oil is added to TMP esters, further addition of synthetic oils will only slightly reduce the scar diameter. Thus, the most optimum choice is the 60% TMP ester blend and 40% synthetic oil.

6. Conclusion

In this study, the objectives were completed. The effect of the addition of synthetic oils in TMP esters as blends allows for the increase in kinematic viscosity at 40°C and 100°C of the lubricant. This allows the blends to be used in a four-stroke marine engine oil at acceptable operating requirements. The pour point has also significantly reduced as synthetic oils are added to the TMP ester. The pour point of less than -28°C has allowed the lubricant to function at temperatures as low as -18 C, the maximum lowest operational temperature of a four-stroke marine engine. Furthermore, the wear-preventive characteristics of the TMP esters were greatly improved as synthetic oils were added. The addition of synthetic oil in TMP esters has reduced the wear scar diameter on the lubricated steel balls. This shows the lubricant's capability of reducing the friction between two metals in a four-stroke marine engine, which is paramount to improving the longevity and efficiency of the engine.

It can be concluded that the blending ratio of TMP-SO of 40%-60% is the best possible blend to use while maintaining the standard requirement of a lubricant to function in a four-stroke marine engine set by the Society of Automotive Engineers (SAE). This allows the blended lubricant to have a biodegradability potential of up to 40%, which allows the lubricant to be categorised as a biolubricant for marine applications.

The product from palm oil should be considered as a potential source of marine engine lubricants towards halal green for sustainable life and as one of the important ways to preserve the natural environment and its components, i.e., earth, water and air, which are no doubt are considered as essential things for social sustainability and wellbeing. Furthermore, today's consumers are demanding sustainability and transparency in consumable products. This means that there will continue to be growth in demand for Halal consumables. Innovation within the industry is the subsequent challenge for the global Halal market. The halal market is no longer restricted to the bounds of the food area. We all know that Halal Thayyiban is protecting Maqasid Shariah, or it can be said it is compliance with Shariah Law, which prioritises the integrity of production and consumption. Still, from another perspective, we can also see that the Halal Thayyiban concept is stated to be environmentally friendly, aligning with some SDG aims.

7. Recommendation

The research presented poses as a good stepping stone for future research. Many things were learned along the way, and some positive conclusions were reached. There are recommendations for future work on the potential of TMP esters derived from palm oil as marine lubricants. Firstly, this study was limited due to time and resources. Thus, further investigation on the rust resistance capability of the blends should be done as it is a necessary characteristic for all marine engine lubricants that require protection from seawater invasion. Other than that, studies on potential additives can be done to identify their compatibility with TMP ester to improve specific important lubricant characteristics such as thermal stability and wear resistance. Finally, the biodegradability of the blends should be tested as this will be the final test for the lubricant to identify the actual degree of biodegradability of TMP esters and the blends.

In light of religious demands, it is recommended that every human being is responsible for preserving the environment in line with Shariah command that Muslims have been entrusted through the Hadith of the Prophet SAW which means: "Abu Sa'id al-Khudri (may Allah be pleased with him) reported: The Messenger (may Allah's peace and blessings be upon him) said: "Life in this world is sweet and green, and indeed, Allah has made you successors there to see how you will behave." In light of this tradition, several actions are

required to achieve a sustainable environment, such as taking practical steps toward a more sustainable lifestyle, such as the Halal Green lifestyle, i.e., saving the earth, water, air, energy and most notably, in modern lifestyle context by switching to reusable products to reduce reliance on single-use plastics, switching to renewable energy in warehouses, factories, and offices, or reducing the use of single-use plastics in manufacturing. Because of the amount of energy, food, and man-made resources used every day, environmental sustainability is critical. Rapid population growth has increased farming and manufacturing, which has resulted in increased greenhouse gas emissions, unsustainable energy use, and deforestation.

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