Faculty of Resource Science and Technology

Cold Flow Behaviour of Esterified Palm Olein with TiO_2 Nanoadditive for Green Lubricant

Loh Lii Jia

Master of Science
2025

Cold Flow Behaviour of Esterified Palm Olein with TiO_2 Nanoadditive for Green Lubricant

Loh Lii Jia

A thesis submitted

In fulfillment of the requirements for the degree of Master of Science

(Chemistry)

Faculty of Resource Science and Technology
UNIVERSITI MALAYSIA SARAWAK
2025

DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

LOH LII JIA

……

Signature

Name: Loh Lii Jia

Matric No.: 23020022

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

Date: 20/7/2025

ACKNOWLEDGEMENT

I would like to take this opportunity to thank those who have contributed directly or indirectly to this research work. First and foremost, I would like to thank my supervisor, Dr. Diana Kertini binti Monir for her guidance to make this project possible. She gave me a lot of advice, information, assistance, and encouragement through all the stages of my work. Her valuable comments and suggestions idealized the research and the writing report that would help me to complete this degree successfully.

My sincere gratitude to the Centre for Graduate Studies, for the advice and support given during my period of study in Universiti Malaysia Sarawak. A great of gratitude is sent to my faculty, Faculty of Resource Science and Technology that provided bioassay laboratory with advanced instruments which allowed me to do the research. At the same time, I would like to send my thanks to all the lab assistants who provided the chemicals, apparatus, and the equipment as well as the officers handled FTIR, NMR, and SEM analysis assisting me to have the results of research. My deep appreciation is prepared for my parents who provided me a laptop which is important for me to study this degree. They gave me a lot of care, understanding, suggestions, and support for helping me to overcome the obstacles.

Finally, I would like to thank the management of the Universiti Malaysia Sarawak for making it possible for me to complete my study here in Sarawak. I would like to thank God for providing me positive attitude, spirit, and energy to complete this project on time. I feel grateful to have a healthy body in my life and also your love and grace abound me to make this project towards a good direction and completion. Thank you all.

ABSTRACT

The poor cold flow properties of natural palm olein (PO_o) limits its application as a lubricant in low-temperature industrial fluids. To address this, PO_o was converted into large-branched esters via epoxidation, alcoholysis, and esterification. Epoxidation of PO_o with performic acid produced epoxidized palm olein (EPO_o) with a 90.65% yield and 98.14% oxirane conversion, followed by the glycerol-based alcoholysis that incorporated three hydroxyl groups for branching at 85.93% yield. Esterification with oleic, linoleic, and salicylic acids at 140℃ for 4 h produced large-branched oleic acid-esterified palm olein (OA-EPO), linoleic acid-esterified palm olein (LA-EPO), and salicylic acid-esterified palm olein (SA-EPO) with excellent yields of 97.46%, 96.19%, and 99.29%, respectively. The Fourier Transformation Infra-Red (FTIR), proton (^{1}H) and carbon (^{13}C) Nuclear Magnetic Resonance (NMR) spectroscopy analysis confirmed the compound structures. The results showed significant improvement ($P<0.05$) in cold flow of all large-branched EPO, with pour point values ranging from -12 to -7℃ relative to PO_o at 6℃. SA-EPO demonstrated the lowest pour point value of -12℃ followed by LA-EPO (-11℃) and OA-EPO (-7℃). The addition of 0.1% (w/w) titanium dioxide (TiO_2) nanoadditive to LA-EPO further improved its pour point from -11℃ to -12℃. These findings suggest the potential of large-branched esterified palm olein as sustainable feedstock for the development of green lubricant. By exhibiting good performance under cold condition with incorporation of nanoadditive technology, this formulation might be suitable in various sectors supporting the advancement and practical implementation of sustainable lubrication technology.

Keywords: Epoxidation, alcoholysis, esterification, TiO_2 nanoadditive, green lubricant

Kelakuan Aliran Sejuk Olein Sawit Terester dengan TiO_2 Nanoadditif bagi Pelincir Hijau

ABSTRAK

Sifat aliran sejuk olein kelapa sawit asli (PO_o) yang lemah mengehadkan penggunaannya sebagai pelincir dalam cecair industri suhu rendah. Untuk mengatasinya, PO_o telah ditukar kepada ester bercabang besar melalui epoksida, alkoholisis, dan pengesteran. Epoksida PO_o dengan asid performik menghasilkan olein kelapa sawit terepoksida (EPO_o) dengan hasil 90.65% dan penukaran oksirana 98.14%, diikuti alkoholisis berasaskan gliserol yang menggabungkan tiga kumpulan hidroksil bagi bercabang pada hasil 85.93%. Pengesteran dengan asid oleik, linoleik, dan salisilik pada 140℃ selama 4 jam menghasilkan olein kelapa sawit bercabang besar diesterkan asid oleik (OA-EPO), linoleik (LA-EPO), dan salisilik (SA-EPO) dengan hasil cemerlang 97.46%, 96.19%, dan 99.29% masing-masing. Spektroskopi Transformasi Fourier Infra-Red (FTIR), proton (^1H) dan karbon (^{13}C) Resonan Magnetik Nukleus (NMR) mengesahkan struktur kompaun. Keputusan menunjukkan penambahbaikan ketara ($P<0.05$) dalam aliran sejuk semua EPO bercabang besar, dengan nilai titik tuang antara -12 hingga -7℃ berbanding PO_o pada 6℃. SA-EPO menunjukkan nilai titik tuang terendah -12℃ diikuti LA-EPO (-11℃) dan OA-EPO (-7℃). Penambahan nanoadditif 0.1%(w/w) titanium dioksida (TiO_2) kepada LA-EPO meningkatkan lagi titik tuangnya daripada -11℃ kepada -12℃. Penemuan ini mencadangkan potensi olein sawit terester bercabang besar sebagai bahan suapan yang mampan untuk pembangunan pelincir hijau. Dengan mempamerkan prestasi yang baik dalam keadaan sejuk dengan penggabungan teknologi nanoadditif, formulasi ini mungkin sesuai dalam pelbagai sektor yang menyokong kemajuan dan pelaksanaan praktikal teknologi pelinciran mampan.

Kata kunci: *Epoksida, alkoholisis, pengesteran, TiO_2 nanoadditif, pelincir hijau*

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

Page

LIST OF ABBREVIATIONS

Abs	Absorbance
ANOVA	Analysis of Variance
ASTM	American Society for testing Materials
ATR	Attenuated Total Reflectance
AV	Acid value
$BF_3{\cdot}Et_2O$	Boron trifluoride diethyl ether complex
°C	Degree Celsius
C	Carbon
$CaCl_2$	Calcium chloride
CAGR	Compound Annual Grow Rate
$CDCl_3$	Deuterated chloroform
cm	Centimetre
cm^{-1}	Wavenumber
^{13}C-NMR	Carbon Nuclear Magnetic Resonance
df	Degree of Freedom
DMSO	Dimethyl sulfoxide
EPO_o	Epoxidized palm olein
equiv	Equivalent
EV	Ester value
FTIR	Fourier Transformation Infra-red
g	Gram
g/mol	Gram per mol

h	Hour
HCl	Hydrochloric acid
HCOOH	Formic acid
^{1}H-NMR	Proton Nuclear Magnetic Resonance
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
In-situ	In the place
In vacuo	In vacuum
IV	Iodine value
KOH	Potassium hydroxide
LA-EPO	Linoleic acid-esterified palm olein
LA-EPO-TiO_2	Linoleic acid-esterified palm olein with titanium dioxide
mbar	Millibar
mg	Milligram
$MgSO_4$	Magnesium sulphate
MHz	Megahertz
min^{-1}	Per minute
min	Minutes
ml	Millilitre
mmol	Millimole
mol	Mole
MoS_2	Molybdenum disulfide
MS	Mean of squares
MW	Molecular weight
N	Normality

NaCl	Sodium chloride
$NaHCO_3$	Sodium bicarbonate
nm	Nanometre
OA-EPO	Oleic acid-esterified palm olein
OA-EPO-TiO_2	Oleic acid-esterified palm olein with titanium dioxide
OH	Hydroxyl
OOC	Oxirane oxygen content
pH	Potential of hydrogen
pKa	Acid dissociation constant
PO_o	Palm olein
PP	Pour point
ppm	Parts per million
p-TSI	p-Toluene sulfonyl isocyanate
rpm	Revolutions per minute
SA-EPO	Salicylic acid-esterified palm olein
SA-EPO-TiO_2	Salicylic acid-esterified palm olein with titanium dioxide
SEM	Scanning Electron Microscopy
SiO_2	Silica
SS	Sum of squares
SV	Saponification value
T	Temperature
TiO_2	Titanium dioxide
TiO_2-CuO	Titanium dioxide-Copper(II) oxide
µL	Microlitre
U.S.	United States

vol%	Percent by volume
ZnO	Zinc Oxide
% (w/w)	Weight by weight concentration percentage
β	Beta
^{o}	Degree
%	Percentage

CHAPTER 1

INTRODUCTION

1.1 Study Background

Since the industrial revolution, the global economic relies mostly on the factory manufacturing products such as lubricating oils. In industrial era, lubricant becomes demanding in the use of machines to optimize the energy consumption, reduce the friction, mechanical wear, and also corrosion which is expected for an extended period of use (Deuraseh & Deuraseh, 2023). Approximately 37 million tonnes of lubricants from the fossil oil resources are exploited globally every year due to increasing of the demand and population (Unugul et al., 2020). It is estimated to increase to 38.1 million tonnes by 2028.

In lubricant market, most of the lubricants are supplied to the countries in the Asia-Pacific (35%) followed by European regions (23%), North America (22%), Latin America (10%), Africa (6%), and Middle East (4%) (Pinheiro et al., 2021). In general, the lubricant formulation exists in liquid, solid, and gaseous states that mainly comprise of 70% to 99% of base oil. It is ranged at nearly 85% to 90% of lubricants are generated from the non-renewable fossil energy source which known as mineral oils. However, this emerges a huge environmental issue as approximately 50% of the toxic petroleum-based lubricants are discharged into our environment especially the water and soils due to the oil spillage and the accident loss that emerging the environmental pollutions and health problem as one kilogram of carcinogenic acids in the crude oils could damage a million litres of potable water (Almasi et al., 2021).

In fact, the development of today's modern machines still be subjected to the lubricating oils based on mineral oils due to their high operating efficiency. Nevertheless,

these mineral based lubricants are hazardous, non-renewable, and low biodegradability that cause a lot of environmental damage which it discharges more than 24 million tonnes of waste oil in global every year (Suhaimi et al., 2022). To concern the sustainability issue, the crude oils which are extracted from the earth's crust may face depletion in one day due to the high industrial demand on the supply of lubricants. That is the reason why the natural compounds are developed to replace the petroleum products nowadays.

From the research view, the vegetable oil-based bio-lubricant is a suitable candidate to supersede the petroleum-based lubricant due to its high biodegradability and low toxicity (Aziz et al., 2020). Oleochemical-based lubricants are environmentally benign which suit for different applications. The advantages of using bio-lubricants derived from the vegetable oils are their high availability meaning in an abundant resources which are more sustainable in the storage and shipping as well as their intermediate products are reusable for the application of biorefineries (Nogales-Delgado et al., 2021).

We can see that the global bio-lubricant market is growing as it is expected to increase from 1.9 billion in year 2020 to 2.5 billion by 2026 in U.S. lubricant market with a 5.2% of Compound Annual Grow Rate (CAGR) (Nurazira et al., 2022). This is caused by the enforcement of government regulations that restrict the use of petroleum-graded lubricants in some regions. To explore a new sustainable lubricant, the researchers start to focus their attention on the use of different vegetable oils to be their raw materials in the design of research. In this new trend, the explorations of plant oil-oriented lubricants have been initiated actively but not yet in an extensive application as some research gaps still be able to discover in the research area of vegetable oils especially on palm olein.

Palm olein is one of great potential sources to be developed as an alternative green lubricant through chemical modification techniques. From the oil palm tree, the edible semi-

solid crude palm oil is mainly extracted from the fleshy orange-red mesocarp of oil palm fruits. Palm olein (PO_o), a refined crude palm oil, is the liquid fraction derived from the industrial fractionation process (Syarifah-Noratiqah et al., 2020). PO_o is selected instead of conventional palm oil because PO_o shows better fatty acid configuration with higher contents of oleic acid (43.9%) and linoleic acid (13%) with more unsaturated double bonds than palm oil (Jadhav et al., 2021). The amphiphilic molecules in the PO_o belongs to the polar ester groups associated at the non-polar hydrocarbon chains. This amphiphilic characteristic satisfies the required requirements as the boundary and hydrodynamic lubricants. PO_o is renewable and less hazardous so it is forecasted to replace 90% of the petroleum oil to reduce the production of non-recyclable waste (Hussein et al., 2021).

In environmental and sustainability concerns, PO_o has high biodegradability that more than 95% so it can degrades in a rapid rate that ranged at 20% to 30% faster than the mineral oil-based lubricants (Owuna et al., 2020). PO_o is renewable, less hazardous, and also cheaper in price (Hambali & Puspita, 2021; Tajau et al., 2020). Moreover, Suhami and her research partners have reported that palm oil is more sustainable compared to the mineral oil because mineral oil has a relatively poor biodegradability between 0% and 40% (Suhaimi et al., 2022). Thus, PO_o stands as a promising substitute to the petroleum oils that also demonstrating a stable thermo-viscosity property with high flash and fire points which is safe over the temperature change (Rahman et al., 2023).

Besides, Malaysia is ranked as the second leading country in the worldwide production of the palm oil which owned 5.9 million hectares of oil palm trees and 423 palm oil operating factories (Abubakar et al., 2021). The yield of oil palm tree per unit land area in Malaysia is relatively high that up to 10 times more than other crops (Loh & Muzzammil, 2021). It is known that the palm oil production has reached as high as 75 million tons in

2020 (Almeida et al., 2021). Therefore, PO_o is eligible to become the replenishable feedstock to be manufactured into the bio-lubricant in order to support the growing market demand of lubricants for lubrication, abrasion resistance, and the formation of strong protecting films between the contacting surfaces in the machines.

Although these outstanding advantages are mentioned as above, the vegetable oils including PO_o share a major drawback of poor cold flow behaviour. This weakness will restrict the direct application of PO_o as the lubricant in the refrigeration system of food industry as well as its usage in the seasonal countries as it tends to solidify at low temperature (Norhayati et al., 2022). Solidification is commonly happened at the linear triacylglycerols of the lubricating oil because of the uniform shape which allows the individual molecules to link the network together into the crystal lattice via nucleation or crystallization at cold condition. Saturated fatty acid in the oil is susceptible to clump faster than the unsaturated fatty acid into the macro-crystals (Salih & Salimon, 2021). To summarize, the molecular structure and the presence of saturated fatty acids are the main concern to affect the fluidity of plant oils at low-temperature applications.

For the molecular structure, there are some reactive functional groups polymerized in the fatty acid chains of plant oils but with very low functionalities that limit the application. The triglyceride structure of PO_o comprises of a mixture of ester moiety derived from the glycerol and the free fatty acid chains mainly with the saturated palmitic and stearic acids together with the unsaturated fatty acid chains like linoleic and oleic acids (Shahdan & Hirzin, 2021). To synthesize the bio-lubricant, the chemical modification action is required on the reactive sites of the triglycerides such as the carbon-carbon double bonds of the plant oils (Li et al., 2020). The unstable double bonds in the triglycerides can be actively converted into high reactivity of oxirane ring which is a beneficial functional group suitable

for further functionalization (Stavila et al., 2023). The unsaturation can be used to react with the reactive peracid reagents of performic or peracetic acid via epoxidation.

Epoxidation is a well-known strategy to model the epoxide groups due to its simple and low-cost production with a high level of selectivity. However, epoxidation is an exothermic reaction that may causes thermal runaway so the experimental temperature should be controlled by the cooling medium with the chemical dosing in the dropwise rate (Dominguez-Candela et al., 2022). The thermal runaway may causes the collapse of the oxirane rings that impact the quality and the yield of products due to the presence of protons during the epoxidation (Meng et al., 2023).

Although there are some molecular structure changes by the epoxidation, the epoxidized plant oils still cannot completely substitute the mineral-processed lubricating oils because it lacks of promising lubricating performance (Sarma et al., 2021). To improve the oil's performance, the ring-opening reaction via alcoholysis is conducted after the epoxidation. The oxirane ring opening of epoxidized fatty acids can be carried out by various nucleophiles such as alcohols with the catalysts to generate valuable ring-opening intermediates (Sharma et al., 2022). By the way, the hydroxyl groups are inserted into the active sites of plant oil to synthesize the bio-polyols. The bio-polyols behaves low acid value, low viscosity, and with small molecular weight distribution (Stavila et al., 2023).

Even though the epoxidation and the ring opening reactions have enhanced some chemical properties of the starting oil but its damaging characteristic of poor cold flow behaviour still exists so it should proceed with the esterification reaction. The purpose is to correct the unstable β-hydrogen atom in the structure. This is declared by Almasi and other researchers in 2021. During the esterification reaction, the alkoxy group of ester acts as a good leaving group in the nucleophilic substitution mechanism (Soodoo et al., 2023). The

ester creates the lubricity feature by presenting the strong dipole moments at the polar sites that adhere strongly to the moving contact surfaces which can reduce the friction and wear.

Besides the friction-reducing ability, the synthetic esters also display a low-temperature property and high oxidative stability after increasing the oil's branch length and molecular weight through esterification (Raof et al., 2022). The fatty acid-based esters are proven to be versatile lubricant alternatives to the standard petroleum based-lubricant. However, there is still no much exploration using the solvents of toluene and acetonitrile during esterification reaction between oleic acid, linoleic acid, and salicylic acid with polyol intermediates respectively. In this study, the ester moiety was incorporated into the structure of PO_o using different reagents and solvents in the presence of catalyst to increase its mid-chain length between the fatty acid backbones.

In addition, the utilization of suitable nano-additive technology is allowed to develop an excellent nano-additive based lubricant which is significantly more effective than traditional bio-based lubricants to reduce the friction. The selection of a proper lubricant additive depends mostly on the additive's ability to compatible with the lubricating oils to perform the desired function. This can be seen from the hardness, concentration, and the particle size of the nano-additive (Zilabi et al., 2022). Theoretically, the addition of nanoparticles into the lubricating oils enhance the lubricating performance by acting as a nano-ball bearing to roll between two contacting surfaces or by forming a triple protective film to reduce the coefficient of friction (Yunus et al., 2020).

To design a nano-additive based lubricant, it is prepared by a small amount of nanoparticles from 0.2% to 0.5% to disperse with the vegetable oil derivatives using the ultrasonic and mechanical agitation methods (Karmakar et al., 2020). The inorganic nanoparticles are difficult to create a stable suspension in the vegetable oil due to its high

surface activity (Waqas et al., 2021). In this sense, it is assisted by the presence of surfactants to link with the hydroxyl and carboxyl groups on the surface of lubricating oil to stabilize the structure. In this manner, the dispersion of nano-powders in the non-polar mediums become more stable (Abdel-Rehim et al., 2021).

Additionally, the conditions of nano-dispersions are strongly correlated on the concentration of nano-powders as an insufficient amount could affect the lubricating property while an excess amount could form the discontinuous oil film (Río et al., 2022). The tribological behaviour of the nano-lubricant is controlled by the shape and the size of nanoparticles as spherical shaped nanoparticles result in higher load-bearing capacity. This can be observed from earlier research findings that the titanium dioxide (TiO_2) nano metal oxide particles by 0.01% of volume have improved the load-bearing strength by 40% (Singh et al., 2020). Other than the tribological performance, the oxidative and thermal stability are also improved by the dispersion of nano-particles in the vegetable oil derived lubricants (Sadiq et al., 2022). The metal oxide (TiO_2) nanoparticles are suggested in this study as the pour point improver due to its benefits of easily obtainable, non-toxic, and also considered as non-hazardous for human handling (Shashavali et al., 2021).

From the particular point of view, the yield of the intermediates and products are controlled predominantly by the operating reaction conditions (Zora et al., 2021). The reaction temperature and the reaction time are chosen as the variable controls in the experiment. This study could explore the potential of chemically modified PO_o as a green lubricant to replace the conventional petroleum-based lubricants that not just limited to engines but also relevant for textile industries, food industries, hydraulic fluids, metalworking lubricants, greases, machinery and many others. Most research investigations have concluded the effectiveness of TiO_2 nano-additive in the tribology property of the