

**SYNTHESIS OF BIO-LUBRICANT THROUGH THE  
ESTERIFICATION OF OLEIC ACID AND  
TRIMETHYLOLPROPANE CATALYSED BY  
SULFATED TIN (II) OXIDE**

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Thesis submitted in partial fulfilment of the requirements  
for the award of the degree of  
Bachelor of Chemical Engineering

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JANUARY 2014

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## ABSTRACT

Bio-lubricant has been proclaimed as a renewable alternative to mineral oil based lubricant due to the growing concern to the environmental impact and sustainability issue of the mineral oil based lubricant. Synthetic esters produced from the esterification of polyols and fatty acids are the bio-lubricant that can replace the mineral oil based lubricants in several applications. In this study, the synthesis of bio-lubricant, trimethylolpropane (TMP) oleate, using sulfated tin (II) oxide was carried out. TMP oleate is most common and widely used in hydraulic fluids. The heterogeneous sulfated tin (II) oxide has been chosen as catalyst because of the shortcomings of the homogeneous catalysts such as difficulty to be separated from the products and reused. The sulfated tin (II) oxide was synthesized by precipitation followed by impregnation and characterized for its physicochemical properties. The catalytic activity was examined through the esterification of TMP and oleic acid (OA) under constant rate of stirring of 800rpm, 0.3 wt. % catalyst with particle diameter of,  $d_p \leq 63 \mu\text{m}$  to eliminate the resistance of external and internal diffusion. The molar ratio of TMP to oleic acids was varied from 1:2.7-1:3.3 and reaction temperature was varied from 120°C-180°C. The TMP oleate synthesized was tested for its total acid number and viscosity. The results indicated that the highest conversion of OA, 91.2% was achieved at temperature of 180°C and the molar ratio of TMP: OA was 1:2.7. Apparently, the reaction temperature has more significant effect on the conversion of OA as compared to molar ratio of reactant, verifying that the reaction is controlled by surface reaction. The catalyst synthesized in this work is expected to provide a simpler and cheaper separation process with the catalyst reuse, reduced waste generation, and increase in yield of TMP oleate at optimum parameters.

## ABSTRAK

Bio-pelincir telah diisytiharkan sebagai alternatif kepada minyak pelincir yang berasaskan mineral kerana kebimbangan yang semakin meningkat disebabkan pelincir minyak mineral yang memberi kesan negative kepada persekitaran kita dan isu kemampanan. Ester sintetik berdasarkan polyols dan asid lemak boleh menggantikan minyak pelincir berasaskan minyak mineral dalam beberapa aplikasi. Dalam kajian ini, sintesis bio- pelincir, trimethylolpropane (TMP) oleate telah dijalankan dengan mengguna pemangkin sulfated timah oksida. TMP oleate biasanya diguna secara meluas dalam cecair hidraulik. Heterogeneous sulfated timah (II) oksida telah dipilih sebagai pemangkin kerana pemangkin homogeneous mempunyai beberapa batasan seperti kesusahan dalam pengasingan catalyst daripada produk dan kebolehgunaan pemangkin. Ia telah disintesis daripada cara mendakan berikut dengan penyuburan dan ujian untuk ciri-ciri fizikokimia telah dijalankan. Aktiviti pemangkin telah diperiksa melalui pengesteran TMP dan asid oleik (OA) di bawah kadar kekacauan 800rpm, 0.3 wt % pemangkin dengan diameter zarah ,  $d_p \leq 63 \mu\text{m}$  untuk menghapuskan rintangan penyebaran luaran dan dalaman. Nisbah molar TMP kepada asid oleik telah diubah dari 1:2.7-1:3.3 dan suhu eksperimen telah diubah dari 120°C - 180°C.. TMP oleate disintesis telah diuji untuk jumlah nombor asid dan kelikatan. Keputusan menunjukkan bahawa penukaran tertinggi OA, 91.2 % telah dicapai pada suhu 180°C dan nisbah molar TMP: OA adalah 1:2.7. Konklusinya, suhu eksperimen mempunyai kesan yang lebih besar ke atas penukaran OA berbanding dengan nisbah molar bahan. Hal ini telah mengesahkan bahawa tindak balas kimia ini dikawal oleh tindak balas permukaan pemangkin. Pemangkin disintesis dalam kerja ini dijangka boleh memudahkan proses pemisahan dengan harga yang lebih murah, meninggikan penggunaan semula pemangkin, mengurangkan sisa dan meningkatkan hasil TMP oleate pada parameter optimum.

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## LIST OF ABBREVIATIONS

$(\text{Al}_2\text{O}_3)_4(\text{ZnO})$	Doped alumina
$\text{Al}_2\text{O}_3$	Alumina
BET	Brunauer-Emmett-Teller
$\text{CH}_3\text{COONH}_4$	Ammonium acetate
$C_{\text{titrant}}(\text{M})$	Concentration of titrant (mol/L)
FESEM	Field Emission Scanning Electron Microscope
Fe-Zn	Ferrum- Zinc
FTIR	Fourier Transform Infrared Spectroscopy
$\text{H}_2\text{SO}_4$	Sulfuric acid
KOH	Potassium hydroxide
$m_{\text{sample}}(\text{g})$	Mass of sample (g)
$\text{MW}_{\text{KOH}}(\text{g/mol})$	Molecular weight of KOH (g/mol)
NPG	Neopentyl glycol
OA	Oleic acid
OH	Hydroxyl group
PE	Pentaerythritol
$\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$	Tin (II) chloride dihydrate
SnO	Tin oxide
$\text{SO}_4^{2-} / \text{SnO}_2$	Sulfated Tin (II) Oxide
TAN	Total acid number
$\text{TAN}_0$	Total acid number at time zero
$\text{TAN}_t$	Total acid number at time t
TMP	Trimethylolpropane
$V_{\text{titrant}}(\text{mL})$	Volume of titrant (mL)
XRF	X-Ray Fluorescence



# 1 INTRODUCTION

## *1.1 Background of Study*

Mineral oil based lubricants have been widely used in the industry. The consumption of lubricants is enormous and has been estimated at 37 million metric tonnes per year. Around 50 percent of this amount is lost to the environment as a result of leakages, volatility, accidents and total loss application where fresh lubricant is supplied at specific intervals while used lubricant is discarded to the environment. These losses are detrimental to the environment by causing the contamination of soil, groundwater and air (Akerman et al., 2011). With the raising of public awareness to the environmental impact of the mineral oil based lubricants, demand for the bio-lubricant which is biodegradable has been increased to substitute the mineral oil based lubricant as hydraulic fluid. Biodegradability has become one of the most significant design parameters both in selection of based fluid and in the overall formulation of the finished lubricant. The synthetic oleo chemical esters have been shown to possess high biodegradability under both aerobic and anaerobic conditions (Rudnick & Erhan, 2006). In addition, mineral oil is not sustainable, it is getting depleted. Bio-lubricant is more promising as it is sustainable and it has more desirable physical properties such as better cold flow properties, wider range of viscosities and higher lubricity after numerous studies are being conducted for the improvement on the physical properties in order to compete as an economical alternative with mineral oil based lubricants.

Although bio-lubricant can be superior to mineral based lubricant in many applications, but the price of bio-lubricant is generally about three times more expensive than mineral based lubricant. This initial acquisition cost may deter potential buyers, but it is counterbalance by reducing energy costs resulting from the higher lubricity of the bio-lubricants. The operating energy requirement contributes 96.02% which is high majority to the cost of operating a machine (Cliff, 2007). The high lubricity of the bio-lubricant eventually generates large savings in energy and maintenance costs by lowering the energy input. By reducing the frictional coefficient of the machine, the gradual degradation of a machine will be minimized hence reducing maintenance costs of the machine. Therefore, the increased cost of the lubricant is negligible when compared to the cost savings in energy and maintenance costs. Bio-lubricant can lowers the frictional

coefficient at the pitch point more efficiently than mineral based lubricant. Bio-lubricant is a more promising alternative to use in various high temperature applications such as injection moulding equipment or heated presses because of its higher lubricity (Ing, 2009).

Bio-lubricant is synthetic oleo chemical esters normally plant or animal origin synthesized from esterification or transesterification (Akerman et al., 2011). Synthesis of oleo chemical esters is achieved by esterification or transesterification with fatty acids, fatty acid methyl esters or triglycerides and usually with polyhydric alcohols (polyol) like trimethylolpropane (TMP), neopentyl glycol (NPG) or pentaerythritol. There are oleo chemical esters made by reacting with monofunctional alcohol, however the stability of mono oleo chemical esters are weak. The oleo chemical ester synthesised by using polyol is known as polyol esters. Polyol esters are environmentally acceptable base fluids in high performance lubricants. Effective eco-friendly formulations of polyol esters have very good low temperature behaviour, high viscosity index, higher in chemical and thermo-oxidative stability and good resistance from attacks by water molecules as compared to esters of glycerol (Hamid et al., 2012). Bio-lubricants with TMP esters of oleic acid are most common and widely used in hydraulic fluids (Akerman et al., 2011).

Production of TMP esters is catalysed by acidic homogeneous or heterogeneous catalysts. Acidic homogeneous catalysts used in the synthesis of bio-lubricant are sulfuric acid, methane sulfonic acid and p-toluene sulfonic acid (Gunstone, & Black, 1990). The used of heterogeneous catalysts in synthesis TMP ester such as acidic resins, acidic metal oxide (Matsushashi et al., 2001), ion exchange resins (Okuhara, 2002), bio-based solid catalyst such as enzyme lipase (Akerman et al., 2011) and biochar (Dalai et al., 2013) have been reported. Inorganic heterogeneous catalysts such as zeolites (Kiss et al., 2006), carbon based material and sulfated zirconia also has been studied (Moreno et al., 2011). The reusability, simplicity of separation process and economical practicality are the main considerations in choosing the suitable catalyst.

## ***1.2 Problem Statement***

Homogeneous catalysts have several limitations on the reusability of catalyst, separation of the products and loss of catalysts. Some of the catalysts used are hazardous and undesirable from the environmental point of view. In order to produce low cost, and environmental friendly bio-lubricants, heterogeneous catalysts are more favourable because they provide simpler, cheaper separation process and reduced waste generation and reusable for several reaction cycles. Solid acid catalysts such as sulfated metal oxides or heteropoly acids loaded metal oxides are more promising alternatives to such conventional acids. Therefore, sulfated tin (II) oxide deserves better attention. Many studies about heterogeneous catalyst have been reported in catalyzing esterification reactions, sulfated zirconia has been reported exhibits high catalytic activities for various types of reactions among these studies. Sulfated tin (II) oxide was found as the more promising acid solid with strongest acidity (Moreno et al., 2011) and it is expected to be the promising catalyst for the bio-lubricant production through esterification. To date, papers focusing on sulfated tin (II) oxide catalyst are few because of multistep in preparation and the used of sulfated tin (II) oxide in the synthesis of bio-lubricant is still scarce and limited in the literature. In this paper, sulfated tin (II) oxide was employed as the catalyst for the synthesis of TMP esters via the esterification of oleic acid with TMP.

## ***1.3 Research Objectives***

The objectives of the present study are:

- (a) To synthesise and characterise the catalyst sulfated tin (II) oxide
- (b) To examine the activity of the synthesised catalyst

## ***1.4 Scope of study***

The scopes of the present study include:

- (a) Sulfated tin (II) oxide synthesis using precipitation and impregnation methods.
- (b) Sulfated tin (II) oxide characterisation for its porosity, specific surface area, structure, functional group.
- (c) Synthesized catalyst activity testing in the esterification of trimethylolpropane with oleic acid under different reaction parameters such as molar ratio and temperature of the reaction with the presence of catalyst. The ranges of the molar ratio of TMP to oleic acid and temperature are 1:2.7-1:3.3, and 120°C -

180°C respectively. The suitable rate of stirring and catalyst particle size are first identified to minimize the internal and external diffusion limitation.

(d) Bio-lubricant characterisation for its total acid number and viscosity.

### ***1.5 Main contribution of this work***

By identifying a more promising catalyst, sulfated tin (II) oxide, a more economic feasible process could be developed for the production of bio-lubricant. The use of a cheaper bio-lubricant can then eliminate the environmental problems caused by the mineral based lubricants.

### ***1.6 Organisation of this thesis***

The structure of the remainder of the thesis is outlined as follow:

Chapter 2 provides a description of bio-lubricant, its' applications, characteristics and general synthesis routes. Besides, it consists of the reviews on literature related to the synthesis of bio-lubricant in the presence of catalyst. The reviews on reactants used for the esterification and transesterification, comparisons among different types of reactant are made and justified. Lastly, the types of catalyst used for the synthesis of bio-lubricant through esterification reaction from previous studies are presented. The comparisons of catalytic activity of different types of catalyst are provided as well.

Chapter 3 describes about the materials and methods used to synthesis catalyst sulfated tin (II) oxide and conduct the esterification of trimethylolpropane (TMP) and oleic acid catalysed by sulfated tin (II) oxide. Materials descriptions and experimental procedures are covered for both the synthesis of catalyst and bio-lubricant while product analyses are divided into catalyst characterisation and bio-lubricant analysis. A brief explanation of the methods used is also provided in this chapter.

Chapter 4 presents the results and discussion. The results obtained from the catalyst characterisations, esterification reaction and bio-lubricant analysis are presented in this chapter. All the results obtained are analysed and discussed in detailed.

Chapter 5 provides the conclusion made according to the results obtained and recommendations suggested for future work to improve the present study.

## **2 LITERATURE REVIEW**

### ***2.1 Overview***

This chapter consists of the reviews on literature related to the synthesis of bio-lubricant in the presence of catalyst. The reviews can be organized into five main sections. Firstly, the characteristics and applications of bio-lubricant are discussed. Secondly, the production of bio-lubricant by transesterification are introduced and discussed. Thirdly, the reviews on the production of bio-lubricant by esterification are presented. Lastly, the acidic catalytic esterifications are reviewed and discussed. Acidic catalytic esterification can be grouped into homogeneous and heterogeneous catalytic esterification. Under heterogeneous catalytic esterification, the two sections are organic and inorganic heterogeneous catalytic esterification.

### ***2.2 Introduction of Bio-lubricant***

Bio-lubricant is synthetic oleo chemical esters normally plant origin synthesised from esterification or transesterification. In recent years, synthetic oleo chemical esters as a biodegradable lubricant has been demanding in the market as an alternative to mineral oil based lubricant which is a non-renewable natural source. This is due to the growing concern for the impact that mineral oil based lubricant making to our environment. Pollution caused by mineral oil based lubricant is severe because of the non-biodegradable and toxic properties have been causing the soil and water contaminations. Biodegradability has become one of the most significant design parameters both in selection of based fluid and in the overall formulation of the finished lubricant. The synthetic esters have been shown to possess high biodegradability under both aerobic and anaerobic conditions (Rudnick & Erhan, 2006).

Generally, the roles of lubricants are to permit easy starting of engine, maintain adequate viscosity at high temperatures, lubricate and prevent wear, reduce friction, protect against rust and corrosion, keep engine parts clean, cool engine parts and seal combustion pressures to allow engine to perform effectively. The roles of lubricant and it's explanations are summarized in the Table 2.1 ("Chapter 5: Combustion Engine Lubricants," 2009).

Table 2.1: The roles of lubricant (“Chapter 5: Combustion Engine Lubricants,” 2009)

Roles of lubricant	Explanations
Permit easy starting of engine	Most of the engine wear occurs during the start-up, primarily due to lubricant starvation thus the lubricant must have low viscosity at low temperatures so that it is pumpable and reach the engine parts that need lubrication instantaneously.
Maintain adequate viscosity at high temperatures	The maintaining of level of viscosity is to ensure the thickness of the lubricating film in permitting the metal to metal contact and wear. Most of the lubricants having problems of decrease in viscosity as the temperature of the engine increased.
Lubricate and prevent wear	The appropriate thickness of lubricating film to prevent metal surfaces from contacting each other and experiencing wear. There are parts such as the piston rings and cam lobes, which are designed to have metal-to-metal contact and the function of the lubricant is to minimize wear by lubricating films.
Reduce friction	The proper thickness of the lubricant film on the surfaces will reduce friction and wear. It reduces the frictional coefficient of the engine parts during the start-up and idle, when the lubrication is insufficient and the frictional losses occur. Therefore, controlling friction will reduce the energy consumption hence improve the fuel economy.
Protection against rust and corrosion	The rust and corrosion of engine parts initiated by the presence of water, oxygen in acidic condition. With the protection of lubricating film, water and oxygen are not permeable.

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Keep engine parts clean	Engine lubricants are designed to prevent the combustion products such as free radicals, soot, sulfur, and nitrogen oxides from enter the crankcase and interact with the lubricant to form highly polar deposit precursors and corrosive materials by suspending them in the bulk lubricant.
Seal combustion pressures	Surfaces of piston rings, ring grooves, and cylinder walls do not have an ideal fit due to the machining limitations. Lubricants therefore improve the seal by filling spaces with the film thickness of 0.025 mm. This is to prevent the loss of the high combustion and compression pressures eventually result in a reduction of the engine power and efficiency.
Cool engine parts	Lubricant acts as a coolant when the parts cannot be effectively cooled by the coolant, either because of their vicinity, or the part temperature is extremely high, which leads to the rapid evaporation of water.

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The selection of a particular lubricant fluid by the engineer or customers from a practical point of view is based on few important factors such as physical properties, chemical properties, lubrication properties, environmental friendliness and cost. Various of considerations have to be taken such as comparisons of performance of lubricant fluids in that particular applications and environmental conditions, the properties of lubricant can be differ a lot within a lubricant type or between lubricant types and the limitations of the lubricant also need to be taken account. The physical properties of lubricant is characterised by temperature and pressure. Temperature and pressure control the ranges of the liquid lubricant such as the solidification at low temperature and high pressure, the evaporation at high temperature and low pressure. While the chemical properties is characterised by oxidation and radiation which influenced by temperatures. A single special fluid cannot meet all the requirements to becoming an ideal lubricant therefore synthetic or bio-based lubricants are introduced to meet the

performance features that cannot be obtained by mineral oils. Nevertheless, no synthetic lubricant combines all properties in a superior manner to mineral oil, there are also some inferior properties of synthetic lubricant but synthetic lubricant can be made or modified based on the chemical structure to perfectly match the specific application. The application area for synthetic lubricants are illustrated in the Table 2.2 and the inferiority of mineral oil based lubricant to synthetic bio based lubricant and inferiority of synthetic bio based lubricant to mineral based lubricant are summarised in the Table 2.3 (Rudnick, & Bartz, 2006):

Table 2.2: Application areas for synthetic lubricant (Rudnick, & Bartz, 2006)

<b>Areas</b>	<b>Applications</b>
Automotive	Engine oils
	Gear oils
	Brake fluids
	Lubricating greases
Aviation	Turbine oils
	Piston engine oils
	Hydraulic fluids
	Lubricating greases
Industry	Gas turbine oils
	Gear oils
	Bearing and circulation oils
	Compressor oils
	Hydraulic oils
	Metalworking fluids
	Heat transfer and isolating oils
Lubricating greases	



Table 2.3: Inferior characteristics of mineral oil based lubricant to synthetic bio based lubricant and inferior characteristics of synthetic bio based lubricant to mineral based lubricant (Rudnick, & Bartz, 2006)

<b>Inferior characteristics of mineral oil based lubricant to synthetic bio based lubricant</b>	<b>Inferior characteristics of synthetic bio based lubricant to mineral based lubricant</b>
Thermal stability	Hydrolytic behaviour
Oxidation stability	Corrosion behaviour
Viscosity temperature behaviour	Toxicological behaviour
Flow behaviour at low temperatures	Compatibility with other design materials
Volatility at high temperatures	Miscibility with mineral oil
Temperature ranges of application	Compatibility with seal materials
Radiation stability	Additive solubility
Ignition resistance	Availability, in general or in viscosity grades
Biodegradability	Price

### **2.3 *Transesterification***

Plant oil is undergoing chemically modification to improve its performance as lubricant. The chemical modifications of plant oil can be categorised into modifications of the carboxyl group and modifications of the fatty acid. Transesterification and esterification are under category of modifications of carboxyl group. Generally, transesterification is one of the methods to produce bio-lubricant. Transesterification of oleo chemical ester is the process of breaking the raw plant oil into their methyl or ethyl esters chemically using an alcohol in the presence of alkaline catalyst such as sodium hydroxide with glycerol as a by-product. The reactions of transesterification with higher alcohols C8 to C14 are used in producing lubricants while the reaction with lower alcohol such as methanol, ethanol and isopropanol are used in production such as biodiesel (Rudnick et al., 2006). In other words, producing methyl, ethyl, propyl fatty acid esters are called as biodiesel whereas octyl fatty acid ester are called as bio-lubricants, which comprises contacting fatty acid triglycerides with or without free fatty acids of vegetable oil with alcohols (Bokade & Yadav, 2007).

Comparing with esterification, production of bio-lubricant through transesterification has been reported by many researchers. Plant oil such as palm (Kamil & Yusup, 2010), soy bean (Schmidt et al., 2006), castor seed (Madankar et al., 2013), jatropha curcas (Resul et al., 2012) and sunflower oil (Kotwal et al., 2009) have been used in synthesising oleo chemical ester through transesterification reaction. Most plant oils are triglycerides that composed of glycerol molecules with three long chain fatty acids attached at the hydroxyl groups via ester linkages. The glycerol part is the same in all vegetable oils whereas the fatty acid chains are similar in length, between 14 and 22 carbons, with varying levels of unsaturation (Fox & Stachowiak, 2007). Fatty acid associated with plant oils can be categorized into saturated, mono-, di-, tri-unsaturated. Oleic acid (*cis*-9-octadecenoic acid) is the most common mono-unsaturated fatty acid found in plant oils that can be used in synthesising lubricants. Although natural triglyceride possess a very rapid biodegradability and is highly effective lubricants (Wagner et al., 2001), plant oil based lubricant is suffering with the drawbacks of sensitivity to hydrolysis and oxidation at high temperatures, poor low temperature flow properties and narrow range of viscosities limit the application as industrial lubricants (Akerman et al., 2011). The example of the reaction of transesterification is shown in the Figure 2.1 (Dossat et al., 2002). In this reaction, the plant oil which is a triglyceride molecule react with alcohol catalysed by lipase to form three molecules of esters in three steps and glycerol are the by-products.

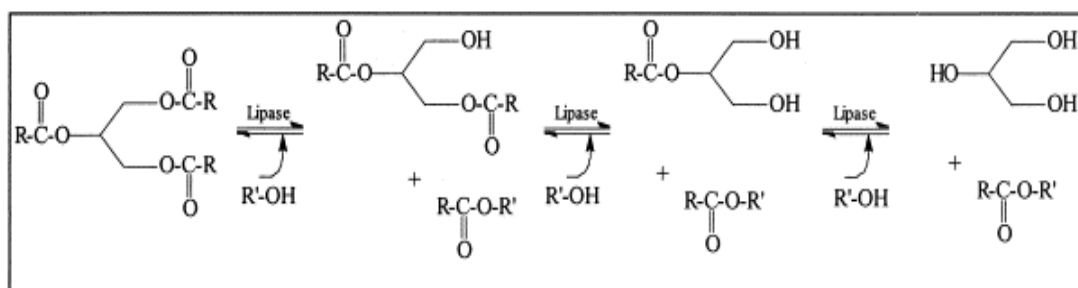


Figure 2.1: Transesterification of plant oil with alcohol catalysed by biocatalyst lipase

The causes for the thermal and oxidative instability of plant oils are unsaturated structure of the fatty acid and the arrangement of the hydrogen atom in the hydroxyl group of glycerol molecules (Gryglewicz et al., 2003). The pour point of a lubricant is good indicator of its low temperature fluidity. The cold flow properties of plant oils are poor and this limits their use in low temperatures applications. Plant oils tend to form macro crystalline structures through uniform stacking at low temperatures. Branching

on the fatty acid chain using transesterification may decrease the internal symmetry of the molecule and thereby improved low temperature properties (Sharma et al., 2008). On the other hand, branching of the fatty acid chain will reduce the lubricity and viscosity index of the lubricant however increased the fatty acid chain length will counterbalance the effect of branching. Therefore, choosing the raw materials to synthesis bio-lubricant is a very crucial step in order to produce lubricant with desired properties. The effect of fatty acids unsaturation, chain length and branching on properties of base fluids are illustrated in the Table 2.4 (Erhan et al., 2006).

Table 2.4 : The relationship of fatty acids unsaturation, chain length and branching with the properties on base fluids (Erhan et al., 2006)

	<b>Lubricity</b>	<b>Viscosity index</b>	<b>Low temperature fluidity</b>	<b>Oxidative stability</b>	<b>Volatility</b>
<b>Chain length</b>	Proportional	Proportional	Inversely proportional	Inversely proportional	Proportional
<b>Chain branching</b>	Inversely proportional	Inversely proportional	Proportional	Proportional	Inversely proportional
<b>Unsaturation</b>	Inversely proportional	No effect	Proportional	Inversely proportional	No effect

In order to overcome the limitations of vegetable oil, the low stability glycerol  $\beta$ -carbon is removed and substituted by polyhydric alcohols (Hamid et al., 2012). Trimethylolpropane (TMP), neopentylglycol (NPG) and pentaerythritol (PE) are the examples of polyol. The method of substituting polyol is known as transesterification which was described earlier in this section. Chemical modifications of hydrocarbon chain in triglycerides such as hydrogenation, epoxidation, alkyl-arylation, cyclisation, acetylation, oxidative scission, carboxylation and olefin metathesis also can be applied to further enhance its stability. Among the methods of modification, epoxidation is one of the most convenient methods to improve the poor thermo-oxidative stability. The formation of oxirane rings at double bond sites in triglycerol molecules by adding reagents of peracids such as performic acid or peracetic acid. The epoxidized plant oils

have better thermal and oxidation stability than vegetable oils by eliminating polyunsaturations and bis-allylic protons from vegetable oil triacylglycerol molecules (Adhvaryu & Erhan, 2002). Plant oils are mostly split into their oleochemical components such as fatty acids or fatty acid methyl esters in order to improve the performance of the lubricant and fatty acid is one of the reactants during the esterification reactions (Wagner et al., 2001).

## 2.4 Esterification

Esterification of oleo chemical ester is the reaction of free fatty acids derived from plant oils and alcohol in the presence of homogeneous or heterogeneous acidic catalyst. Free fatty acids can be extracted from plant oils by hydrolysis using acid catalysts. The acid catalysed esterification proceeds by protonation of carboxylic acid to give an oxonium ion followed by nucleophilic attack of alcohol resulting in ester bond formation and release of water. The alcohols used either having a long alkyl groups such as C8 or complicated hydrocarbon structure with more than one hydroxyl groups. The product obtained by reaction of free fatty acids had desirable cold flow properties and wider range of viscosities in the industrial application according to past studies (Akerman et al., 2011). The paths esterification of free fatty acids extracted from plant oil and transesterification reaction directly from plant oil are shown in Figure 2.2 (Oh et al., 2013).

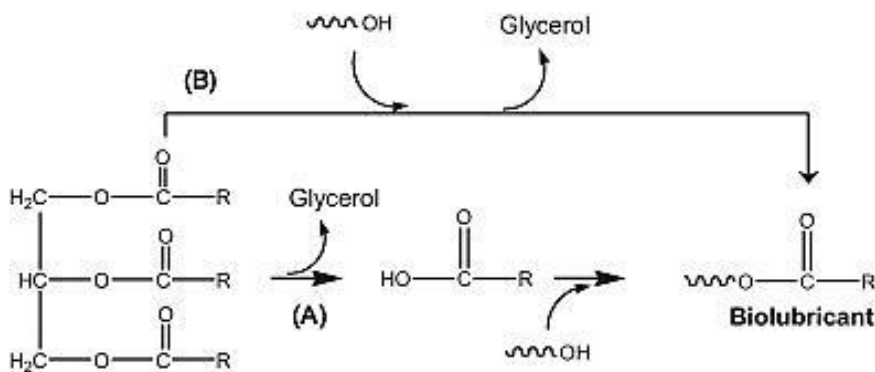


Figure 2.2: Path A: esterification of free fatty acids derived from plant oils

Path B: direct transesterification of plant oils

There are three main types of esters which are acid centred, alcohol centred and polymeric esters. The examples of acid centred ester are monoesters and diesters, for

alcohol centred esters such as polyol esters and the examples for polymeric esters are polyalkyleneglycol esters and complex esters. Monoesters are also known as monocarboxylic acid esters which are derivatives of monofunctional fatty acids such as oleic acid and isostearic acid with a C<sub>8</sub>–C<sub>22</sub> alkyl chain length esterified with branched or linear mono-alcohols. Monoesters have different range of viscosities depends on the alcohol react with (Randles, 2006). Diesters are also known as dicarboxylic acids esters. Dicarboxylic acid esters are synthesised by reacting a linear dimeric fatty acids with branched, monofunctional alcohol. The examples of linear dimeric fatty acids are adipic acid, sebacic acid and azelaic acid. These acids can be esterified with alcohols such as 2-ethylhexanol and isodecanol. Diesters have higher viscosities index and lower pour point compare to monoesters because of the structure of diesters. Linear dimeric acids contribute to the higher viscosities whereas branched alcohol contributes to a good pour point (Wagner et al., 2001).

Polyol esters are alcohol centred esters that made by reacting a multifunctional alcohol with a monofunctional acid. Multifunctional alcohols are polyols with a quaternary carbon atom such as neopentylglycol, trimethylolpropane and pentaerythritol. Polyol esters have extraordinary stability due to the absence of secondary hydrogen in the  $\beta$ -position or beta-hindered and the presence of a quaternary C-atom in the centre. Polyol esters have similar pros and cons with diesters, however polyol esters have higher thermal and hydrolytically stability than diesters (Schmidt, 2006). Besides, polyol esters have a good resistance from attacks by water molecules (Hamid et al., 2012). Complex esters are polymeric esters produced by the esterification of polyols with mixtures of mono-, di-, and tricarboxylic acid esters. Complex esters have very high viscosity and generally shear-stable (Wagner et al., 2001). The summary of the typical physical properties of esters lubricant is illustrated in Table 2.5 (Schmidt, 2006).

Table 2.5: Typical Physical Properties of different types of esters lubricant (Schmidt, 2006)

	<b>Monoester</b>	<b>Diesters</b>	<b>Polyol esters</b>	<b>Complex esters</b>
Viscosity index	150 to 230	0 to 90	40 to 170	130 to 230
Pour point (°C)	-35 to 25	-70 to -40	-60 to 7	-60 to -20
Flash point (°C)	180 to 220	200 to 260	250 to 320	240 to 280
Oxidative stability	Fair	Good	Excellent	Fair
Biodegradability	Excellent	Good	Excellent	Excellent

From Table 2.5, polyol esters have overall better physical properties, therefore it deserves more attention. As mentioned earlier, the reactants used in synthesising polyol esters are polyhydric alcohols such as neopentylglycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) and with a monofunctional fatty acid such as oleic acid (Akerman et al., 2011), linoleic acid (Oh et al., 2013), valeric acid (Akerman et al., 2011), caprylic acid (Akerman et al., 2011). Polyol has been chosen to replace glycerol in the synthesis of oleo chemical ester in order to improve the viscosity and reduce the pour point of the product due to the higher molecular weight, higher number of functional groups –OH and the higher degree of branching of polyols. Pentaerythritol is more thermally stable than TMP and neopentyl glycol but because TMP is at moderate price level and reacts in lower temperature thus reducing the cost of production, it is being used widely (Resul et al., 2012). The lubricating properties are depending on the structure of the fatty acids and alcohol. The number of functional group or the size or the degree of branching, less symmetrical of the molecules, long chain of fatty acids helps to improve the viscosity of the product and reduce the pour point and biodegradability (Eychenne & Mouloungui, 1998). The number and type of hydrogen bonds of fatty acid chain has been shown to have major effect on the oxidative stability of esters. The primary carbon-hydrogen bond (CH<sub>3</sub>) is the most stable, following by secondary carbon-hydrogen (CH<sub>2</sub>) bond and lastly tertiary carbon-hydrogen bond (CH). The mechanism of esterification reaction between trimethylolpropane (TMP) and a fatty acid is shown in Figure 2.3 and the typical physical properties of polyol esters are illustrated in Table 2.6 (Akerman et al., 2011; Schmidt, 2006):

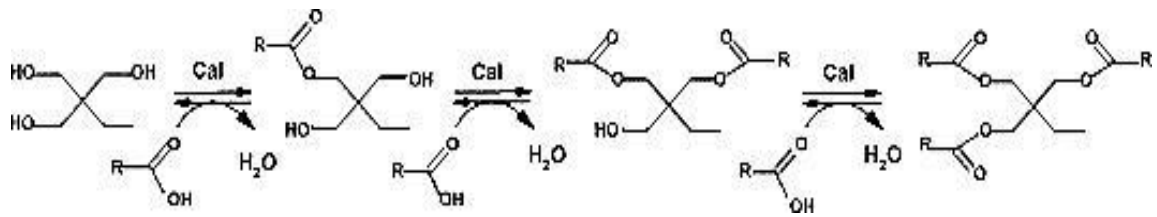


Figure 2.3: Esterification reaction between trimethylolpropane (TMP) and a fatty acid

Table 2.6: Typical physical properties of polyol esters

Polyol	Fatty acid	Viscosity index	Pour point (°C)	Biodegradability (%)	References
NPG	Oleic acid	207	-24	100	Schmidt, 2006
PE	Oleic acid	141	-21	98	Schmidt, 2006
TMP	Oleic acid	190	-39	100	Schmidt, 2006
	Valeric acid(C5)	80	-75	100	Akerman et al, 2011
	Caprylic acid(C8)	114	-45	100	Akerman et al, 2011

The application range of lubricants is determined by the physico-chemical properties which is the ability to remain as liquid form over a wide range of temperature. The pour point and the flash point of lubricants are the good indicators for the physico-chemical properties. Pour point is the lowest temperature at which oil tends to solidify and no longer flowing (“Technology Dictionary,” 2008) while flash point is the lowest temperature at which the vapour of the oil will ignite in the air (“Your Dictionary: Science,” 2013). TMP valerate are useful for low temperature applications such as lubricants in cutting oils and lubricant basestocks when present in a mixture with other esters (Beran, 2001). TMP caprylate can be used in the applications requiring high viscosity and high stability. It also can be used as dielectric coolants and as rail or wheel lubricants (Waara et al., 2004). TMP-oleate is the most widely used biolubricant product for hydraulic fluids. TMP oleate is more preferable after comparing the physico-chemical properties. TMP esters of oleic acid (TMP oleate) are most common and

widely used in low temperature applications and hydraulic fluids (Akerman et al., 2011). Hydraulic fluids transmit power to moving parts of many types of machines including cars, tractors and heavy equipment under pressure. TMP oleate is suitable in low temperature applications because it has 100% degradability, high thermo-oxidative stability and renewability, low temperature pumpability and fire resistant (Rudnick et al., 2006).

## ***2.5 Acidic Catalytic Esterification***

Bio-lubricant as known as oleo chemical esters synthesis through esterification in the present study is more preferable using acidic catalysts. There are two major types of catalyst used in the esterification of polyol and fatty acids, acidic homogeneous and heterogeneous catalyst. Homogeneous catalyst is the catalyst present in the same phase as the reactants, in this case the reactants are in liquid state. On the other hand, heterogeneous catalyst is the catalyst present in a different phase as the reactants; in this case heterogeneous catalyst is in solid form ("The Bigger.Com," 2013).

### **2.5.1 Acidic Homogeneous Catalytic Esterification**

Acidic homogeneous catalysts such as sulfuric acid (Silitonga et al., 2013), methane sulfonic acid, p-toluene sulfonic acid (Jong et al., 2009) are the most common acid catalysts in past studies. In previous study, p-toluene sulphonic acid has been used as catalyst for the esterification of myristic acid with isopropanol and n-propanol at the range of temperature 75°C-130°C. By using p-toluene sulfonic acid, the conversion for the free fatty acid was around 80% in the esterification of myristic acid with isopropanol and n-propanol (Jong et al., 2009). Sulfuric acid was employed as the catalyst in the past study on esterification of adipic acid with isopropyl alcohol. The conversion of adipic acid in this study by using catalyst sulfuric acid was around 90% (Hasegawa et al., 2012). Another study on sulfuric acid as catalyst was done by mixing pure oleic acid with refined sunflower oil and react with ethanol. The conversion of free fatty acids in this study was also around 90% (Marchetti & Errazu, 2008). In the esterification of palmitic acid with deuterated methanol, p-sulfonic acid was employed as catalyst. The conversion of palmitic acid in this research was around 90%. The same researchers also applied sulfuric acid as the catalyst in the study, the conversion of palmitic acid was 90% as well (Fernandes et al., 2012). The catalysts used in previous studies can be summarized in the Table 2.7: