SYNTHESIS OF BIO-LUBRICANT BY ESTERIFICATION OF PELARGONIC ACID WITH 2-ETHYLHEXANOL OVER AMBERLYST 36

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ABSTRACT

In recent years, the demand of bio-lubricant has greatly increased due to the environmental and sustainability issue created by mineral oil based lubricant. This study addresses the issue of low oxidative stability of the current bio lubricant by substituting one of the raw materials with saturated base oil. Homogeneous catalyst employed in the current production process is also replaced by Amberlyst 36, a heterogeneous catalyst to eliminate the complications in product separation and the occurrence of side reaction. This work presents the synthesis of bio-lubricant, 2-ethylhexyl pelargonate through the esterification of pelargonic acid and 2-ethylhexanol. In this study, a batch reactor completed with dean stark apparatus was used to study the effect of important operating parameters such as mixing speed, temperature, reactant ratio and catalyst loading. The samples withdrawn were titrated for its total acid number (TAN) and the best condition to achieve highest conversion was attained. It was found that the mixing speed of 300rpm has minimised the external mass transfer resistances. Under the external diffusion-free regime, the maximum conversion, 96% was achieved at the temperature of 140^{o}C, catalyst loading of 2.5wt% and reactant molar ratio of pelargonic acid to 2-ethylhexanol of 1:5. The bio-lubricant produced possessed the kinematic viscosity of 4.44 cSt at 40^{o}C and 1.92 cSt at 100^{o}C with a viscosity index of 366.247. The excellent viscosity properties are better than current commercial petro-lubricant and bio-lubricant available. However, the cloud point and pour point of 2-ethylhexyl pelargonate were observed at -18^{o}C and -24 ^{o}C respectively which were still not in par with the commercial petro-lubricant although better than current bio-lubricant available. It is recommended that this work can be further studied by addition of additive e.g. antioxidant to enhance its lubrication properties and commercialised due to its high potential to replace petro-lubricant.

ABSTRAK

Dalam tahun-tahun kebelakangan ini, permintaan bio-pelincir telah banyak meningkat kerana isu alam sekitar dan kemampanan dicipta oleh pelincir berasaskan minyak mineral. Kajian ini menangani isu kestabilan oksidatif rendah daripada minyak pelincir bio semasa dengan menggantikan salah satu bahan mentah dengan minyak asas tepu. Pemangkin homogen digunakan dalam proses pengeluaran semasa juga digantikan dengan Amberlyst 36, pemangkin heterogen untuk menghapuskan komplikasi dalam pengasingan produk dan berlakunya reaksi sampingan. Kerja ini membentangkan sintesis bio-pelincir, 2-ethylhexyl pelargonate melalui pengesteran asid pelargonic dan 2-ethylhexanol. Dalam kajian ini, reaktor batch siap dengan peralatan sekali Dekan telah digunakan untuk mengkaji kesan parameter operasi penting seperti kelajuan pencampuran, suhu, nisbah bahan tindak balas dan pemangkin loading. Sampel telah ditarik balik dititratkan untuk bilangan jumlah asid (TAN) dan keadaan yang terbaik untuk mencapai penukaran tertinggi telah diperolehi. Ia telah mendapati bahawa kelajuan pencampuran dari 300rpm telah meminimakan rintangan pemindahan jisim luaran. Di bawah rejim resapan bebas luaran, penukaran maksimum, 96% telah dicapai pada suhu 140^{o}C, loading pemangkin 2.5wt% dan nisbah molar bahan tindak balas asid pelargonic untuk 2-ethylhexanol 1: 5. Bio-minyak pelincir yang dihasilkan mempunyai kelikatan kinematik 4.44 cSt pada 40^{o}C dan 1.92 cSt pada 100^{o}C dengan indeks kelikatan 366.247. Sifat kelikatan yang sangat baik adalah lebih baik daripada semasa komersial petro-pelincir dan bio-minyak pelincir yang ada. Walau bagaimanapun, titik awan dan mencurahkan titik 2-ethylhexyl pelargonate diperhatikan di -18^{o}C dan -24^{o}C masing-masing yang masih tidak setanding dengan komersial petro-pelincir yang walaupun lebih baik daripada semasa bio-minyak pelincir yang ada. Ia adalah disyorkan bahawa kerja ini boleh dikaji lagi dengan penambahan contohnya tambahan antioksidan untuk meningkatkan sifat pelinciran dan dikomersialkan kerana potensi yang tinggi untuk menggantikan petro-pelincir.

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LIST OF ABBREVIATIONS

2EH	2-Ethylhexanol
2EHP	2-Ethylhexyl Pelargonate
ASTM	American Society for Testing and Materials
FFA	Free Fatty Acid
FA	Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
KHP	Potassium Hydrogen Phatalate
NaOH	Sodium Hydroxide
PA	Pelargonic Acid
TMP	Trimethyolpropane
rpm	Rotation per Minute
rps	Rotation per second
wt%	Weight Percentage
XRF	X-ray Fluorescent

1 INTRODUCTION

1.1 Background and motivation of Study

Lubricants are comprehensively used in industries and automotive sectors for machineries and tools lubrication. The world demand of lubricant is growing at 2.4 percent annually and projected to reach 43.6 million metric tons by 2017(Freedonia, 2013). Lubricants principally serve as a thin protective film between moving or sliding parts of machinery by reducing its friction. Apart from that, it also removes heat from parts during operation as a heat transfer agent. Viscosity of lubricant is also a very important parameter as it indicates the forces required to overcome its own intermolecular forces for sliding motion between components.

Typically, lubricants are made of fossils but the overly consumed earth fossil energy has urged the substitution of petroleum base oil by renewable sources. Although petro-based lubricant has great lubricating properties, it is also highly toxic, non-renewable and non-biodegradable. Hence, vegetable oil based lubricants is the best known new alternative.

Vegetable oil based bio-lubricants are environmentally friendly, renewable, non-toxic and completely biodegradable and they have excellent high lubricating properties such as high flash point and high viscosity index, low volatility and good contact lubricity(Sharma & Dalai, 2013).

1.2 Statement of problem

Bio-lubricants are synthesized by the esterification of long carbon chain alcohols with fatty acids. The reaction is commonly catalysed by acidic homogeneous or heterogeneous chemical catalysts. The common homogeneous acidic catalysts for esterification are sulphuric or phosphoric acids. Homogeneous catalysts has its drawbacks such as promoting side reactions, causing corrosion to the equipment and generating acid-containing waste. In view of this, the replacement of homogeneous catalyst with heterogeneous catalyst is favorable. Heterogeneous catalysts with high selectivity and good thermal stability did not create corrosion problem (Knothe & Gerpen, 2010; Silva, 2011). The heterogeneous catalysts reported in literature include ion-exchange resin such as Amberlyst 15, Amberlyst 36, Amberlyst 70, Amberlite IRA-900, Amberlite IRC-72, Amberlite IRC-93, Dowex HCR-W2, Diaion PK208, aminophosphonic acid resin D418 and Nafion (Kitakawa et al., 2007; Liu et al., 2013; López et al., 2007; Özbay et al., 2008; Tsai et al., 2011)and metal based catalysts such as sulphated zirconia ,alumina, tin (ii) oxide, doped alumina/tin oxide, mesoporous Mg-Al mixed-metal oxides and Li-doped magnesium oxide (Mello et al., 2011; Patel et al., 2013; Wen et al., 2010).

There are numerous types of esters and the two most notable classes are monool esters and polyol esters. Monool esters are produced by reaction between a monofunctional acid with a monofunctional alcohol. There are several mono-oleates being used as bio-lubricants including methyl oleate, 2-ethylhexyl oleate, decyl oleate and iso-propyl oleate. Polyol esters are synthesised through the reaction of monobasic fatty acids and polyhydric alcohols. There are several polyol esters being used as bio-lubricant including trimethylpropane trioleate, trimethylpropane heptanoate, pentaerythritol heptanoate and neopentylglycol pelargonate. Monoester will be synthesised in the present study due to its high viscosity index, fairly low pour point and high flash point. To date, the study about monool esters such as 2-ethylhexyl pelargonate as lubricant is scarce. 2-ethylhexyl pelargonate is commonly used in the cosmetics industry and as weapons lubricant (Johnson & Fritz, 1989; Milne, 2005).

1.3 Objectives

In this study, esterification of the pelargonic acid with 2-ethyl hexanol over Amberlyst 36 ion-exchange resin catalyst is studied to determine the best operating condition. Its lubrication properties are measured.

1.4 Scope of this research

In the present study, several important parameters are investigated. These parameters are temperature, ratios of fatty acid to alcohol, amount of catalyst used and mixing speed. 2-ethylhexyl-pelargonate synthesized is tested for its viscosity, oxidative stability, flash point and pour point. The ranges of the reaction operating parameters used in the present studyare as below:

i. Mixing speeds of 100-500rpm
ii. Temperature is between 110-150 ℃
iii. Amount of catalyst is between 0.5-1.5 wt% of solution
iv. Ratios of fatty acid to alcohol are 1:2, 1:3, 1:4 and 1:5 in molar

1.5 Significance of the study

This section includes the significances of this study given in the areas of educational, technological and environmental. To future researchers, this study serves as a guide on the performance of mono-esters as bio-lubricants and way to synthesise it. To industries, this study gives a clear comparison on its properties to petrol-lubricant and addresses the use of heterogeneous catalyst in production to minimise damage on equipment. Lastly, this study helps to create awareness from using bio-degradable materials as lubricants as fossil sources' rapid depletion and its severe impacts towards the environment.

2 LITERATURE REVIEW

2.1 Chapter Overview

In this chapter, the literature review is organised into four main sections. Firstly, the properties of bio-lubricant are compared against petroleum based lubricant. The characterisation and tribological evaluation of bio-lubricant are then discussed. Then, the bio-lubricant synthesis routes are compared. The reactants and catalysts used for bio-lubricant synthesis through direct esterification reaction are deliberated.

2.2 Lubricants

Lubricants are the substances introduced between two moving surfaces to minimise friction between moving elements. Friction is a force that resists the movement of two objects in relative motion from sliding or rolling towards another. Friction will increase the workload of machinery to generate movement and the usage of lubricant will increase machine's efficiency as less energy required to generate motion. Under microscopic resolution, two surfaces moving across each other is mountain like ranges rubbing against one another. Lubrication helps this situation by creating a thin film to ease their movement. Apart from that, lubricant also helps removing wear debris as movements between two solid surfaces tends to generate abrasive particles. The usage of lubricant could help as fewer particles will break off the material surface due to movement. Lubricant removes frictional heat generated by motion and hence the expansion caused by local frictional heat could be greatly reduced. Lubricants also prevent materials from corrosion and rust as the humidity in the atmosphere will cause rusting on equipment, by lubrication it can prevent the parts from directly contacting it (Li, 2004).

Materials that used for lubricating purposes has been greatly widened over the past decades, apart from oils and greases, plastics, solids and even gases are being applied. The selection of materials is only based on limitations including their ability to replenish themselves, to dissipate frictional heat generated, their usability at high temperature and their stability in combined environments. Extensive care is needed in choosing the material and application method to avoid damage to applied part and currently there are many types of lubricants available including petroleum fluids, synthetic fluids, greases, solid films, working fluids, gases, plastics, animal fat, metallic and mineral films, and vegetable oils (Oberg et al., 2004).

Lubricants are a broad blend of base oil and additives in which the base oil composed of more than 80%. Seldom, lubricants are being marketed are without additive. The usage of additive is developed for particular application and commonly they are added for modifying the physical and chemical properties to improve lubricant's performance. While for the base oil being used, petrol-based and bio-based are the two most common types.

Petroleum derivative lubricants dominated the market due to several reasons. Petroleum lubricant has a lower production cost over all other types of base oil and thus greatly applied and included in wide variety of production goods. It is easily and readily available to sustain global high demand. On top of these, petro-lubricant has generally longer drain interval which is measurement of operating life for lubricant that other types of similar. It also possess good tribological quality of lubricant including high temperature resistance, high viscosity index, high oxidative stability, low pour point and low viscosity (Ing, 2009).

Nevertheless, petro-lubricants impose a huge impact to the environment from production, usage to disposal stage and millions tonnes of lubricant are disposed into the environment yearly. European Union alone had 600,000 tonnes of used lubricant disposed uncontrolledly. Petroleum derived lubricant is non-biodegradable and contains toxic aromatic hydrocarbons and sulphur compounds. Furthermore, it may leech into water systems causing severe infections or even fatalities if disposed improperly. The awareness on petroleum usage and its rapidly depleting source has created space for petro-lubricant alternatives to grow (Gryglewicz et al., 2013).

There are many alternatives available to petro-lubricant including synthetic oils or animal fats lubricant. However, lubricants derived from vegetable and plant oil have better acceptance for many uses as they are not only non-toxic and biodegradable but possesses the comparable physical properties with the petro based lubricant. The only drawback of bio-lubricant is that it suffers from lower oxidative stability if compared to petro-lubricant. Oxidative stability it is dependable on the types of reactant used in bio-lubricant synthesis as the usage of saturated fats and oils will remove the vulnerable side for oxidative attack which is the cause for its low stability. Table 2.1 compares the advantages and disadvantages of the petro-lubricant and bio-lubricant.

Table 2.1: Summary of advantages and disadvantages for petro-lubricant and bio-lubricant

	Petro-lubricant	Bio-lubricant
Advantages	• Cheaper and readily accessible for global demand. • Longer operating life • Low pour point • High oxidation stability	• Low toxicity • Low viscosity • High flash point • Biodegradable
Disadvantages	• Toxic • Non-biodegradable • Hazardous waste disposal	• Poor oxidative stability • Higher cost of synthesis

2.3 Tribological Properties and Performance of Lubricants

Tribology is the study of science and technology of interacting surfaces in relative motions which mainly includes the principle of friction, wear and lubrication. Tribology is important to maintain a sustainable growth of industry as the friction and wear which cause high energy consumption and damage to the system can be analysed and rectified. The savings on monetary and environmental impact could be greatly improved through this (Sahoo, 2005). There are several important tribological properties which defines lubricant’s performance namely viscosity, volatility, flash point, pour point, oxidative stability and total acid number.

Viscosity is the most important property for lubricant as it determines the thickness of lubricant film when being used for lubrication. High viscosity will give a thicker lubricating film and more energy is required for motion. Low viscosity will give a thinner film however if the film is too thin, asperity of the surface will be very close with each other and increasing the friction. The measurement of viscosity for lubricant is based on viscosity index (VI) which is an arbitrary number used to characterize the variation of the kinematic viscosity of a lubricant with temperature. The standard test method for viscosity index is ASTM D2210-93 which is the standard practice for calculating viscosity index from kinematic viscosity at 40 and 100^{o}C (Sahoo, 2005; Torbacke et al., 2014).

Volatility is a measure of lubricant’s tendency to vaporise under its vapour pressure. In a closed system, the vapour and liquid phase are in equilibrium. Lubricant with high vapour pressure will vaporise easier at any temperature. The volatility of lubricant is dependent on base fluids used, lower molecular weight molecules have high vapour pressure and will vaporise easier compared to heavier molecules. This implies that low viscosity base fluid is more volatile. In high temperature application, a balanced mix of base fluid is required in order to maintain its low volatility and low viscosity for higher performance. For lubrication applications, a lower volatility is desired to avoid generating vapour and to reduce fire hazards. The standard test method for volatility is ASTM D5800-10 which is used to test on the evaporation loss of the lubricating oils by NOACK method (Booser, 1997; Sahoo, 2005; Torbacke et al., 2014).

Flash point is the lowest temperature for lubricant to ignite in air. At this temperature, lubricant will burn even there is no ignition source. The flash point is used to identify the safety operating condition for lubricant, where a high performance lubricant should have a high flash point for high temperature application. The standard test method for flash point is ASTM D92-05 which is a test for identifying flash and fire points by Cleveland open cup tester (Kajdas et al., 1990; Sahoo, 2005; Torbacke et al., 2014).

Pour point is the lowest temperature at which lubricant will flow. When lubricant applied reaching its pour point, it may not reach contact of targeted area and potentially causing wear or seizure. The molecules can move freely in lubricant’s base fluid, however its movement decreases when temperature going down as they will always be positioned in a pattern that is energetically favourable. When pour point temperature is reached, lubricant solidifies due to crystal lattice formed. The standard test method for pour point is ASTM D97-05(Sahoo, 2005; Theo, 2014; Torbacke et al., 2014).

Cloud point is another temperature indicator of lubricant's cold flow behaviour where the dissolved solids in fluid are no longer completely soluble and begin to separate from oil. As the temperature declines, precipitate as a second phase giving the fluid a cloudy appearance. Lubricants must be maintained above cloud point to prevent clogging occurrence during equipment application (Torbacke et al., 2014).

Oxidative stability is the resistance of lubricant to oxidation when it is stored statically in an oxygen atmosphere at elevated temperature. Oxidation activity will increase when metal and oxygen in contact at elevated temperature. Thus, in order to reduce oxidation, oxygen contact should be decreased or the temperature of application should be reduced. The rate of oxidation is doubled every 10^{o}C and become significant at temperature above 60^{o}C. The standard test method for oxidation stability is ASTM D942-02 by oxygen pressure vessel method (Bruce, 1988; Sahoo, 2005; Torbacke et al., 2014).

Total acid number (TAN) is a measurement for lubricant's base fluid condition. Lubricants may contain acidic component such as organic and inorganic acids, esters or acidic additives and acids formed through lubricants age. The condition of lubricant can be characterised through measurement of acid value and the acid value should be kept at low all time to prevent corrosion occurrence in the applied system. The standard test method for TAN is ASTM D974 which determines the acid and base number by colour-indicator titration (Pirro & Wessol, 2013; Sahoo, 2005; Torbacke et al., 2014). Table 2.2 gives the brief description about the important tribological properties of the lubricants.

Table 2.2: Characterisation and tribological evaluation of bio-lubricant

Properties	**Description**
Viscosity	• Determines the thickness of lubricant film when being used for lubrication. • High viscosity will give a thicker lubricating film and more energy is required for motion.

	• Low viscosity will give a thinner film however if the film is too thin, asperity of the surface will be very close with each other and increasing the friction.
Volatility	• Measure of lubricant’s tendency to vaporise under its vapour pressure. • For lubrication applications, a lower volatility is desired to avoid generating vapour and to reduce fire hazards.
Flash Point	• The lowest temperature for lubricant to ignite in air. • At this temperature, lubricant will burn even there is no ignition source.
Pour Point	• The lowest temperature at which lubricant will flow. • When pour point temperature is reached, lubricant solidifies due to crystal lattice formed.
Cloud Point	• Temperature at which dissolved solids in lubricants no longer dissolve and give a cloudy appearance. • Lubricants must be maintained above cloud point to prevent clogging occurrence during equipment application
Oxidative Stability	• The resistance of lubricant to oxidation when stored statically in an oxygen atmosphere at elevated temperature. • Oxidation activity will increase when metal and oxygen in contact at elevated temperature.
Total Acid Number (TAN)	• Measurement for lubricant’s base fluid condition. Lubricants may contain acidic component such as organic and inorganic acids, esters or acidic additives and acids formed through lubricants age.

2.4 Bio-lubricant Synthesis Routes

Transesterification is a process of using an alcohol in the presence of a catalyst to chemically break down the molecule of the raw vegetable oils into their alkyl esters with glycerol as a by-product (Ganesan et al., 2009). Transesterification is an equilibrium reaction and the reaction become slower after achieving certain yield and selectivity(Baroi & Dalai, 2013). Transesterification with lower alcohols ($< C_6$) yields biodiesel while higher alcohol (C_6-C_8) produces bio-lubricant (Sreeprasanth et al., 2006). Type of catalyst, alcohol/vegetable oil or animal fat molar ratio, temperature, time of the reaction, water and free fatty acid content have significantly influence the transesterification reaction (Bokade & Yadav, 2007). Conventionally, transesterification reaction can be catalysed by both acidic and base catalyst to increase its reaction rate and yield. Vegetable oil such as palm, soy bean, rapeseed, sunflower, cotton and peanut oil has been used in synthesizing of bio-lubricant through transesterification reaction. However, vegetable oil based lubricant synthesised through transesterification is suffering with the shortcomings of sensitive to hydrolysis, oxidised at high temperatures, poor low temperature flow properties and narrow range of viscosities which limit the application for industrial purposes (Åkerman et al., 2011).

Esterification of free fatty acids (FFA) with long chained alcohols (typically > C8) can also form bio-lubricant. This reaction is catalysed by acid through protonation of carboxylic acid to give an oxonium ion followed by nucleophilic attack of alcohol resulting in ester bond formation and release of water(Åkerman et al., 2011). Excess alcohol and removal of water will greatly improve the conversion and yield of bio-lubricant according to Le-Chatelier's. The bio-lubricant produced through esterification possesses desirable cold flow properties and wider range of viscosities in the industrial application while maintaining its biodegradability. In view of this, esterification will be studied in the present work. Saturated fatty acids have relatively high oxidation stability. The oxidation stability decreases with increasing unsaturation in the molecule (Ajithkumar, 2009).

2.5 Reactants for Synthesis of Bio-lubricant Through Esterification

Bio-lubricant base stocks that employing fatty acid raw materials are essentially ester which is the product of the chemical reaction between an acid and an alcohol. Due to a large number of acids and alcohols available, myriads of ester formations with different physical properties are possible. The esters produced can be classified into three main groups: monoesters, diesters and polyol esters.

Monoesters are produced by reaction between a monofunctional acid (e.g., oleic, isostearic) with a monofunctional alcohol (C_1-C_{22}). Monoesters are most notable for its relatively low viscosity. It also possess high viscosity index as it remain stable and do not vary much in viscosity over the temperature range. They are commonly used in metalworking applications. For example, 2-ethylhexyl pelargonate is used as a weapons lubricant base and isodecyl heptanoate is used as a motor additive for its low temperature properties (Johnson & Fritz, 1989).

Diesters are formed by the reaction of dibasic acids and monohydric alcohols. Diesters have very good viscosity index and pour point because of the “dumb-bell” configuration. Good viscosity index is contributed by the linear diacid portion while the branched alcohols end gives good pour point. Diesters have a disadvantage of low molecular weight that limits its viscosity range. The main usage of diesters in the industry is as plasticizer for example di-2-ethylhexyl phthalate which is the principal plasticizer for polyvinyl chloride resins(Johnson & Fritz, 1989; Rudnick, 2005).

Polyol esters are synthesised through the reaction of monobasic fatty acids and polyhydric alcohols. Polyol esters such as pentaerythritol tetraheptanoate and trimethylolpropane trioleate with the complicated structure are used as lubricant base stocks in a variety of fields. Most of the properties of polyols esters are similar to the diesters except they are more hydrolytically and thermally stable than diesters. (El-Magly et al., 2013; Padmaja et al., 2012; Wu et al., 2013). Table 2.3 shows the comparison of monoesters, diesters and polyol esters in terms of their physical properties.

Table 2.3: Comparison of properties for monoester, diesters and polyols (Rudnick, 2005)

Properties	**Monoester**	**Diesters**	**Polyols**
Viscosity at 40°C(cSt)	4 to 30	6 to 46	7 to 320
Viscosity at 100°C(cSt)	1 to 6	2 to 8	2 to 30
Viscosity index	150 to 230	0 to 90	40 to 170
Pour point (°C)	-35 to +25	-70 to -40	-60 to +7
Flash point(°C)	180 to 220	200 to 260	250 to 320
Oxidative stability	Fair	Good	Excellent
Biodegradability	Excellent	Good	Excellent

Monoester will be synthesised in the present study due to its high viscosity index and fairly low pour point and high flash point. The oxidative stability will be improved by adopting the saturated fatty acid.

2.6 Catalyst for the Synthesis of Bio-lubricant Through Esterification

Esterification reactions to produce bio-lubricant are commonly catalysed by acid homogeneous or heterogeneous catalyst. Mineral acids are common example of homogeneous catalyst while cation-exchange resin serves as heterogeneous catalyst. Homogeneous catalyst has several drawbacks; such has the difficulties in separating the catalyst from the products and also the presence of side reactions, equipment corrosion and acid-containing waste. These disadvantages can be eliminated by replacing it with a heterogeneous catalyst because it is non-corrosive and thermal stable while yielding a high selectivity. There are many literatures for esterification that uses heterogeneous acidic catalysts such as H-ZSM-5, niobic acids, heteropolyacids, and zeolites-T membrane (Sharma et al., 2012). For example, the esterification of methanol and octanoic acid over H-ZSM-5 yielded conversion of methyl octanoate at 95% under 773K, 1 atm at molar ratio acid to alcohol of 6:1 (Danuthai et al., 2009). Esterification of lactic acid and ethanol catalysed by zeolite-T-membrane has resulted an almost complete conversion of 99% and zeolite T membrane worked steadily over long time(Tanaka et al., 2002). Heteropolyacids supported on HPA hydrates was used for liquid phase esterification for hexanoic acid to methanol at ratio 1:20 under 60°C ambient pressure yielded full conversion at time more than 2 hours (Alsalme et al., 2008). Kitakawa et al. (2007) carried out esterification using triolein and methanol. The performance for various ion-exchange resins PK208, PA308, PA306, PA306s, HPA25 were compared and they found out that PA306s with lowest cross-linking density and the smallest particle size gave the highest reaction rate. Izci and Hosgun (2007) used maleic acid and methanol for esterification and compared the performance of Indion-170, Amberlyst-36, Amberlyst-15, Amberlite IRA 120 and 20% DTP/K-10 (dodecatungstophosphoric acid supported on K-10 clay). Indion-170, Amberlyst-36, Amberlyst-15 were observed to be the most effective catalyst. It was observed that the catalyst chosen has excellent reusability and was not deactivated.

Izci and Hosgun (2007) carried out esterification of propionic acid and isobutanol over Amberlyst 15 and high 90% conversion was achieved while solid-liquid external mass transfer resistance was negligible at speed above 400 rpm. Oliveira et al. (2010) carried out esterification of oleic acid with ethanol by 12-tungstophosphoric acid supported on zirconia at different catalyst loading. An optimum reaction performance of 88% oleic acid conversion was achieved at 20 wt% loading, 100^{o}C, 4 hours reaction and 1:6 (acid:ethanol) molar ratio. However, a small leaching of 8 wt% of the initial mass of the catalyst was observed at the end of the reaction. Jiang et al. (2013) carried out the esterification of oleic acid and ethanol over Sulfonated Cation Exchange Resin, SCER, CH-A (average size of 0.77 mm) in the H+ form. Under the acid to alcohol molar ratio 9:1 with reflux at 82^{o}C, 20g catalyst loaded and 8h reaction time used, the conversion of 93% was achieved.

Kuzminska et al. (2015) investigated the effect of Amberlyst 36, Purolite CT842 and Purolite CT275DR over the esterification of trimethyolpropane and oleic acid for the production of trimethylolpropane trioleate(TMPTO) in an open batch reactor at 3:1 molar ratio of OA:TMP, 1.6% wt. of catalyst, 400rpm mixing speed under 180^{o}C. Conversion of oleic acid over Amberlyst 36 reached 65% after 1500 min of reaction, while Purolite CT482 attained 90% conversion at 990 min and Purolite CT275DR achieved similar conversion at 880 min. Oh et al. (2013) used sulphated zirconia to catalyse the esterification reaction of 1-octanol over stearic acid, oleic acid, linoleic acid and linolenic acid. The reaction was performed using 6.25 mmol of FA together with 7.5 mmol of alcohol under 140^{o}C and 100mg of catalyst for 4h. Conversion of stearic acid achieved 97.8% followed by oleic acid (90.4%), linoleic (86.3%) and linolenic acid (82.7%).

Åkerman et al. (2011) synthesised esters from trimethylolpropane (TMP) and carboxylic acids from C5 to C18 over various heterogeneous catalysts (silica–sulphuric acid, Amberlyst-15, and immobilised lipase B from Candida Antarctica). Silica–sulphuric acid was found to be the most efficient catalyst followed by Amberlyst-15, especially when using short chain carboxylic acids under 70 ℃. Table 2.4 shows the summary of the heterogeneously catalysed esterification for bio-lubricant synthesis.

Table 2.4: Esterification over heterogeneous acidic catalyst for bio-lubricant synthesis.

References	Reactants	Catalyst	Result
(Danuthai et al., 2009)	Methanol/Octanoic acid	H-ZSM-5	95% conversion at 773K, 1 atm, $M_{A/OH}$=1:6
(Tanaka et al., 2002)	Lactic acid/ Ethanol	Zeolite-T-membrane	>99% conversion, no deactivation over time
(Alsalme et al., 2008)	Hexanoic acid/ Methanol	Heteropolyacids on HPA	Full conversion >2h, $M_{A/OH}$=1:20, 60°C, 1atm
(Kitakawa et al., 2007)	Triolein/Methanol	Ion-exchange resins PK208,PA308,PA306, PA306s,HPA25	PA306s gave the highest reaction rate.
(Yadav & Thathagar, 2002)	Maleic acid/Ethanol	Indion-170, Amberlyst-36, Amberlyst-15, Amberlite IRA 120, 20% DTP/K-10	Indion-170, Amberlyst-36, Amberlyst-15 were the most effective and was not deactivated.
(Izci & Hosgun, 2007)	Propionic acid/ Isobutanol	Amberlyst-15	High conversion 90%; above 400rpm mass transfer resistance negligible.