SYNTHESIS OF BIOLUBRICANT BY ESTERIFICATION OF OLEIC ACID AND PELARGONIC ACID WITH TRIMETHYLOLPROPANE OVER 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

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JAN 2014

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ABSTRACT

Increasing demand of biolubricant nowadays due to the promotions replacement of non-renewable raw materials by renewable resources and minimisation of the environmental impact that caused by improper disposal issue. Current biolubricant production processes which involving the reaction of vegetable oil and alcohol with the presence of homogeneous catalyst causing the catalysts cannot be recycled, soap formation, high separation cost during the downstream of reactions and etc. To overcome these problems, researches were done by using solid catalysts. However, the research using heterogeneous catalyst, metal oxide is scarce. So, this paper presents the best operating condition for the synthesis of biolubricant through the esterification of oleic acid(OA) and pelargonic acid(PA) with trimethylolpropane(TMP). Fatty acid(FA) were reacted with TMP using different molar ratios and operating temperatures with the presence of tin(II) oxide under atmospheric pressure. The samples withdrawn were titrated for its total acid number (TAN). The reaction was proven not limited by both external and internal diffusions. The highest conversion of 80.49% was achieved at the molar ratio OA:TMP of 1:2.4 and operating temperature of 150 ℃. An identical conversion was achieved with lower FFA for the synthesis of biolubricant using PA. Trimethylolpropane tripelargonate(TMTP) with lower viscosity and FFA value would prevent corrosion and reduce friction in the engine. The fresh and used catalysts were characterized by Fourier transforms infrared spectroscopy (FTIR) and proven that tin(II) oxide can be reuse after the reaction. The initial rates and K values is determined. The findings of the present work are useful for the optimisation of the biolubricant production in future. The activation energy for the esterification were found to be 48.612 kJ/mol for the formation of TMTO and 52.303 kJ/mol for the formation of TMTP. The rate constant and equilibrium constant were found to be increased with temperature. The thermodynamic properties of the reaction OA with TMP were found to be Gibbs free energy, ΔG=-82.159kJ/mol, enthalpy, ΔH=- 81.9511kJ/mol and entropy ΔS=0.208 kJ/mol. The thermodynamic properties of the reaction PA with TMP were found to be ΔG=-71.357kJ/mol, ΔH=- 71.176kJ/mol and entropy ΔS=0.181 kJ/mol.

PENGHASILAN BIOLUBRICANT DARI ASID OLEIK DAN ASID PELARGONIK DENGAN TRIMETHYLOLPROPANE MELALUI TIN(II) OKSIDA

ABSTRAK

Permintaan biolubricant yang semakin meningkat pada masa kini kerana penggantian pasaran bahan-bahan mentah yang tidak boleh diperbaharui dengan sumber yang boleh diperbaharui dan mengurangkan kesan alam sekitar yang disebabkan oleh isu pelupusan yang tidak wajar. Proses penghasilan biolubricant yang melibatkan tindak balas minyak sayuran dan alcohol dengan pemangkin tidak boleh dikitar semula, pembentukan sabun berlaku, kos pemisahan yang tinggi di akhir tindak balas dan lain-lain. Penyelidikan telah dijalankan bagi mengatasi masalah tersebutdengan menggunakan pemangkin pepejal. Walaubagaimanapun, kajian tersebut mendapati pemangkin yang digunakan iaitu oksida logam adalah terhad. . olehitu, kajian ini dijalankan bagi menyediakan keadaan operasi yang terbaik untuk menghasilkan biolubricant melalui pengesteran asid oleik (OA) dan asid pelargonik (PA)dengan trimethylolpropane (TMP). Asid lemak (FA) telah bertindak balas dengan TMP menggunakan nisbah molar yang berbeza dan suhu operasi dengan pemangkin Tin (II) oksida di bawah tekanan atmosfera. Sampel yang diambil akan diuji menggunakan kaedah titrasi untuk menentukan jumlah asid yang terhasil. Tindak balas telah terbukti tidak dihadkan oleh kedua-dua proses penyerapan luaran dan dalaman. Penukaran yang paling tinggi dicapai pada nisbah molar OA : TMP suhu 1:2.4 dan operasi 150 ℃ iaitu sebanyak 80.49%. Penukaran FFA yang sama telah dicapai dengan lebih rendah untuk sintesis biolubricant menggunakan PA. Trimethylolpropanetripelargonate (TMTP) dengan kelikatan yang lebih rendah dan nilai FFA akan menghalang kakisan dan mengurangkan geseran dalam enjin. Pemangkin baru dan yang telah digunakan telah dikelaskan menngunakan Fourier transforms infrared spectroscopy (FTIR)dan membuktikan bahawa Tin (II) oksida boleh digunakan semula selepas tindakbalas. Kadar awal tindak balas dan nilai-nilai K telah ditentukan .Hasil kajian ini adalah berguna untuk pengoptimuman pengeluaran biolubricant pada masa akan datang.

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LIST OF ABBEVIATIONS

A	Alcohol
DE	Diester
E	Enzyme
FA	Fatty Acid
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
HM	Homogeneous
HT	Heterogeneous
ME	Monoester
OA	Oleic Acid
PET	Pentaerythritol
POME	Palm Oil Methyl Ester
PTSA	p-Toluenesulfonic Acid
SZ	Sulphated Zirconia
TE	Triester
TiZ	Titania Zirconia
TMP	Trimethylolpropane
TMTO	Trimethylolpropane trioleate
TMTP	Trimethylolpropane tripelargonate
WZ	Tungstated Zirconia

CHAPTER 1

INTRODUCTION

1. 1 Background of Study

In order to reduce metal to metal contact and reduce the frictional force and heat generation, certain foreign substances are introduced between rubbing surfaces which keep them apart and these substances are called lubricant. Lubricating oil is an important resource and a petroleum base product. It reduce wear and tear of substances by avoiding direct metal to metal contact and reduce expansion of metal result of frictional heat and destruction of material. It also acts as coolant of metal due to heat transfer, and reduces the power loss in internal combustion engines (Carnes & K, 2004).

From a global perspective, total lubricant demand is expected to be about 41.8 million metric tons or about 13 billion gallons. Growth is expected to be about2% per year through 2010. The fastest growth will be in the Asia Pacific region especially China is the major gainer (Bremmer & Plonsker, 2008). Asia pacific consumed 36.7% of lubricant, North America consumed 28%, 12.5% by Western Europe and the rest of world about 22.8%. According to Biolubricants Market Data Sheet at 2004, automotive industry consumed 47% of lubricant in Europe, 32% of the total lubricant in market consumed by the industries which include hydraulic oils, process oil consumed 11.3% and 9.4% consumed by marine and aviation.

Since 1991, the world demand for lubricants has been around 35 million tons per year and is anticipated to increase by 1.6% per year (Nagendramma & Kaul, 2012). However, about 5 to 10 million tons of petroleum products enter the environment every year. National Oceanic and Atmospheric Administration (NOAA) estimates that over 700 million gallons of petroleum enter the environment per year (Kovanda, 2011). More than half of it end up polluting the environment through total loss applications, accidental spillage, no recoverable usage, volatility, industrial and municipal waste, urban runoff and refinery process (Carnes & K, 2004). It is estimated 70 to 80% is the loss of hydraulic fluids. These petro-based lubricants are highly toxic to the environment and have poor biodegradability causing soil, water and air contamination (Horner & D, 2002).

1. 2 Motivation

Due to the concern to the environment and the growing regulations to protect the environment have increased the need for renewable and biodegradable lubricants, there has been a lot of research being done. This prove that there is a need to search for alternative sources for producing lubricants since the petroleum sources is limited and effect on polluting the environment is long term.

As compared to petroleum-based lubricants, biolubricants produces a cleaner and less toxic environment which causes fewer dermatological problems for those working with engines and hydraulic systems. Biolubricants has higher flashpoint, constant viscosity and less oil mist and vapour emissions which are safer to use compared to petroleum-based lubricant (Biolubricants, 2011). It is over 90% biodegradable (Biolubricants Market Data Sheet, 2004) and thus, accidentally spilled or leaks biolubricant will not contaminate streams nor the wildlife. Plus, it costs less over the product's life cycle since less maintenance, storage and disposal requirement (Biolubricants, 2011).

Biolubricants, bio-based lubricant or bio-lubes are made up of esterification of long carbon chain alcohols with fatty acids (Bányai et al., 2011). This reaction is catalyzed by acid or alkaline nature of homogeneous or heterogeneous chemical catalysts and the equilibrium is reached in a few hours usually under temperature around 150 ℃ (Silva, 2011).

According the research done in 2004, industry claimed that if over 90% of all lubricant could be replace by biolubricant, the market could be have up to 9 million tons of biolubricant consumption per year (Biolubricants Market Data Sheet, 2004). Due to the rapid depletion of world fossil fuel reserves and increases of awareness of concern on environmental pollution from petroleum based lubricant use, biolubricant market has increased approximately 10% annually in the last ten years (Erhan et al., 2008). Therefore, research and development work of biolubricant should be done intensively to maximize the production with minimum cost.

1. 3 Problem Statement

1.3.1 Polyol based biolubricant

In the previous studies, most of the alcohol used to react with fatty acid with single alcohol (Sripada, 2012) or mixture of alcohol-fusel oil (Nemestóthy et al., 2012), but not polyol. In order to reach a satisfactory ester production from fatty acid and monol, it is necessary to renew the alcohol several times or to use a very large stoichiometric excess of it which is more than ratio of 1:10 (Bondioli, 2004). Polyol esters are excellent substitutes for mineral oil because of their low volatility, high flash point, low toxicity, excellent biodegradability and good thermal stability. One of the most commonly used polyol is Trimethylolpropane, TMP due to its branching structure and low melting point (Arbain & Salimon, 2011).

1.3.2 Heterogeneous catalyst

The common catalysts for esterification are sulphuric or phosphoric acids which are acidic based, sodium methoxide or ethoxide which are basic based, enzymatic catalyst such as lipase, triacyl ester hydrolases and solid resins (Silva, 2011). The use of basic homogenous catalyst would result in large amounts of soap formation during the reaction. The solution must be washed and neutralized at the end of the reaction (Arbain & Salimon, 2011).Meanwhile; enzymatic based catalyst is costly due to its special cares handle. The study on the biolubricant production using heterogeneous catalyst, metal oxide is scarce. Zinc oxide has been used by Bondioli et al. (2003) for synthesis of TMP complex ester. The removal of the last traces of catalysts can be done using simple filtration which simplified the steps of production of biolubricant (Bondioli, 2004). Besides, heterogeneous catalyst will not facing leaching problem as homogeneous catalysis (Gracia et al., 2008). In the present study, biolubricant polyester will be synthesized through the esterification reaction by heterogeneous catalyst. In the present study, the performance of tin(II) oxide heterogeneously catalyzed esterification of polyol, TMP with fatty acid will be examined in a batch reactor (Silva, 2011).

1. 4 Objective

The objective of the present study is to determine the best operating condition for the synthesis of biolubricant through the esterification of oleic acid (OA) and pelargonic acid (PA) with trimethylolpropane (TMP) and to develop the suitable kinetic model for the reaction.

1. 5 Scope of Study

The operating parameters that will be varied include catalyst used, size of the catalyst, reaction time, and reaction temperature and reactant molar ratio. The performance of the catalyst Tin(II) oxide will be compared with sulfated zirconia under same operating condition. Based on the previous research studies done by other researchers, reaction temperature will be varied from 100 to 150 ℃. Molar ratio of TMP: fatty acid will be varied from 1:2.4 to 1:3.3 (Arbain & Salimon, 2011). The samples will be collected for every hour and its' acid value will be analysed. Important properties of biolubricant such as its viscosity and total acid number also will be determined. Finally, the experiment data will be fitted into suitable kinetic data and the thermodynamic properties of the reaction will be determined.

CHAPTER 2

LITERATURE REVIEW

2. 1 Chapter Overview

The review about the synthesis of biolubricant can be organized in eight sections. Firstly, biolubricant was compared with the petrobased lubricant. The application for biobased lubricant is summarized. The characterisation and tribological evaluation of biolubricants were discussed in this chapter as well. Besides, the processes employed for biolubricant synthesis were reviewed. These processes include expoxidation, transesterification and esterification. Then, the reactants and catalysts used for biolubricant synthesis through esterification reaction were assessed. Lastly,the effect of mass transfer to the synthesis of bio-lubricant was reviewed.

2. 2 Lubricant

Lubricants are mineral oil that is omnipresent due to the widespread use as automotive transmission fluids, hydraulic fluids, metal working fluids, cold rolling oils, fire resistant fluids, industrial gear oils, neat cutting oil and automotive gear lubricants. Lubricants are primarily used to reduce friction stress between surfaces. It serve great applications in industries, automobiles and machinery by not only reduce the friction, but the removal of wear particles, increase it efficiency, minimizing energy losses and uniformly distribution of heat (Nagendramma & Kaul, 2012). By reducing wear, a lubricant extent the operational life of surface and by reducing friction, the energy required to move surfaces is reduced and the heat generated by the moving part is transferred (Hayhock & Hillier, 2004). In addition, a lubricant mist provides a liquid seal at moving contact and removes wear particles (Sripada, 2012). Lubricant can also be antioxidants, antifoaming agents, rust and corrosion inhibitors, demulsifying and emulsifying agents. Synthetic lubricants are used in turbines, vacuum pumps, and semiconductor devices. Some lubricant can be used as a paint pigment and as a catalyst (Application of Lubricants, 2013). Table 2.1 discussed more detail on applications of biolubricants.

Table 2.1: The descriptions applications of biolubricants

No	Application	Description
1	Hydraulic fluid	• Transmit power in hydraulic machinery (Givens & Michael, 2003). • Used in environmentally sensitive applications when there is a risk of an oil spil (Placek, 2006). • Filterability, antiwear, corrosion control, adequate viscosity, proper viscosity that minimize internal leakage, high viscosity index (Jain & Suhane, 2013).
2	Metalworking fluid	• Reduce metal particles in industrial machining and grinding operations. • Excellent lubricity, better thin film strength, less smoke and risk of fire (Dwight Smith 2010).
3	Metal forming	• Separate the work piece and tool surfaces • Reduce interface friction and ease metal flow • Increase tool life (Jain & Suhane, 2013).
4	Cutting Fluids	• Improve tool life, reduce thermal deformation, improve surface finish (Frazier & Smith, 2010).
5	Grease	• Sealants that prevent water entry • Bearings with grease have greater frictional characteristics due to properties of high viscosity (Jain & Suhane, 2013).
6	Concrete Mould Release Agent	• Prevent freshly poured concrete from sticking to its mould or formwork (Jain & Suhane, 2013).

7	Chain Saw Oils	• Excellent lubricity and good ageing stability (Jain & Suhane, 2013).
8	Gear Oil	• Excellent protection against micro pitting • Eliminate or reduce smoke (Jain & Suhane, 2013) • Increase too life up to 100% (Frazier & Smith, 2010). • Lesser tool change can increase productivity 20% or more.
9	Grinding operation	• Coolants that reduce friction and cause the abrasive grains to stay sharp longer • Wheel life and accuracy is improved • Reduce heat generated and allow feed rates increase without introduce excessive heat into the part (Jain & Suhane, 2013).
10	Drilling Fluid	• Keep drill bit cool and provide hydrostatic pressure to prevent fluid entering into the well bore, hence avoid corrosion (Chilingarian & Vorabutr, 1983). • Able to withstand the harsh and challenging downhole environment conditions and the residual fluid able to meet the environment standards which offer a cleaner and safer approach (Jain & Suhane, 2013).

Lubricants are composed of more than 80% base oil and a smaller amount of functional additives (Arbain & Salimon, 2009). Therefore, the base oil mainly determines lubricant properties. Examples of base oils are mineral oils, synthetic oils and vegetable oils and 85% of the base oils in the market are refined from crude petroleum (Yunus et al., 2005). Petroleum is a natural product of decaying living organisms includes plants, bacteria and animals (Tissot & Welte, 1978). Most common type is petroleum derived lubricant where share many similar physical properties with biobased lubricants but have much different on environmental impact. They are commonly used due to cheaper price and satisfy the demands. Petrobased lubricants are attractive for application or inclusion into a wide variety of consumer goods due to its cheap price. It has longer operating life which lower the downtime of the machine as completely changing the lubricant takes a significant amount of time. However, improperly disposal of petrobased lubricants may leach into water system and cause infection and death to organisms. Especially, the Industrial machines that used in offshore drilling or agriculture require machine to be in close proximity with a water source, have higher potential harm the environment (Ing, 2009). Concerning the impact that lubricant exerts on environment, more than 10millions tons of it include engine, industrial and hydraulic oils are estimated returned into environment. Indirectly, spilling of the lubricant oil on ground and water can inhibit the growth of trees and can be toxic to aquatic life (Sánchez et al., 2011). The comparison of the properties of petrobased and biobased lubricant is summarized as in Table 2.2.

Table 2.2: Comparison of the properties of petrobased and biobased lubricant

	Petrobased Lubricant	Biobased Lubricant
Advantages	• Cheap price • Abundant readily accessible satisfy global demand • Longer operating time-Lower downtime of machine changing lubricant. (Ing, 2009) • High oxidation stability • Low pour point (Biolubricants,2011)	• Low toxicity • High viscosity • Higher flash point(higher safety) • Biodegradable (Biolubricants, 2011) • Less emissions • Cost savings on disposal costs, storage (Biolubricants Market Data Sheet, 2004)
Disadvantages	• Non-renewable • Toxic to environment • Hazard disposal (Biolubricants Market Data Sheet, 2004)	• Poor oxidative stability (Biolubricants, 2011) • Price is 1.5-5 times more expansive than conventional lubricants (Biolubricants Market Data Sheet, 2004)

		• High pour point • Low thermal stability (Ing, 2009)

2. 3 Tribological Evaluation and Characterization

The most important properties of lubricants which determine their applicability and efficiency are viscosity, oxidative stability, flash point, pour point, moisture content and total acid number (Sripada, 2012).

Pour point defined as lowest temperature below which it would cease to flow or the temperature at which a fluid begins to flow (Vocabulary Term, 2012). As such, it can become the determining factor in selecting one lubricant from among a group with otherwise identical properties. Standard test method for pour point is ASTM D97-12 (ASTM International, 2013). Cloud point is the temperature at which the dissolved solid in the fluid are no longer completely soluble and precipitate as second phase which give the fluid a cloudy appearance (Nie, 2012). Standard test method for cloud point is ASTM D2500-11 (ASTM International, 2013). Flash point is the lowest temperature which the liquid can vaporize to form an ignitable mixture in air. This point is the temperature where lubricant loss to the surrounding (Sripada, 2012; Vocabulary Term, 2012). Results of this test method ASTM D6450-12 for flash point may be used as elements of a fire risk assessment, which takes into account all of the factors that are pertinent to an assessment of the fire hazard of a particular end use (ASTM International, 2013). The higher the different of pour point and flash point, the broader the range of temperature over which the lubricant could be used safely. Viscosity index (VI) is a measure of the amount of the change in the viscosity of a fluid with a change in temperature (Sripada, 2012). Oxidative stability is the property by which the lubricant is able to resist oxidation and it will be reduced if substantial amount of polyunsaturated fatty acids such as linoleic or linolenic acids in biolubricant (Nie, 2012). Total acid number defined as milligrams (mg) of potassium hydroxide needed to neutralize the acid in one gram of lubricant. The standard unit of measure is mg KOH/g (A Comprehensive Look At The Acid Number Test, 2007). ASTM