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Development of Biolubricants from Vegetable Oils for Non-Internal Combustion Engine Applications

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Abstract

With the emerging bio-economy and increasing concerns over sustainability, biobased complex esters (CEs) are coming back to the fore, notably due to their renewability and biodegradability attributes and low toxicity to the environment. The promise of biobased CEs in the lubrication industry lies in their ability to provide superior lubrication, thermal stability, and compatibility with various metals. Therefore, biobased CEs are likely to play a significant role in meeting the demanding requirements of modern machining and forming processes.

The presence of unsaturated free fatty acids in the carbon chain of triglycerides and tertiary β-hydrogen group in the glycerol backbone causes low thermal and oxidative stability. Thus, this study investigated a methodology that has been developed to produce biobased CEs with improved thermal and oxidative stability. This involves the conversion of vegetable oil triglycerides into trimethylolpropane (TMP) esters through a two-step transesterification-transesterification and a two-step hydrolysis-esterification process. To further increase the thermal and oxidative stability, an epoxidation reaction was performed in order to remove the C=C double bonds in the canola oil trimethylolpropane (COTMP) ester structure using tert-butyl hydroperoxide (TBHP) as an oxidizing agent in the presence of a heterogeneous catalyst. The conversion, selectivity, oxirane oxygen content (OOC), and iodine value of the final epoxidized canola oil trimethylolpropane (ECOTMP) ester were 95.2%, 98.62%, 4.12%, and 3.4 mg I_2/g, respectively.

This work has focused on the conversion of vegetable oils to saturated complex esters through several chemical modifications (e.g., hydrolysis, esterification/transesterification, and epoxidation) and demonstrated the effective use of metal complexes as heterogeneous catalysts in the epoxidation reaction. The novelty of this study is the formulation of biolubricants with outstanding wear scar diameter (WSD) from vegetable oils and the development of a heterogeneous catalyst for epoxidation reaction in order to increase the conversion, selectivity, and OOC of the final product.

Keywords

Biolubricants; vegetable oils; biobased complex esters; biodegradability; thermal stability; oxidative stability; biobased high-performance hydraulic fluids; chemical modification; transesterification; hydrolysis-esterification; epoxidation; heterogeneous catalyst.

Summary for Lay Audience

As concerns about sustainability grow and the bioeconomy gains traction, biobased complex esters (CEs) are regaining attention for their renewable, biodegradable, and environmentally friendly properties. These CEs show great promise in the lubrication industry, offering superior lubrication, thermal stability, and compatibility with various metals. They are poised to meet the rigorous demands of modern machining and forming processes. However, traditional biobased CEs often suffer from low thermal and oxidative stability due to the presence of unsaturated fatty acids in triglycerides. To address this, a study explored a cost-effective method to produce biobased CEs with improved stability. The process involves converting vegetable oil triglycerides into trimethylolpropane (TMP) esters through two-step transesterification-transesterification or a novel two-step hydrolysis-esterification process. Additionally, an epoxidation reaction is used to remove double bonds in the ester structure, enhancing stability.

The resulting epoxidized canola oil trimethylolpropane (ECOTMP) ester showed high conversion, selectivity, oxirane oxygen content (OOC), and reduced iodine value, indicating improved stability. The study focused on transforming vegetable oils into saturated complex esters through chemical modifications, such as hydrolysis, esterification/transesterification, and epoxidation. It also demonstrated the effective use of metal complexes as heterogeneous catalysts in the epoxidation reaction.

This research not only develops biolubricants with exceptional wear scar diameter (WSD) from vegetable oils but also introduces a novel heterogeneous catalyst to enhance conversion, selectivity, and OOC in the final product. Overall, this work contributes to the advancement of sustainable lubrication solutions, leveraging abundant vegetable oil resources and innovative chemical processes to meet the evolving needs of the industry while minimizing environmental impact.

Co-Authorship Statement

Chapter 2 Literature Review

Authors: Behzad Kamyab, Ramon Filipe Beims, Darren W Chambers, Chunbao Charles Xu, Amarjeet S. Bassi

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Chapter 3 Synthesis of TMP esters as a biolubricant from canola oil via a two-step transesterification-transesterification process

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The experimental work, sample characterizations, and data analysis were conducted by Behzad Kamyab under the supervision of Dr. Chunbao Charles Xu and Darren W Chambers. The biodegradability analysis was conducted by Chonlong Chio under the supervision of Dr. Wensheng Qin. The manuscript was reviewed and revised by Drs. Ramon Filipe Beims and Chunbao Charles Xu.

Chapter 4 Preparing vegetable oils-based metalworking fluids by a hydrolysis-esterification two-step process

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Chapter 5 Production of high-end bio-lubricant products via epoxidation of canola oil trimethylolpropane (COTMP) esters

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Table of Contents

List of Tables

List of Figures

List of Abbreviations and Symbols

Abbreviation/Symbol	Meaning
CEs	Complex esters
HPHFs	High performance hydraulic fluids
HFs	Hydraulic fluids
TMP	Trimethylolpropane
FAAEs	Fatty acid alkyl esters
FAME	Fatty acid methyl ester
FAEE	Fatty acid ethyl ester
FAEs	Fatty acid esters
FFAs	Free fatty acids
NPG	Neopentyl glycol
PE/PTE	Pentaerythritol
ME	Monoester
DE	Diester
TE	Triester
TAG	Triacylglycerol
PAG	Polyalkylene glycols
PEG	Polyethylene glycols
PAO	Polyalphaolefin
TMPTE	Trimethylolpropane triester
PP	Pour point (ºC)
FP	Flash point (ºC)
COTMP	Canola oil trimethylolpropane
ECOTMP	Epoxidized canola oil trimethylolpropane
TBHP	Tert-Butyl hydroperoxide
API	American petroleum institute
ATF	Automatic transmission fluid
AW	Anti-wear
WSD	Wear scar diameter (mm)
EHL	Elastohydrodynamic lubrication
EP	Extreme pressure
ESBO	Epoxidized soybean oil
EVOs	Epoxidized vegetable oils
FDA	Food and Drug Administration

OECD	Organization of Economic Cooperation and Development
NSF	National Sanitation Foundation
FRH	Fire resistance hydraulic
HEES	Hydraulic oil environmental ester synthetic
HEPG	Hydraulic oil environmental polyglycol
HETG	Hydraulic oil environmental triglyceride
HO-TMPTE	High oleic trimethylolpropane triesters
HOSO	High oleic sunflower oil
SFO	Sunflower oil
HVI	High viscosity index
VI	Viscosity index
VII	Viscosity index improver
OIT	Oxidation induction time (min)
PPD	Pour point depressant
R&O	Robust and oxidation inhibitors
RBOT	Rotary bomb oxidation test
STOU	Super Tractor Oil Universal
UTTO	Universal Tractor Transmission Oil
TGA	Thermogravimetric analysis
ZDDP	Zinc dithiophosphates
ZDTP	Zinc dithiophosphate
BSTFA	N,O-bis(trimethylsilyl)-trifluoroacetamide
MSTFA	N-methyl-N-trimethylsilyltrifluoracetamide
COEE	Canola oil ethyl ester
GC-MS	Gas chromatography-mass spectrometry
NMR	Nuclear magnetic resonance
FTIR	Fourier-transform infrared spectroscopy
T600	Time to 600 ºC (s)
T400	Time to 400 ºC (s)
T200	Time to 200 ºC (s)
Vmax	Maximum cooling rate (ºC/s)
Tvmax	Temperature at maximum cooling rate (ºC)
V300	Cooling rate at 300 ºC (ºC/s)
TMS	Tetra-methyl silane
AV	Acid value (mg KOH/g)
ADA	Adipic acid

COF	Coefficient of friction
OSPE	Oil soluble phosphate ester
XRD	X-ray diffractometry
SEM	Scanning electron microscopy
EDS	Energy dispersive X-ray spectroscopy
OOC	Oxygen oxirane content (%)
RCO	Relative conversion to oxirane (%)
PVC	polyvinyl chloride
BSE	Backscattering electron
IV	Iodine value (mg I_2/g)
μ_0	Dynamic viscosity (Pa.s)
T_A	Absolute temperature (ºC)
E_ν	Epoxy value (mol/100g)

Chapter 1

1 Introduction

1.1 Background and Knowledge Gaps

Fossil fuel is now widely recognized as an unsustainable resource with depleting supplies and increasing costs [1,2]. In addition, the use of more-aggressive petroleum extraction techniques, impelled by the decrease in fossil fuel sources, transportation, and industrial processes for oil refining has resulted in many environmental problems such as oil leakage, low degradability of wastes and toxic effluents, contamination of water with gasoline and additives, and accumulation of carbon dioxide in the atmosphere [3]. Currently, industries are searching for new, less costly, and renewable raw materials in order to produce liquid transportation fuels and oleochemicals with high biodegradability, low toxicity, and low environmental impact [4]. One of the renewable alternatives for liquid fuel is biodiesel, a renewable, non-toxic, biodegradable, and eco-friendly fuel consisting of fatty acid alkyl esters (FAAEs) obtained from renewable sources like vegetable oils and animal fats [5-7]. Biodiesel is more advantageous than conventional petroleum-based diesel fuel in terms of sulfur content, flash point, aromatic content, and cetane number [8]. The usage of biodiesel can reduce the emissions of SOx, CO, particulate matter, and hydrocarbons in exhaust gas compared with petroleum-based diesel fuel [9], while the properties of biodiesel are similar to those of petroleum-based diesel fuel, so it can be used as a fuel blend or as a substitute for petroleum-based diesel fuel [10-12].

Nowadays, commercially available lubricants are produced mainly from mineral and synthetic oils. The world market for finished lubricants is around 35 million tonnes per year, with biolubricants accounting for about 1% of the total production capacity [13]. While the market for mineral-based finished lubricants has been stagnant, the market for biolubricants has shown an average growth of 10% per year over the last 10 years [14]. Biolubricants, mostly composed of fatty acid esters, are preferred as they are considered “green products” with excellent biodegradability [15], and hence their use prevents environmental pollution caused by possible leaks and disposal of the used products. Vegetable oils are good candidates because they are environmentally friendly and structurally similar to long-chain hydrocarbons in mineral oils [16]. Thus, vegetable oils can be environmentally friendly bio-feedstocks for biolubricant production [17]. However, direct use of vegetable oils is limited by their high melting point, prohibitively high viscosity and low oxidative stability, which are not desirable properties for lubricants [18]. To overcome this limitation, a two-step conversion process has been commonly adopted, i.e., the step-1 transesterification of vegetable oils (triglyceride) usually with **methanol** into fatty acid esters (FAEs), followed by step-2 transesterification of FAEs with polyols such as trimethylolpropane (TMP) and neopentyl glycol (NPG) [19-21]. Polyol esters can have good viscosity levels and a satisfactory pour point, although the final characteristics of the product depend on the polyol used, the chain sizes of the fatty acids, and the number of unsaturated bonds and their positions in the chain [22]. Saturated fatty acids have significantly higher melting points than unsaturated fatty compounds and, in the mixture, they crystalize at a temperature higher than the unsaturated ones [23]. Unsaturated fats tend to have a lower melting point than saturated analogues; as a result, they are often liquid at room temperature.

Vegetable oils, such as Castor oil, Palm oil, Sunflower oil, and Canola oil, have been used to produce biolubricants. For example, Canola oil consists of about 64% oleic acid (C18:1), 20% linoleic acid (C18:2), and 10% α-linolenic acid (C18:3) as free fatty acids (FFAs) [24]. Esterification of FFAs or transesterification of FAEs with polyols such as TMP, NPG, and pentaerythritol (PE) leads to the production of complex esters such as TMP ester of vegetable oils, which are potential biolubricants derived from renewable sources. The molecular structures of triglyceride in vegetable oil, common vegetable oil free fatty acids and the TMP, NPG and PE polyols are shown in **Figure** 1.1**.**

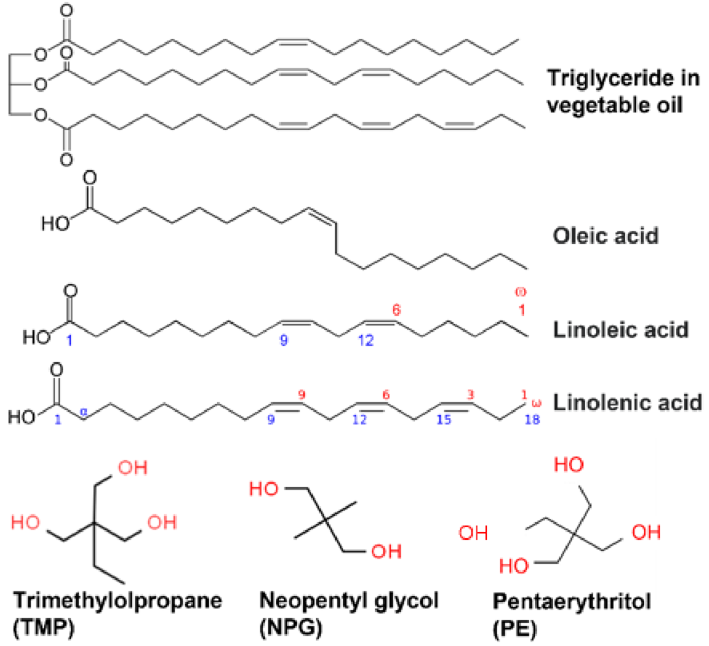

Figure 1.1: Molecular structures of triglyceride in vegetable oil, common vegetable oil fatty acids and the TMP, NPG, and PE polyols.

As shown in the scheme (**figure** 1.1**)**, the polyols are all branched polyols that have no labile hydrogen atoms in their structure which are equivalent to the β carbon of glycerol. Therefore, esters of these polyols have greater thermal stability than simple esters of the same fatty acids [25]. TMP is a colorless triol (three hydroxyl groups) with the formula of $CH_3CH_2C(CH_2OH)_3$. TMP is often used to produce triester (TE) compounds of fatty acid as vegetable oil-based biolubricants with improved properties to substitute the triacylglycerol (TAG) lubricants [26,27]. Previously, Yunus et al. [28] synthesized TMP esters with palm oil fatty acids and fractions of palm oil fatty acids. The product materials were reported to have improved pour point (PP) (as low as –37 ºC). In a separate study, Arbain & Salimon, [29], reported that the PP of Jatropha curcas TAG oil was 10 ºC, while the trimethylolpropane triester (TMPTE) of Jatropha curcas fatty acids had a PP of –37 ºC. However, the presence of free fatty acids and multiple C=C bonds in the carbon chain of triglycerides was reported in previous studies to be prone to accelerating oxidative degradation, and the presence of the tertiary β-hydrogen group in the glycerol backbone resulted in low thermal and oxidative stability [30].

According to the aforementioned paragraphs, the knowledge gaps are as follows:

(1) Methanol has been widely used in the Step-1 transesterification reaction of vegetable oil to FAEs and most commonly produced from fossil resources. Thus, there is a strong need to replace methanol with a lower-toxicity and renewable alcohol (such as bioethanol) for transesterification of vegetable oil to FAEs.

(2) Sodium methoxide has been widely applied as an effective base-catalyst in the Step-2 transesterification of FAEs to complex esters such as TMP esters in many studies. However, sodium methoxide is not the most suitable catalyst for industrial-scale reactions as it can be easily deactivated. In addition, sodium methoxide powder is highly caustic, and can react with water in air rapidly to give methanol vapor, so it is highly corrosive, volatile, and flammable, as well as expensive. Thus, it is necessary to explore an inexpensive way to make complex esters as biolubricants from vegetable oils for industrial applications.

(3) Wear and friction properties of biolubricants from vegetable oils are highly important for industrial applications. However, by far there is still a lack of research on the wear and friction of metalworking biolubricants derived from vegetable oils. In addition, there is almost no information about the quenching characteristics of vegetable oil TMP esters.

(4) Since the performance of the final biolubricant products is strongly dependent on the compositions of the vegetable oil used. **Canola oil, abundantly produced in Canada with annual production of 20 million tonnes**, has however not been much explored as feedstock for biolubricants production [31]. In this study, canola oil will be used for synthesis of canola oil TMP (COTMP) esters, and the optimum conditions will be investigated to achieve better product yields and properties.

(5) Hydrolysis reaction of vegetable oils to FFAs has been investigated by many researchers in supercritical conditions (high temperature/pressure), which are not economical for industrial application. Consequently, it is more desirable to develop a more efficient process for hydrolysis of vegetable oils to FFAs, which operates at moderate temperatures/pressures and produces higher yields of FA and glycerol.

(6) In the realm of vegetable oils, industry commonly employs epoxidation processes that utilize peracids as oxidizing agents, coupled with strong mineral acids as catalysts. However, these methods come with notable drawbacks, as they lack selectivity, contribute to equipment corrosion, and generate significant residue. The use of transition metal complexes as homogeneous or heterogeneous catalysts eliminates many of these problems and also

provides a reaction that is very selective. Therefore, it is crucial to use another oxidizing agent such as tert-Butyl hydroperoxide (TBHP) in presence of a heterogeneous catalyst in order to improve efficiency and selectivity of the final product.

Thus, the motivation of this PhD project was to develop a process to produce biolubricant oils with improved thermal and oxidative stability from vegetable oils (in particular Canola oil, abundantly produced in Canada) for non-internal combustion engine applications, by converting vegetable oil triglyceride into TMP esters via the 2-step transesterification-transesterification process or a novel 2-step hydrolysis-esterification process, followed by an epoxidation reaction in presence of $[MoO_2(acac)_2]$@K10-ETA as heterogeneous catalyst to remove the C=C bonds.

1.2 Objectives

The overall objective of this PhD work is to develop a process to produce biolubricant oils with improved thermal and oxidative stability from vegetable oils (in particular Canola oil, abundantly produced in Canada) for non-internal combustion engine applications. specifically, this thesis aimed to: **(1)** Develop and optimize the 2-step transesterification-transesterification process to convert vegetable oil triglyceride into TMP esters as a biolubricant. The target biolubricant is expected to have the following characteristics: a) high viscosity index as desired for lubricants; b) high thermal and oxidative stability; c) low volatility; d) high chemical stability against acids (low scar test values or high anti-wear properties); e) good miscibility for mineral oils and additives. **(2)** Develop and optimize the 2-step hydrolysis-esterification process to convert vegetable oil triglyceride into TMP esters as a biolubricant. **(3)** Improve the thermal-oxidative stability of the COTMP esters by epoxidation reaction in the presence of $[MoO_2(acac)_2]$@K10-ETA as a heterogeneous catalyst.

1.3 Thesis overview and research approaches

Chapter 1 introduces the general background, significance, and knowledge gaps of biobased lubricants. The research objectives, approaches, contributions, and thesis structure are also presented.

Chapter 2 introduces the most important performance indexes that a hydraulic fluid must have in order to have the desirable performance in various industrial applications, reviews the most common types of esters used in making hydraulic fluids, and provides an in-depth discussion on two chemical modification methods widely employed in the production of biobased HPHFs from vegetable oils. Finally, the current challenges, knowledge gaps, and future perspectives on the sustainable development of biobased HPHFs are analyzed.

In **Chapter 3,** a process was developed to produce biolubricant complex esters with improved thermal and oxidative stability from vegetable oils (in particular Canola oil, abundantly produced in Canada) for non-internal combustion engine applications, by converting vegetable oil triglyceride into TMP esters via a 2-step transesterification-transesterification process. In this work, ethanol as a renewable alcohol was used as a substitute for methanol in 1^{st} step transesterification reaction.

Chapter 4 aimed to synthesize biodegradable esters, compatible with mineral or synthetic oils. Their combination with base oils and appropriate additives demonstrates exceptional wear and friction properties, bolstering the performance of anti-wear and coolant operations in metalworking systems.

Chapter 5 evaluates the synthesis of epoxidized canola oil trimethylolpropane (ECOTMP) ester using TBHP as an oxidant agent and a heterogeneous catalyst obtained by immobilization of bis(acetylacetonate)dioxo-molybdenum (VI) [$MoO_2(acac)_2$] with montmorillonite (K10)-ethanolamine.

Chapter 6 summarizes the main conclusions from this project and suggests future research perspectives.

1.4 Contributions and novelties

The main contributions and novelties of this thesis can be summarized as follows:

- Summary of the most important performance indexes of HPHFs, and the most common important esters used as base stocks in hydraulic fluids.
- Development of innovative approaches for chemical modification of vegetable oils to produce esters and complex esters as biolubricants for non-internal combustion engine applications.
- Optimized process for manufacturing of biolubricants from vegetable oils.
- Formulation of ultimate lubricants (e.g. metalworking fluids) uisng the complex esters obtained from this project.
- Discovering anti-wear characteristics and quench properties of the lubricant uisng the complex esters in the final formulation
- Development of an affordable process for epoxidation reaction of COTMP ester in order to remove C=C bonds, using TBHP as an oxidizing agent and a heterogeneous catalyst.

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Chapter 2

2 Sustainable production of high-performance bio-based hydraulic fluids from vegetable oils: Recent advances, current challenges, and future perspectives

Abstract

The significant benefits of sustainability, biodegradability, and non-toxicity have led to a dramatic increase in the utilization of vegetable oil-based hydraulic fluids across various industries. Therefore, knowing how to formulate biobased high-performance hydraulic fluids with various types of base oils (e.g., petroleum-based oils, esters, complex esters, and estolides) and their essential physical and chemical properties are the key factors. This review provides an overview of the most important performance indexes of high-performance hydraulic fluids and the most common important esters used as base stocks in hydraulic fluids. Recent advances in chemical modification of vegetable oils as one of the most popular methods to achieve an ideal base oil for the formulation of high-performance hydraulic fluids and two examples of estolide esters and epoxidized vegetable oils are extensively reviewed. More ways to convert vegetable oils into esters with better stability and fluidity, expected to provide new applications of bioresources and green chemistry, are introduced. Furthermore, current challenges and future perspectives of the production of high-performance vegetable oil-based hydraulic fluids are discussed.

2.1 Introduction

At present, a wide market for bio-based hydraulic oils exists, with numerous companies predominantly located in the USA and Europe. Major players in the lubricant industry, such as Mobil (USA), Shell (USA), and Chevron Texaco (USA), are among the prominent manufacturers [2]. According to the market research future website, in 2022, the hydraulic fluid market reached a value of $20.75 billion. Industry projections indicate significant growth, with the market expected to increase from $21 billion in 2023 to $25.93 billion by 2030, reflecting a compound annual growth rate (CAGR) of 2.19% during the forecast period [3]. In addition, after engine oils, HFs are the second-largest group of lubricants, mostly employed in static industrial installations (70-80%), and, to a lesser extent, in engines, aerospace [4], and military [5] industries [6]. Hence, HFs must meet the critical standards in that application, and an improper choice could result in the reduction of the longevity of other components of the hydraulic system and maintenance periods, thus increasing operating expenditures due to erosion-corrosion problems.

Industrial manufacturers generally determine the type of hydraulic fluid (HF) based on the technical specifications required by their hydraulic systems (e.g., operating temperature and pressure, fluidity at high or low temperatures, water miscibility, operating conditions of the hydraulic pump, etc.) [7,8]. A high-performance hydraulic fluid (HPHF) must have properties such as biodegradability, high thermal and oxidative stability, excellent low-temperature performance, low copper activity, high hydrolytic stability, excellent rust and corrosion preventative performance, efficacious demulsibility characteristics, high anti-wear protection, low pour point, acceptable viscosity-temperature properties, high oxidation and foam resistance, and extremely high film strength. For example, Asaff et al. [9] examined the overall effects of typical contaminants on the oxidation stability and hydrolysis stability of commercial biodegradable hydraulic fluid samples. Their findings indicated that these fluids were susceptible to contamination from solid copper particles, oxygen (leading to oxidation), water (causing hydrolysis), common mineral-based hydraulic fluids, and exposure to elevated temperatures. Consequently, this degradation of the oil results in the generation of acidic compounds, an elevation in oil viscosity, reduced additive efficacy, and the formation of varnish. Their study revealed that the biodegradability of biobased hydraulic fluids is notably diminished by their combination with mineral oil, experiencing a decline of 10 to 12%.

The most prevalent HFs are usually those based on mineral oils due to their lower prices and accessibility. However, due to the increasing importance of the biodegradability of lubricants in industries, the use of natural and synthetic esters in the manufacture of HFs has grown drastically worldwide [10]. The main concern of most lubricant companies is to eliminate the risks of accidental oil spills, which can cause irreparable damage to the environment [10,11]. Consequently, advancing toward the production of bio-based hydraulic fluids (BHFs) has become a priority. BHFs are currently formulated with vegetable oils (e.g., rapeseed, sunflower, corn, soybean, canola, coconut, etc.) or synthetic esters [12,13]. Regueira et al. [14] conducted a study to evaluate the compressibility of high oleic soybean oil (HOSO) and compared its performance with that of conventional synthetic and mineral-based oils. Through comparisons with findings from previous studies, they determined that bio-based oil demonstrates superior power transmission properties (in hydraulic systems) when compared to mineral-based oils. Furthermore, high-quality and pure base oils, such as vegetable oils, are known to facilitate faster air release, a crucial factor in hydraulic oil selection (Mang and Dresel, 2007) [15]. Rogoś [16] found that when refined rapeseed oil was used as the base oil, the air release rate for bio-based hydraulic oils exceeded the specified standard PN-C-96057-6 by sevenfold. In another study, Nagendramma et al. [17] conducted a study where bio-based hydraulic fluids were effectively synthesized through the esterification reaction. The resulting polyol esters demonstrated lower pour points and superior biodegradability when compared to commercial VG-22 mineral hydraulic oils.

In addition to biodegradability and lack of toxicity, high-temperature stability, high shear stability, low volatility, high flash point, and viscosity index, excellent lubrication, fluidity as well as low health and safety risks, and ease of disposal are other advantages of using natural or synthetic esters from carboxylic groups [18]. In contrast, they have some inherent disadvantages such as poor performance at low temperatures, oil polymerization and sensitivity to hydrolysis, and oxidative instability caused by the multiple unsaturated fatty acids [19]. Chemical modification of fatty acid methyl esters (FAME), employing suitable additives compatible with BHFs, or even creating them through de novo synthesis [20], represents potential strategies for addressing the limitations of BHFs. However, this approach may help mitigate the increased overall costs associated with scaling up production.

Nowadays, about 80% of the base stocks used worldwide in synthetic lubricants fall into generic groups, such as synthesized hydrocarbons (~50-55%) and organic esters (~25%). Other categories include polyglycols (~10-15%) and phosphate esters (~5-10%) [21,22]. Applying high-performance hydraulic fluids (HPHFs) requires the use of non-mineral-based oils (most often Group V base oil) as well as the use of chemically modified esters. As for environmentally friendly fluids for insoluble HFs in water, hydraulic oil environmental ester synthetic (HEES) fluids and hydraulic oil environmental triglyceride (HETG) vegetable oil-based fluids have received more attention because of their significant biodegradability. For HETG-type base stocks, the most important vegetable oils that are used in the synthesis of esters are rapeseed and sunflower [18]. They withstand lower thermal and oxidative loads than mineral oils and are used for low-pressure applications and medium temperatures, where reservoir temperatures do not exceed 70°C. It should be noted that this type of fluid can become unstable if exposed to water. An illustration of HETG-type fluids is demonstrated in the research conducted by Jabal et al. [23], which investigated the utilization of non-edible sunflower oil as a bio-hydraulic fluid. Their findings indicated that under various loads, the tested samples displayed lower friction torque and coefficient of friction compared to mineral-based fluid alternatives. For HEES-type base stocks, the most widely used synthetic esters are simple or complex chemically modified esters (e.g., diesters, trimethylolpropane (TMP), and neopentylglycol (NPG) esters) [24-26]. For instance, Bahadi et al. [27] highlighted the suitability of a TMP triester derived from palm kernel fatty acids for use in food processing machinery. In a separate study, Bahadi et al. [28] proposed di-trimethylolpropane tetraester as a candidate for food-grade hydraulic oil. This compound is synthesized through the transesterification reaction of palm kernel oil and di-TMP, possessing a viscosity index of 140, a flash point of 392°C, and a pour point of -6°C.

Much effort has been made in developing HFs from vegetable oils, such as rapeseed, soybean, passion fruit, moringa, and sunflower oils with a high oleic acid content [29]. Kamalakar et al. [30] focused on the use of unsaturated fatty acid-rich rubber seed oil (82%, unsaturation) for lubricant base stock preparation. According to ISO 15380 (standard for environmentally acceptable hydraulic fluids) requirements, their synthesized esters show good performance in terms of HF specifications. Erhan et al. [31] reported the development of diester derivatives of soybean oil through epoxidation and ring-opening reactions of vegetable oils. These diester derivatives of triglyceride (TG) were reported to have excellent oxidative stability and well-low-temperature performance properties and utility as HFs, metal-working fluids, drilling fluids, and greases. However, to increase the cold flow property, pour point depressant (PPD) additives and diluents need to be used.

Since hydraulic oils form a big part of industrial oils (15% in Europe and 22% in the USA (222 million gallons)) [7], it is necessary to provide a guide to the industries on the types of biobased hydraulic oils that have high quality and performance for various industrial applications [32]. This study aims to review the effects of different types of base oil (mineral, synthetic ester, or triglyceride) in the production of hydraulic oil on the final properties of HF products and the environmental aspects of HF products.

In addition, this review introduces the most important performance indexes that a hydraulic fluid must have in order to have the desirable performance in various industrial applications, reviews the most common types of esters used in making hydraulic fluids, and provides an in-depth discussion of two chemical modification methods widely employed in the production of HPHFs from vegetable oils. Finally, the current challenges, knowledge gaps, and future perspectives on the sustainable development of HPHFs are analyzed.

2.2 Methodology

A thorough review of the literature was conducted utilizing prominent international interdisciplinary research platforms such as Science Direct, Scopus, and Web of Science. The search employed combinations of keywords including "biobased hydraulic fluids," "chemical modification," "esters and complex esters," "epoxidation reaction," and "estolides." Given the considerable variation in hydraulic oil characteristics across industrial applications, this review specifically concentrates on investigations related to high-performance hydraulic fluids. It delves into their formulation with diverse base oils, esters, and additives. The subsequent sections of this article are organized as follows: Section 2.3 explores the classification of hydraulic fluids (HFs) and various base oils, while Section 2.4 provides an overview of the key parameters associated with high-performance hydraulic fluids. Section 2.5 delves into the application of esters in hydraulic systems, and Section 2.6 discusses the chemical modifications applied to esters derived from vegetable oils. The challenges and future prospects of bio-based hydraulic fluids in this research domain are addressed in Section 2.7, with the study's primary conclusions presented in Section 2.8.

2.3 Classification of hydraulic fluids (HFs) and base oils

Knowing the conditions of the oil consumption is an important key for choosing the suitable kind of hydraulic fluid in order to achieve the desired performance. The classification of various HFs according to ISO 6743-4 (Lubricants, industrial oils, and related products (class L) Classification

- Part 4: Family H (Hydraulic systems)) is shown in **Table** 2.1 [12].

Table 2.1: Classification of HFs based on ISO 6743-4.

Mineral oil-based HF		**Fire resistant HF**		**Environmentally acceptable HF**		**Food grade lubricant**	
DIN 51524	ISO 11158	DN 51502		ISO 15380		NSF and FDA	
		Water containing	Water free	Non-water soluble	Water soluble	NSF H1	NSH H2
HL HLP HLPD HVLP HVLPD	HH HL HM HR HV HS HG	HFAE HFAS HFB HFC	HFDR HFDS HFDT HFDU	HETG HEES HEPR	HEPG	White oil PAO	White oil Mineral oil PAO

Note: DIN 51524: Mineral-based hydraulic oil of the HLP type classification; ISO 11158: The minimum requirements for new mineral oil hydraulic fluids; DIN 51502: Designation of lubricants and marking of lubricant containers, equipment, and lubricating points; ISO 15380: Requirements for environmentally acceptable hydraulic fluids; NSF: National Sanitation Foundation; FDA: The Food and Drug Administration; H1: Lubricants used in applications where they might touch food; H2: Lubricants used in locations where there is no possibility that the lubricant or lubricated surface contacts food; HH: Mineral lubricants without corrosion inhibitors; HL*: HH lubricants with oxidation-reduction and anticorrosive additives; HM: HL lubricants with wear reducing additives; HR: HL lubricants with a high viscosity index; HV: HM lubricants with a high viscosity index; HG: HM lubricants with shock-resistant features; HS: Synthetic liquids; HL: Mineral oil with active ingredients to increase the corrosion protection and resistance to aging; HLP: Mineral oil with further active ingredients in addition to HL oil to reduce wear and increase resistance in the mixed friction area; HLPD: Like HLP and with additives to improve particle transport, dispersion capacity, and active ingredients to increase the corrosion protection; HVLP: Like HLP and with increased resistance to aging and improved viscosity index; HVLPD: Like HLPD with improved viscosity index; HFAE: Emulsions (>80% water), HFAS: Synthetic aqueous fluids; HFB: Emulsions (>40% water); HFC: Glycol solutions; HFDR: Synthetic phosphate esters (without water); HFDS: Chlorinated hydrocarbons (without water); HFDT: HFDR/HFDS mixtures; HFDU: Synthetic anhydrous liquids (without water).

The quality and performance of HFs depend on the quality of the base oil, and the combination of the additives/additive package [24]. **Table** 2.2 presents the classification of base oils commonly used in the lubricating industry. These base oils are widely used in the formulation of different lubricants based on the desired viscosity (at 40°C and 100°C) and viscosity index (VI). Groups I, II, III, IV, and V are those classified according to the American Petroleum Institute (API), and Groups II+, III+, and VI are those obtained by some chemical processes on API category base oils to promote fuel efficiency and help reduce CO_2 emissions.

Table 2.2: Classification of base oils according to the American Petroleum Institute (API) and Petroliam Nasional Berhad (PETRONAS).

Group	Classification	Manufacturing process	Viscosity Index (VI)	Most used in industry
Group I	API	Solvent refining (paraffinic)	80-120	SN 90, SN 150 SN 500, SN600 SN 650, BS150
Group II	API	Hydro-processing (Naphthenic)	80-120	SN180, SN 350 CN 70, CN 110 CN 225
Group II+	PETRONAS	Hydrotreating	Minimum 110-115	SOC4
Group III	API	Severe Hydrocracking (Catalytic de-waxing)	≥ 120	ETRO 4 ETRO 6 ETRO 8
Group III+	PETRONAS	Gas to Liquids (GTL) process	Minimum 130-140	ETRO 4+ ETRO 8+
Group IV	API	Chemical reactions (synthesizing)	-	PAO 10 PAO 40
Group V	API	Esters, complex esters	-	PAG
Group VI	-	Synthesis process of PAOs	-	PIO

Note: SN: Solvent Neutral, BS: Bright stock, CN: percentage of naphthenic, SOC4: a paraffinic base oil with very high viscosity index, ETRO: a very high-quality Group III base oil, PAO: Poly-alpha olefins, PIO: Poly-internal-olefins.

Group I base oils fall under the classification of having less than 90% saturates, sulfur content exceeding 0.03%, and exhibiting a viscosity-index range between 80 to 120. Their operational temperature range spans from 0 to 65°C. Employing a solvent-refining technique, Group I base oils undergo a simplified refining process, contributing to their affordability, thus positioning them as the most economical option within the base oil market. Group II base oils, featuring over 90% saturates, sulfur content below 0.03%, and a viscosity index of 80 to 120, are produced via hydrocracking, offering superior antioxidation properties and clearer color compared to Group I base oils. Despite their higher cost, they are increasingly prevalent in the market and competitively priced relative to Group I base oils. Group III base oils, with over 90% saturates, less than 0.03% sulfur, and a viscosity index surpassing 120, undergo thorough refining, including severe hydrocracking, to achieve purity. Despite being derived from crude oil, they are often termed synthesized hydrocarbons. These oils, akin to Group II base oils, are gaining prominence in the market due to their enhanced properties, despite the intensive refining process involved. Group IV base oils, known as polyalphaolefins (PAOs), are synthetically produced through a synthesis process. These oils have a broader temperature range, making them ideal for use in both extremely cold conditions and high-temperature applications. Group V base oils encompass various types like silicone, phosphate ester, PAG, polyol esters, and biolubes. They are often blended with other base stocks to enhance properties. Esters, for instance, enhance the properties of the base oil, particularly when exposed to high temperatures. They also provide better cleaning abilities compared to PAO synthetic base oils, thus extending the operational lifespan [33-35].

Group II+ base oils are refined from conventional crude oil through advanced hydroprocessing techniques, resulting in oils with even higher purity and improved properties compared to standard Group II base oils. They typically have lower levels of impurities, such as sulfur, and exhibit enhanced viscosity index, oxidative stability, and thermal stability. Similarly, Group III+ base oils are produced through more extensive hydrocracking and purification processes compared to standard Group III base oils. This advanced refining results in base oils with exceptionally high purity, superior oxidative stability, and enhanced viscosity index. Group III+ base oils are often regarded as "synthetic" base oils due to their purity and performance characteristics, although they are still derived from crude oil feedstocks. Both Group II+ and Group III+ base oils are prized for their superior performance in lubricant applications, offering improved fuel efficiency, longer equipment life, and better protection against wear and corrosion compared to lower-grade base oils. Group VI base oils are a category of synthetic base oils, specifically referred to as PAOs. These synthetic oils are not derived from crude oil but are instead synthesized through chemical processes. Polyalphaolefins are linear hydrocarbons with a high degree of purity and uniformity in molecular structure. Due to their exceptional properties, Group VI base oils are commonly used in high-performance lubricants for automotive, industrial, and aerospace applications, where reliability, durability, and efficiency are critical [35].

These base oils are highly suitable for hydraulic fluids due to their exceptional performance characteristics. In hydraulic systems, where smooth and efficient operation is crucial, Group VI base oils offer advantages such as high thermal stability, excellent viscosity-temperature behavior, and low volatility. These properties ensure consistent fluidity and lubrication performance across a wide range of operating temperatures, while also minimizing the risk of fluid breakdown or vaporization, which can lead to equipment failure or reduced efficiency. Additionally, their compatibility with seals and elastomers reduces the risk of leaks and ensures the integrity of hydraulic systems over extended periods of use. For biobased hydraulic fluids, Group VI base oils can serve as an ideal foundation when combined with biodegradable additives or ester-based formulations. This combination allows for the creation of environmentally friendly hydraulic fluids that offer comparable performance to conventional petroleum-based alternatives while also meeting stringent environmental regulations and sustainability goals.

In addition, vegetable oils present an ideal foundation for the formulation of biobased hydraulic fluids, offering a renewable and sustainable alternative to traditional petroleum-based oils. Derived from plant sources such as soybeans, sunflowers, or rapeseeds possess inherent biodegradability and low toxicity, making them environmentally friendly options for hydraulic fluid applications. Additionally, vegetable oils exhibit excellent lubricating properties and high natural viscosity indexes, which can be further enhanced through processing and additives to meet the performance requirements of hydraulic systems. With advancements in refining and modification techniques, vegetable oils can overcome challenges such as oxidative stability and temperature sensitivity, ensuring reliable performance even in demanding operating conditions. **Table** 2.3 indicates various types of vegetable oils/esters/complex esters and their physicochemical characteristics as base stock for biobased HFs.

Table 2. 3: Various vegetable oils and their characteristics as base oils for biobased HFs.

Properties	Base oils for biobased HFs			Ref.
	Mineral oil	HOSO	HOSO with additives	
V@40 (cSt)	48.7	39.3	42.1	[36]
V@100 (cSt)	8.3	8.5	8.8	
VI	145	202	196	
Pour point (°C)	-34	-3	-27	
OIT (min)	>120	8	71	
Biodegradability (%)	Non biodegradable	85±5	89±7	
AN (mg KOH/g)	0.54	0.06	0.78	
Seizure load	126	160	160	
WSD (mm)	0.52	0.82	0.52	

	TMP trioleate (HOSO)	PAO-8	soybean	
V@40 (cSt)	47	47	31	[37]
V@100 (cSt)	9.5	7.9	-	
VI	190	142	-	
Pour point (°C)	-45	-50	-9	
Biodegradability (%)	90±5	30	>70	

	Canola (85% oleic acid)		Canola (75% oleic acid)	
RBOT (min)	335		180	[38]
Viscosity change (%)	0.4		0.5	
DRY TOST (h)	2712		2700	
TAN increase (%)	0.4		0.5	

	HOSO*	HOSO	Conventional soybean oil	
V@40 (cSt)	250	49	252	[39]
RBOT (min)	49.6	39.9	48.8	
Initial total acid number (mg KOH/g)	0.4	0.5	NA	
Final total acid number (mg KOH/g)	0.8	1.1	NA	

	Rape seed (46)	PEG (46)	Synthetic ester (68)	
V@40 (cSt)	44	46	72	[40]
V@100 (cSt)	10	9.8	13	
VI	210	215	187	
Pour point (°C)	-33	-36	-42	
Biodegradability (%)	97	70	85	

	Passion fruit oil	Epoxidized passion fruit oil	Epoxidized Moringa oil	
V@40 (cSt)	31.78	185.65	80.37	[41]
Acid value (mg KOH/g)	1.12	0.83	0.2	
WSD (mm)	0.076	0.131	0.145	
Oxidative stability (min)	7.5	16.89	24.57	

	Crude pomace oil	
V@40 (cSt)	39.93	[42]
V@100 (cSt)	8.54	
VI	199	
Pour point (°C)	-9	
TAN (mg KOH/g)	0.32	
Density at 20°C (g/cm^3)	0.918	

	Acylated derivatives of Castor oil	Methyl 12-Acyloxy Octadecenoate-Rich Fatty Acid Methyl Esters	2-Ethyl-hexyl 12-Acyloxy Octadecenoate-Rich Fatty Acid Esters	
V@40 (cSt)	112.6	8.22	8.64	[43]
V@100 (cSt)	14.84	2.47	3.54	
VI	136	122.75	144.82	
Pour point (°C)	-24	-21	-36	
RPVOT (min)	15	5	5	
NOAK evaporation loss (%)	3.25	37.36	22.87	
Weld load (kg)	150	130	140	

Note: VI: Viscosity Index; HOSO: High Oleic Sunflower Oil; HOSO*: High Oleic Soybean Oil; OIT: Oxidation Induction Time; AN: Acid Number; WSD: Wear Scar Diameter; PAO: Polyalphaolefin; PEG: Polyethylene glycol; RBOT: Rotating Bomb Oxidation Test; TAN: Total Acid Number; TOST: Turbine Oil Oxidation Stability Test; RPVOT: Rotating Pressure Vessel Oxidation Test.

2.4 Performance Indexes of high-performance hydraulic fluids (HPHFs)

The most important performance indexes of HPHFs are the viscosity index, low-temperature properties, oxidation stability, volatility, biodegradability, and anti-wear scar properties. On the other hand, bio-based oils are suitable for preparing HPHFs owing to mainly their higher viscosity index and better biodegradability. Examples of such bio-based oils include chemically modified vegetable oil-derived esters where the glycerol has been replaced by complex polyols, such as trimethylolpropane (TMP), neopentyl glycol (NPG), or pentaerythritol (PET) to have higher thermal-oxidative stability [44]. In terms of biodegradability, however, the performance of fully bio-based esters is generally better than that of PAO and mineral-based fluids (Groups I, II, and III) [45,46]. Furthermore, it is worth noting that the performance of biobased HPHFs in low-temperature conditions and their anti-wear characteristics can be significantly improved by carefully integrating appropriate additives [47].

2.4.1 Viscosity

Viscosity is a key performance index of HFs and has a significant impact on the performance of hydraulic system components. An inappropriate selection of base oil viscosity can cause serious damage to the hydraulic system due to the reduction in efficiency and corrosive problems. A high viscosity index (HVI) and thermal attributes of the system would maximize the performance of hydraulic systems [1]. For instance, lubricants with HVI increase the pumping capacity and efficiency at low temperatures as well as improve sealing and abrasion protection at high temperatures [48]. Therefore, it is important to pay attention to the viscosity and viscosity index (VI) of the base oil for making hydraulic oils of different grades (ISO 32, 46, and 68), and also consider their working temperature ranges.

BHFs inherently have a high viscosity index due to their chemical structure. As illustrated in **Figure** 2.1, the viscosity decreases with the reduction in the chain length of the alkane, carboxylic acid, or alcohol, resulting in a lower molecular weight, whereas a higher percentage of polyunsaturated fatty acid esters in the structure of lubricant results in higher viscosity [1,49]. The viscosity index determines the range of viscosity changes with temperature. A comparison between three readily biodegradable fluids and mineral oil (**Table** 2.4) shows a considerable difference between their viscosity and VI [50]. As shown in **Table** 2.4, the VI for unsaturated HEES fluid is higher than saturated HEES fluid, suggesting that the presence of double bonds in the structure of vegetable oils leads to increased VI [33]. In addition, the high VI (210-250) for rapeseed oil has made it one of the most desired oils in the industry as a base stock for HETG.

Asadauskas et al. [18] investigated the effects of various factors such as molecular architecture, double bonds, ester linkage, and VI improvers as additives on the VI of HF base stocks. At low temperatures, large polymer particles are tightly entangled, but as the temperature increases, the molecules gradually open up and take on more hydrodynamic volume, resulting in reduced VI [51]. Obviously, when using polymeric viscosity index improvers (VIIs) to increase the VI of hydraulic oils under high shear stress, it is crucial to consider the shear stability of the oil as an important parameter and the need to maintain a minimum value of viscosity for lubrication [52].

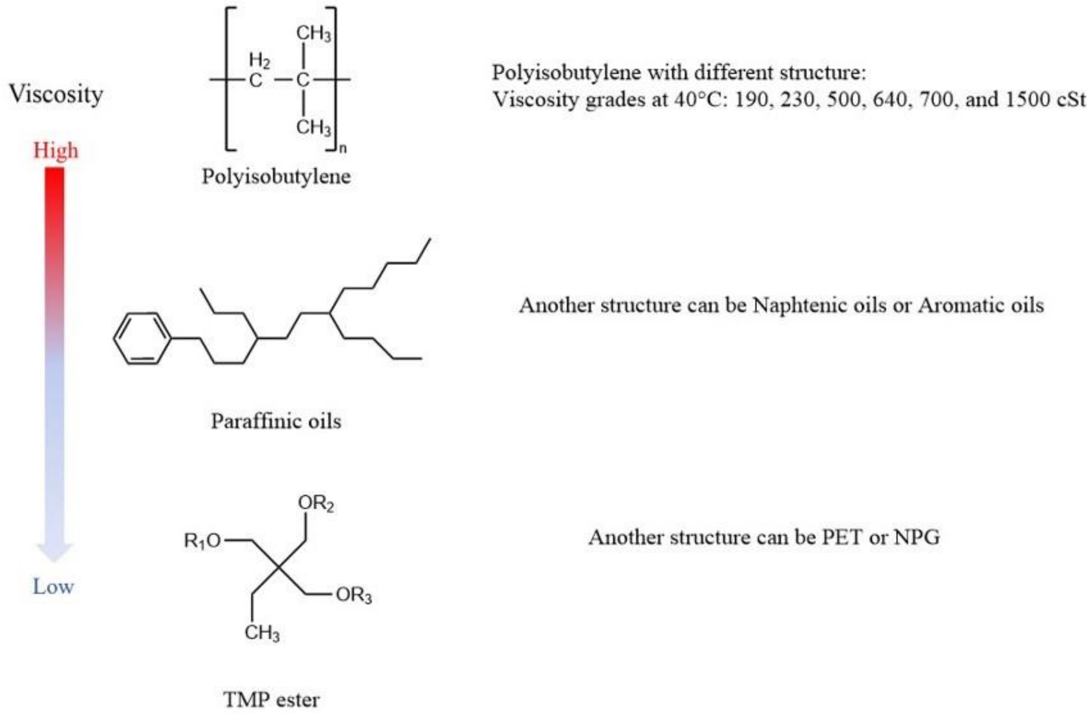

Figure 2.1: Variation of viscosity of different backbones of polyisobutylene (as VI) and paraffinic oils and TMP ester (as base oil). (R1, R2, and R1 are carboxylic acids) [49].

Table 2.4: Comparison of viscosity and VI of three readily biodegradable fluids with mineral oil [33,50].

Property	ASTM	Mineral oil SN 150	HETG (Rapeseed Type Oil)	Unsaturated BIO HEES	Unsaturated BIO HEES	Saturated HEES
ISO grade		32	32	32	46	32
Pour point (°C)	D97	-6	-33	-58	-54	-58
Viscosity @ 40°C (mm2/s)	D445	28.7	34	33.6	45.86	31.8
Viscosity @ 100°C (mm2/s)	D445	5.2	8	8	10.96	5.8
Viscosity index	D2270	105-115	210-250	220-230	230-250	140-150

The relationship between viscosity and pressure for HFs has not been clearly investigated. This characteristic is mainly related to the elastohydrodynamic lubricating layers. In general, the viscosity-pressure behavior depends on the chemical structure of the material as well as the geometry of its molecules [53]. The parameter to investigate the viscosity-pressure behavior of HFs is the viscosity-pressure coefficient (α). The higher the value of α, the more effective the lubrication of oil under high pressure [32]. An exponential dependence of the viscosity on the pressure was reported for lubricants, indicating that the viscosity increases rapidly with increasing pressure [54]. Paredes et al. [55] investigated the viscosity-pressure behavior of two hydraulic mineral oils and two vegetable oils. Experiments were carried out at three different temperatures (313.15, 343.15, and 363.15 K) and pressures up to 250 MPa using a high-pressure falling-body viscometer. The obtained results from the film thickness measurement demonstrated that vegetable-based oils due to their higher lubricity provide a thinner protective layer (not too thin) than their mineral counterparts. The thicker the oil film, the less contact of the metal to metal, resulting in less wear and friction. Hence, higher pressure–viscosity coefficient (α) values lead to less wear and friction and better separation of moving surfaces in the friction zone [18].

In contrast, as shown in **Figure** 2.2, esters derived from vegetable oils, with comparable viscosity, remained unaffected by increasing pressure, unlike mineral-based stocks [55]. In the case of mineral and ester oils, the effects of pressure on their viscosity correlate well with the effects on their corresponding VI. In addition, it is essential to carefully adjust the molecular structure of selected esters for the fluidity requirement in HF applications [18,55]. For example, in hydraulic systems operating at low pressure, changes in viscosity with pressure are often neglected. However, at high pressures, the viscosity changes are quite palpable, which is of great importance considering the desired filtration and lubrication. In addition, hydraulic systems are designed with safety factors to keep working pressures below critical failure points. Monitoring pressure is vital to prevent exceeding working pressure limits, ensuring system integrity, minimizing downtime, and preventing safety hazards. Hence, to achieve the desired viscosity-pressure properties, the composition of materials used in the HF formulation should be properly designed.

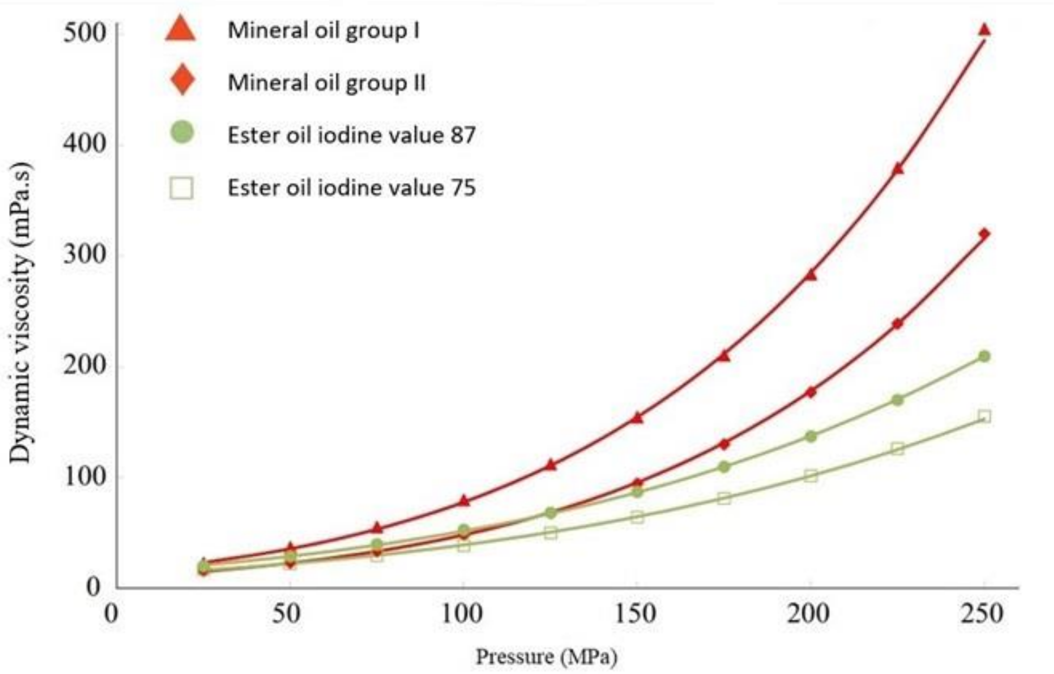

Figure 2.2: Effects of high pressures on dynamic viscosity of formulated lubricants, from group I (probably paraffinic (contain alkanes)), group II (probably naphthenic (contain cyclic aliphatic hydrocarbons)) mineral base stocks, and two ester base stocks with approximate iodine values of ~ 87 and ~ 75 mg I_2/g, respectively [55]. Copyright 2014 Elsevier B.V., Reprint permission obtained.

2.4.2 Low-temperature properties

The low-temperature behavior of fluids is usually characterized by pour point (PP). The PP is the lowest temperature at which HFs can flow under gravity. When the temperature is less than the PP of a fluid product, it cannot be stored or transferred through a pipeline. Consequently, it is very important to pay attention to the fluidity of HFs at low temperatures, especially in cold weather conditions. Normally increasing the saturation and molecular weight of vegetable oils results in increased pour points, and *cis* unsaturation and hydroxyl groups cause decreased pour point values [56]. The poor low-temperature behavior of vegetable oil-based esters limits their prospect as biodegradable lubricants. The bio-based esters start freezing at a temperature around −10°C, in contrast to mineral oils that have a pour point around −21°C. This poor low-temperature behavior of bio-based esters can be critical in several applications. For instance, hydraulic systems used in marine vessels, offshore rigs, and underwater equipment may encounter cold seawater temperatures, especially in polar regions or during deep-sea operations. Hydraulic fluids with low pour points are necessary to prevent fluid thickening and maintain hydraulic system functionality in these environments [57]. Thus, the low-temperature properties of HFs are of the utmost importance in determining the potential applications of the HFs.

The degree of unsaturation, number of carbon atoms, and branching of vegetable-based esters are structural characteristics affecting their pour points. The degree of unsaturation and branching of fatty acids have a positive effect on lowering PP. It should be pointed out, however, the effect of unsaturated fatty acids containing one or more double bonds with a terminal carboxylic group (–COOH) on reducing the PP is greater than branched fatty acids with similar carbon chain lengths [58]. In addition, vegetable oil-based esters containing aromatic groups have a positive influence on maintaining a low PP [59]. Hence, chemically modified vegetable oils can lead to a significant reduction in PP.

In addition, the use of a small amount of PPD additives with diluents can also lower the pour point and increase the low-temperature properties of lubricants [60,61]. **Figure** 2.3 indicates the general interaction of PPD additive with molecules of vegetable-based oil. As can be seen, PPD penetrates into the structure of the oil, which prevents the formation of crystals and their precipitation at low temperatures. The PP values are highly dependent on the fatty acid structure of the vegetable oils [60]. For instance, base fluids with a high content of oleic acid show excellent low-temperature properties, with pour points of –35°C for high oleic sunflower oil (HOSO) and –50°C for high oleic trimethylolpropane triesters (HO-TMPTE) [38].

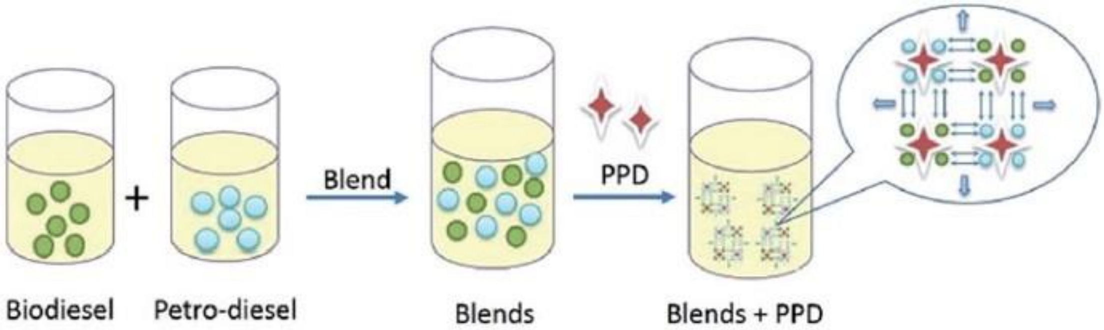

Figure 2.3: Crystallization behavior of vegetable oil molecules with PPD [62]. Copyright 2015

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The commonly used PPD additives are not biodegradable, thus biodegradable PPD additives must be developed to not compromise the overall biodegradability of industrial HFs. Two biodegradable multifunctional PPD additives were derived from sunflower oil (SFO) by Ghosh et al. [63], and the characteristics of these additives are illustrated in **Table** 2.5. It can be seen that the PP of base oil decreases as the loading of the additive increases.

Table 2.5: Biodegradable polymers as lubricant PPD additives [64]. Copyright 2014 by the Author(s), Reprint permission obtained.

Samples	Base oils	% (w/w) loading of the additive and its properties											
		2%			3%			4%			5%		
		THK	PP (°C)	VI	THK	PP (°C)	VI	THK	PP (°C)	VI	THK	PP (°C)	VI
P-1	BO1	2.761	-6	113	3.822	-9	126	5.177	-12	131	6.208	-15	131
	BO2	1.01	-9	101	1.567	-12	127	2.19	-15	163	3.135	-15	205
P-2	BO1	2.841	-6	121	3.935	-9	131	5.432	-15	128	6.807	-18	131
	BO2	1.093	-9	103	1.619	-12	130	2.259	-15	164	3.198	-18	207

Note: THK: Thickening values; P-1: Thermally prepared SFO polymer; P-2: Homopolymer of SFO prepared by microwave irradiation (MI) method; PP: pour point; VI: viscosity index, BO: Base oil.

2.4.3 Thermal-oxidation stability

The β-CH group in the glycerol backbone of triglycerides causes hydrolytic, thermal, and oxidative instability. The β-hydrogen atom can be easily eliminated from the molecular structure in the presence of oxygen and moisture, which would lead to the cleavage of the esters into acid and olefin. In addition, the rate of hydrolytic reaction increases at higher temperatures as a result of the decomposition of ester linkage into free fatty acids (FFAs) and alcohol, which also lowers the thermal-oxidative stability of the esters [65]. Furthermore, the oxidative stability of vegetable oils (triglycerides, esters composed of various natural fatty acids, and glycerol) increases with decreasing amounts of polyunsaturated acids. A good example of an ester that is highly stable to oxidation is a fully saturated diester [66], while the presence of one double bond in the structure such as oleic acid (C18:1) is indispensably necessary for good low-temperature behavior. Thus, high oxidative stability requires a low percentage of polyunsaturated fatty acids (linoleic and linolenic acids) in the structure of vegetable oils. For instance, high oleic sunflower oil (HOSO) with more than 77% oleic acid is highly oxidatively stable (32 h) compared to palm oil (12 h) with only 47% oleic acid [67]. In another study, Erhan and Sharma [68] reported that the rotary bomb oxidation test (RBOT) and oxidation induction time for HOSO (RBOT: 768 min, OIT: 98.1 min) are higher than those of a commercial biodegradable hydraulic fluid (RBOT: 278 min, OIT: 42.6 min). Schneider [37], from the point of chemistry, studied the process of oxygen attack on unsaturated fatty acids and reported that HOSO and polyol esters derived therefrom (e.g., HOSO-TMP ester) have higher oxidation stability than bio-esters with polyunsaturated fatty acids.

Vegetable oils (e.g., rapeseed and soybean) that are not high in oleic acid might be modified through various chemical processes, such as selective hydrogenation or epoxidation of polyunsaturated fatty acids. Silva et al. [41] synthesized a new biobased hydraulic fluid by epoxidation of passion fruit and moringa oils via performic acid, where the oxidative stability of the epoxidized moringa oil was found to increase from 24 min to 311 min, although some oxidation stability promoting additives were used. Similarly, Erhan et al. [31] enhanced the oxidation stability of three high-oleic vegetable oils (safflower, sunflower, and soybean oils) through a combination of chemical additives, PAOs, and high-oleic vegetable oils, demonstrating that the lubricant formulated with high-oleic sunflower, 20% PAO-8, antioxidants, and PPD had oxidation stability of 768 min and OIT of 98.1 min. The comparative performance of paraffinic mineral oil, vegetable oils, and different types of synthetic hydraulic fluids and their most important characteristics are shown in **Table** 2.6 [32].

Table 2.6: The relative stability for several synthetic hydraulic fluids.

Product	**Thermal stability**	**Oxidation stability**	**Hydrolytic stability**	**Volatility**	**Low-temperature properties**	**Toxicity**	**Biodegradability**
Mineral oil (parafinic)	G	F	E	LF	L	F	L
Vegetable oils	F	G	F	L	F	L	E
Polyalphaolefins	VG	VG	E	VG	G	L	G
Polyalkylene glycols	G	G	G	G	G	L	G
Diesters	G	VG	G	G	G	L	VG
Polyol esters	G	VG	G	G	G	L	VG
Trialkyl phosphates	G	G	F	LF	VG	L	VG
Triaryl phosphates	E	E	G	E	VG	L	VG
Silicones	VG	G	E	E	E	L	L
Silicate esters	VG	G	LF	G	E	L	VG

E: Excellent, VG: Very Good, G: Good, F: Fair, L: Low; LF: Low Fair

In summary, the "β-CH group" in the glycerol backbone of triglycerides, as well as the double bond in the structure of the fatty acid chains are the main causes of the thermo-oxidative instability of vegetable oils [69,70]. Poor thermo-oxidative stability can lead to insoluble deposits, varnish formations, additive depletion, filter plugging, and increased acidity and viscosity, which would in turn result in corrosion of the lubricated parts [71].

2.4.4 Volatility and decomposition

Currently, flash point (FP) measurement, thermogravimetric analysis (TGA), and NOACK volatility analysis are the standard tests to characterize the volatility of HFs. The paramount parameter related to the values of volatility is the content of lower molar mass components. **Figure** 2.4 indicates the short-term volatility of several fluids (e.g., hydrocarbons, monoesters, diesters, and polyol esters) by using the NOACK method. As expected, larger molecules tend to have stronger intermolecular forces, which can reduce their tendency to evaporate at high temperatures. Therefore, fluids with higher molecular weights typically exhibit lower NOACK volatility because they are less prone to evaporate under the test conditions. In addition, no discernible impact from saturation (hydrocarbons) or unsaturation (monoester, diester, or polyol ester) is evident. This could be because, during the NOACK volatility test, the primary mechanism driving evaporation is the energy supplied by the high temperature, which primarily affects the intermolecular forces and molecular weight of the fluid rather than the specific types of bonds present in the molecules.

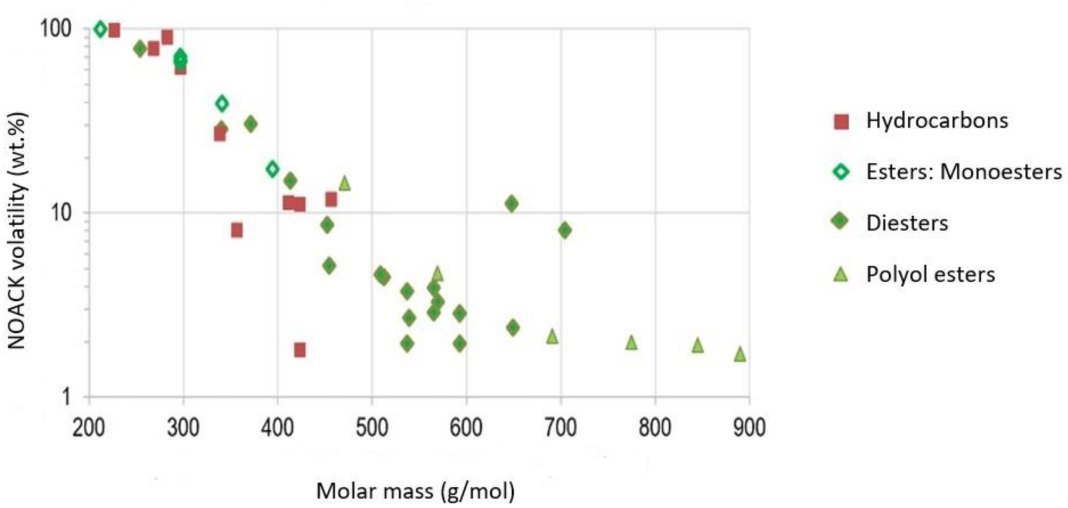


Figure 2.4: Dependece of NOACK volatilities of hydrocarbons and ester-based oils on molar mass [72]. Copyright 2019 by the Author(s), Reprint permission obtained.

Bražinskienė et al. [72] investigated the dependence between the NOACK volatility and the molar mass of several hydrocarbons and esters. They demonstrated that esters with higher polarity showed slower vaporization or less oxidative decomposition than hydrocarbons with similar molar mass (**Figure** 2.5A). Hydroxyl or carboxyl functional groups compared to double C=C bonds, regardless of their negligible effect on oxidative decomposition, have a formidable effect on volatility as oleic acid and oleyl alcohol can readily form hydrogen bonds, which causes lower volatility than that of FAME (**Figure** 2.5B) [72]. Therefore, carboxylic acids are much less volatile than esters, hydrocarbons, or aldehydes of similar molecular weight due to hydrogen bonding [32].

As a novel type of HFs, vegetable oil-based ionic liquids (ILs) have gained attention in the last decade due to their low volatility, non-flammability, high thermal-oxidative stability, low melting point, broad liquid range, and controlled miscibility with organic solvents. The most significant advantage of ILs is their low isothermal compressibility, usually lower than mineral and synthetic hydraulic oils [73]. Compressibility plays an important role in HFs, in particular in hydraulic systems that perform at high-pressure conditions, and low-compressibility fluids are required for efficient power transmission. Jamari and Schipper [74] investigated the isothermal compressibility of several ILs as HFs, compared with synthetic oils, mineral oils, vegetable oils, and water. They observed that ILs with low compressibility were more appropriate as HFs than the other currently applied HFs.

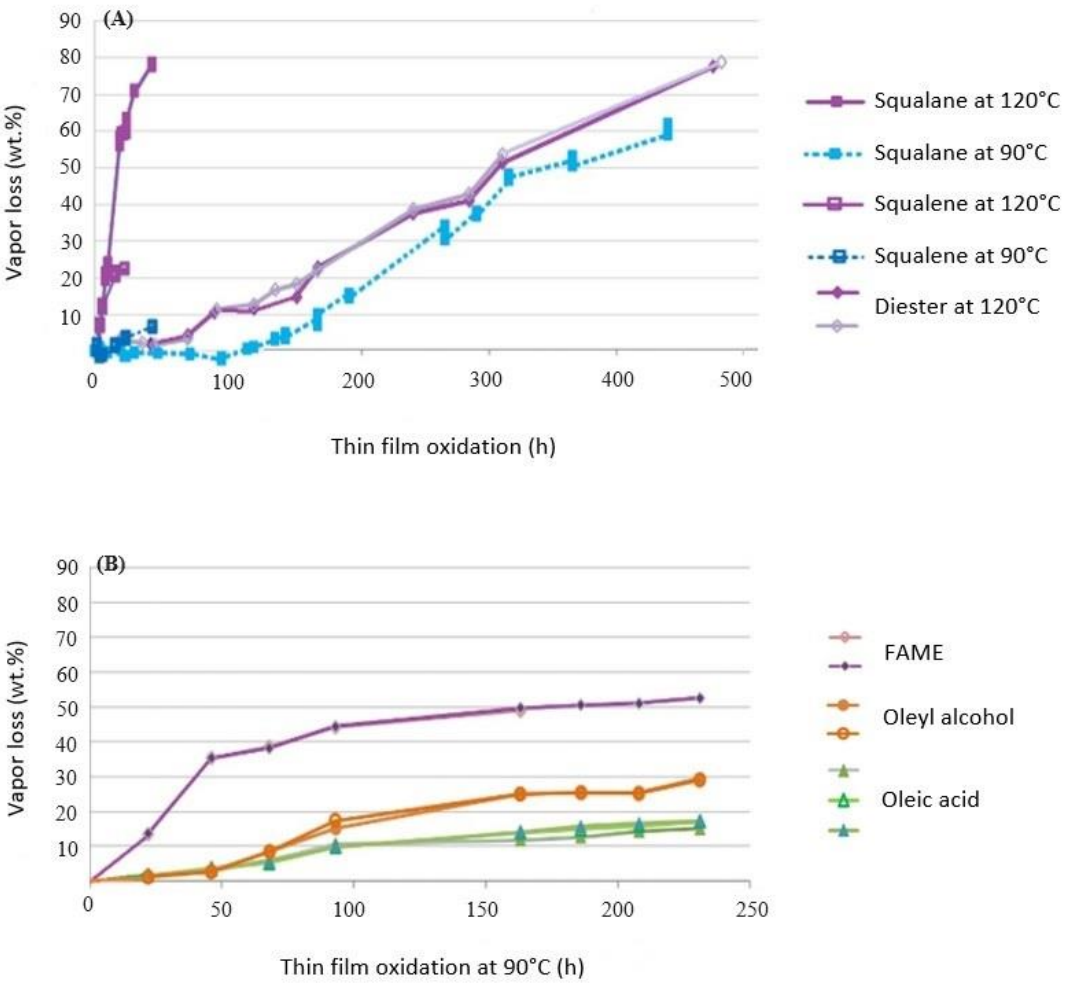


Figure 2.5: Long-term vaporization of hydrocarbons and saturated diester (duplicate) of similar molar mass at 90°C and 120°C (A), and long-term vaporization of FAME, oleic acid, and oleyl alcohol (multiple runs) of similar molar mass at 90°C (B) [72]. Copyright 2019 by the Author(s), Reprint permission obtained.

It should be noted that by oxidative decomposition alone, fully saturated esters and hydrocarbons can lead to nearly 100% volatile emissions through long-term decomposition. In addition, microbial degradation would also contribute to long-term decomposition. In the realm of BHFs, microorganisms (including bacteria and fungi) can metabolize the organic components of these fluids, contributing to their decomposition over time. This microbial degradation process not only affects the fluid's physical and chemical properties but also influences its biodegradability and environmental impact. Understanding and managing microbial degradation in BHFs is essential for ensuring their effectiveness and environmental compatibility in various applications, thus supporting the broader goal of sustainable fluid technologies.

2.4.5 Biodegradability

Biodegradability is a property measuring the hazard level of material decomposition by the action of microorganisms when deployed to the environment. Bio-based fluids are well-known for their higher biodegradability. The biodegradation of a vegetable oil depends on the chemical composition of its fatty acid. Rhee and Bailey [5] evaluated the biodegradability of five biobased HFs among which “Terresolve EL 146” depicted higher biodegradability (~ 85%). Singh et al. [75] reported the biodegradability of various mineral-oil base stocks, formulated vegetable oils, and polyol ester-based fluids using the CEC-L-33-A-94 test procedure. It should be considered that the span of biodegradability improves with developing saturation levels and modifying aromatic, aliphatic, and heterocyclic derivatives [32]. Moreover, microorganisms typically find it easier to degrade unsaturated or aromatic chains compared to saturated chains. Unsaturated chains, containing double or triple bonds, offer accessible sites for microbial attack, while aromatic chains, characterized by benzene rings, similarly present vulnerable points for degradation due to the presence of reactive sites [76]. However, polymeric esters may exhibit higher resistance to microbial degradation due to their more complex and less accessible structure, making them less susceptible to microbial attack compared to simpler unsaturated or aromatic chains [77].

Table 2.7: Comparison of biodegradability and other physicochemical characteristics between HEES, HEPG, vegetable oils, and mineral base fluids [78]. Copyright 2019 The Author(s), Reprint permission obtained. Copyright 2012 by Taylor & Francis Group, LLC, Reprint permission obtained.

	Mineral oils	**Vegetable oils**	**HEES**	**HEPG**
Biodegradability ASTM D5864. %	10-40	40-80	30-80	40-80
Viscosity (cSt)	15-150	32-68	20-300	10-100
Viscosity Index	90-100	100-250	120-220	100-200
Pour point (°C)	-54 to -15	-20 to 10	-60 to -20	-40 to 20
Compatibility with Mineral oils	-	Good	Good	Not miscible
Oxidation stability	Good	Poor to Good	poor to good	poor

Service life	2 years	6 months to 1 year	3 years	2 years
Relative cost	1	2 to 3	4 to 5	2 to 4

The biodegradability of HFs is commonly measured by the standard method of the Organization of Economic Cooperation and Development (OECD) 301 B (ASTM D 5864). However, the test duration (28 days) itself is a challenge. Rhee et al. [79], developed a bio-kinetic model to predict the biodegradability of HFs. The bio-kinetic model significantly decreased the test time from 28 days to one day and was capable of efficiently predicting the biodegradability of fluids without the use of microorganisms [80].

There are three original classes of biodegradable base fluids: vegetable oils, polyalkylene glycols (PAG), and organic esters. PAG (e.g., polyethylene glycols (PEG)) not only have good lubrication, high VI, and excellent oxidation/hydrolytic stability but also are water-soluble and can be rapidly biodegradable by microorganisms [81]. However, they have very limited solubility in mineral oils [82] or vegetable oils [71], which is a major disadvantage for the application of this biodegradable fluid as a hydraulic fluid, unless they are chemically modified by sophisticated conversion methods. Furthermore, some organic esters (such as adipates), with high VI, excellent thermal and oxidation stability, acceptable low-temperature fluidity, and other desirable properties, are exceptionally qualified biodegradable base fluids [83].

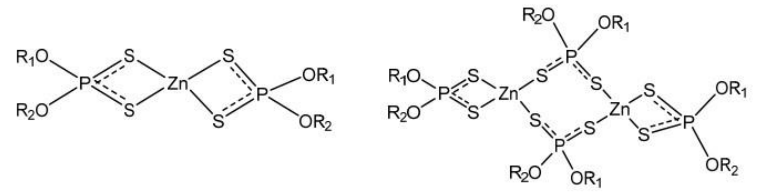
Currently, base stocks with high oleic acid content (70-80%) seem to be the best compromise between performance, price, and biodegradability [84]. Consequently, a popular formulation of BHFs is done with sunflower, canola, soybean, rapeseed, and corn oils, or synthetic esters, which have less toxicity and better biodegradability than conventional HFs. TMP esters of oleic acid, for instance, are among the most universally applied base stocks for HFs [37]. They are not only bio-based, but exhibit excellent biodegradability, moderate oxidative stability, and reasonable price levels. In terms of biodegradability, many studies have been conducted on bio-based fluids in comparison with petroleum-based fluids. For example, Rios et al. [85] evaluated the biodegradability of two biolubricants (BL1 and BL2) synthesized from castor oils using a bio-kinetic model, comparing their performances with fresh vegetable oil and mineral oil, and the two biolubricants have shorter half-lives: around 26 days for BL1 and 20 days for BL2. Lathi and Mattiasson [86] prepared bio-based lubricants from epoxidized vegetable oil whose BOD5-to-

COD ratio was in the range of 0.43–0.63, suggesting that the prepared biolubricants are biodegradable (a compound with BOD5/COD ratio of around 0.5 and higher is considered biodegradable).

Therefore, biolubricants have higher biodegradability and non- or less toxicity than petroleum-based lubricants owing to their straight-chain aliphatic compounds and the non-aromatic structure. Furthermore, polyalkylene glycols (PAGs), despite being non-bio-based, exhibit excellent water solubility, low viscosity characteristics, and good biodegradability.

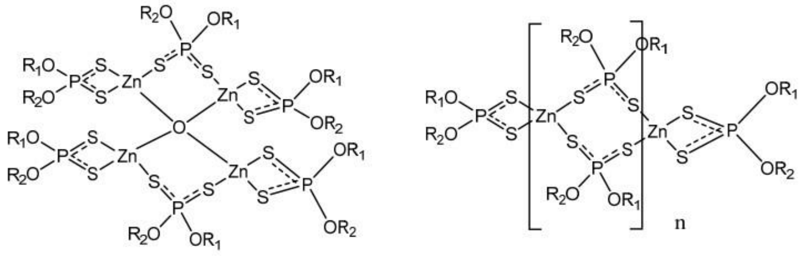
2.4.6 Anti-wear

The addition of anti-wear additives to biobased HFs is mainly to deduct "scuffing" wear between slippery steel surfaces with high loads on the steel [87]. Metal dithiophosphates like zinc dithiophosphates (ZDDP) and activated sulfur-phosphorus compounds are exclusively efficacious anti-wear additives to prevent this wear mechanism [88,89]. Structures of different forms of ZDDP additives are illustrated in **Figure** 2.6. These additives are fundamentally based on chemically bound phosphorus (aryl phosphates) or sulfur/phosphorus compounds that diminish mechanical abrasion via "chemical polishing" effects [90]. Friction modifier additives are indispensable to ensure smooth performance without vibration (adhesive/slip) under difficult conditions such as relatively slow movement between heavily loaded mating surfaces. By selecting an appropriate combination of the corresponding alkyl or aryl groups for the additives, it is possible to dramatically increase the thermal stability of large dithiophosphate molecules [91]. The organic sulfur/phosphorus compounds are described by superior characteristics for hydrolytic and oxidation stability, compared with the conventional dithiophosphate additives (petroleum-based) [92]. In addition, to improve the properties of both thermal stability and anti-wear demeanor of biobased HFs, an appropriate combination of organic (ashless) sulfur/phosphorus compounds can be used. Without the application of a friction modifier additive, there may be a dangerous risk of irregular performance under the conditions of speed, load, or both in hydraulic systems. It was reported that the addition of esters of fatty acids could reduce the static friction coefficient below the kinetic value owing to the increased formation of a surface layer of reaction products between lubricated surfaces under boundary conditions [93].



Monomeric ZDDP

Dimeric ZDDP



Basic ZDDP (tetrameric)

Polymeric ZDDP

Figure 2.6: Structures of various forms of zinc dithiophosphate (ZDDP), where the R group is an alky- or aryl-dithiophosphate [90].

Abrasion process or abrasive wear related to the plastic fatigue process can also occur in hydraulic systems. The greatest effect of surface fatigue is on components that operate under high contact pressure [95]. In this process, small water molecules can be rapidly dispersed and decomposed on the reactive surfaces of the newly-formed microcracks, resulting in the release of hydrogen atoms. Continuing this process would lead to hydrogen embrittlement of the steel, leading to greater crack propagation. Consequently, it is indispensable that hydraulic systems be equipped with satisfactory filters to protect critical equipment and maintain fluid purity at an acceptable level [96].

2.4.7. Compatibility with the seals and rubber hoses

The compatibility of BHFs with seals and rubber hoses is a critical aspect to consider when integrating these eco-friendly fluids into hydraulic systems. Due to their distinct chemical compositions compared to traditional petroleum-based oils, BHFs may interact differently with seal and hose materials, potentially affecting their performance and longevity. It is imperative to assess the compatibility of seals and rubber hoses with BHFs to prevent issues such as swelling, hardening, or deterioration, which could lead to leaks or system failures.

In addition, rubber seals and hoses commonly used in hydraulic systems are typically composed of materials like nitrile butadiene rubber (NBR), fluorocarbon rubber, and polytetrafluoroethylene

(PTFE) [97,98]. While these materials generally exhibit good compatibility with BHFs, prolonged exposure may still result in adverse effects such as swelling or degradation. Therefore, thorough testing and validation of seal and hose materials with specific formulations of BHFs are necessary to ensure reliable performance and long-term durability. For instance, in a study conducted by Honary [99], rubber hosing compatibility was assessed by immersing it in crude soybean oil at a temperature of 104°C for a duration of 94 h. The results revealed a minimal increase of less than 10% across all measurements, with no displacement of water volume observed. The sample exhibited no significant signs of wear, corrosion, or burning. Although some swelling was observed at the hose ends, it was noted to be minor. Overall, the findings suggest that compatibility with rubber hosing does not pose a significant issue for the use of crude soybean oil.

Selecting seals and hoses explicitly designed and rated for use with BHFs is recommended to mitigate compatibility issues. Additionally, ongoing monitoring and maintenance of seals and hoses are essential to detect any signs of degradation or wear over time. By carefully considering seal and hose compatibility with BHFs and implementing appropriate preventive measures, hydraulic systems can effectively harness the benefits of eco-friendly fluids while maintaining optimal performance and reliability. However, the compatibility of elastomers with BHFs may be compromised in the presence of seawater contamination. This can lead to accelerated wear, leakage, or even failure of hydraulic system components, posing operational and maintenance challenges [49].

2.5 Esters used for hydraulic applications

Many manufacturers are interested in using diesters as environmentally acceptable HFs owing to their multiple beneficial characteristics, e.g., low-temperature fluidity, inherent biodegradability, excellent thermal and oxidative stability, and high VI, etc. **Figure** 2.7 shows the synthesis of diesters from oleic acid. However, low molecular weight diesters have drawbacks, such as poor hydraulic stability and the tendency to attack certain paints and elastomers [100]. Complex esters, on the other hand, have better compatibility with elastomers, higher hydrolytic stability, and higher VI compared to diesters. The raw materials used to synthesize complex esters are usually a type of neopentyl polyols such as PET, TMP, or NPG, and a polycarboxylic aromatic acid such as phthalic, pyromalic, or malic acid, as well as aliphatic monocarboxylic acid with 2 to 12 carbon atoms [101]. **Figure** 2.8 shows the synthesis of a complex ester (TMP ester) from vegetable oil [102,103]. Complex esters are particularly suitable as a base stock for lubricating hydraulic systems operating at high temperatures. Notably, despite the low PP of the complex esters, their fluidity at lower temperatures is generally poorer than that of diesters. This defect can be remedied using various methods, e.g., genetic modification, direct addition of additives, and chemical modification [104]. Suitable applications of esters are strongly dependent on the molecular weight and function of the polyol. In fact, esters with low molecular weight acids or low polyol function are highly volatile, while high molecular weight esters are highly viscous. Hence, achieving an ideal lubricant to satisfy both fluidity and volatility properties at low temperatures may require the use of a mixture of acids and polyols [105].

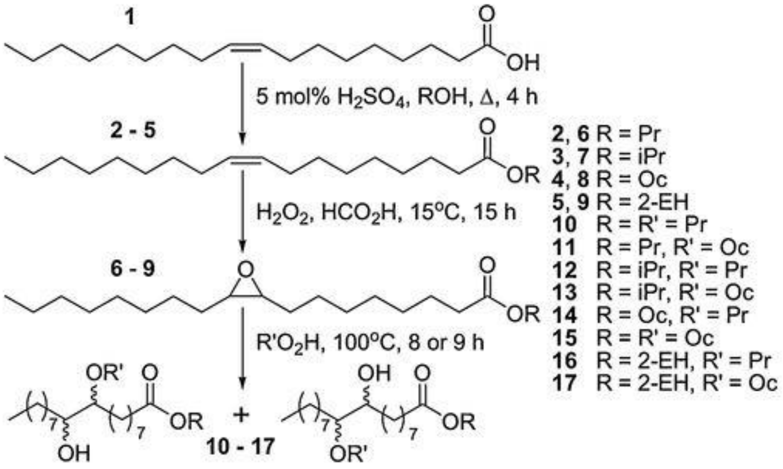


Figure 2.7: Synthesis of diesters from oleic acid. Note: R′: a carbonyl group at carbon 1, resulting in an ester; Pr: propyl; iPr: isopropyl; Oc: octyl; 2-EH: 2-ethylhexyl [106]. Copyright 2007 AOCS, Reprint permission obtained.

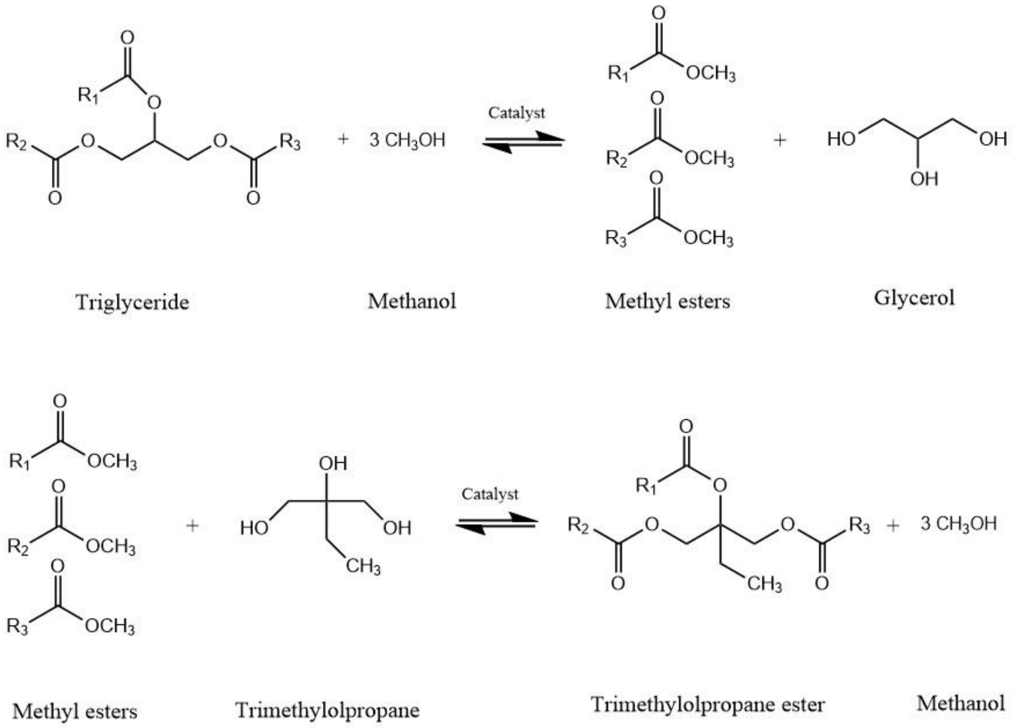
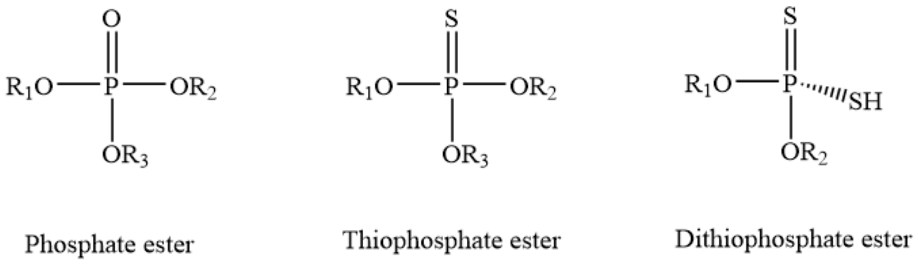


Figure 2.8: Two-step reaction processes of base-catalyzed production of TMP ester [102].

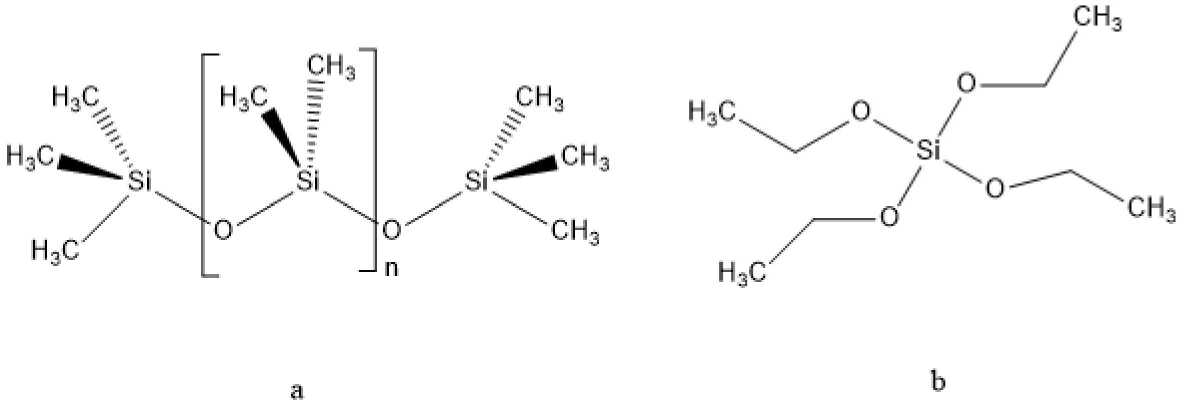
Another common type of ester is phosphate-based esters. Phosphate-based esters are employed principally as fire-resistant base stocks for special applications, including hydraulic systems, compressors, and turbines, although there are disadvantages of using such esters in hydraulic applications, e.g., fire hazards, low VI, poor hydrolytic stability, and strong aggressiveness to many common sealing and coating materials [18,95]. On the other hand, restrained phosphate-based esters (chemically modified or formulated to enhance certain properties) have excellent oxidation stability as well as inherently good anti-wear properties under heavy loading situations [107]. The structures of most common phosphate esters including phosphate ester, thiophosphate ester, and dithiophosphate ester are illustrated in **Figure** 2.9 [88,94].



Phosphate ester Thiophosphate ester Dithiophosphate ester

Figure 2.9: Structures of most common phosphate esters [88,94].

Thus far, much effort has been made in synthesizing phosphate esters from other raw materials in order to better control the performance and reduce the toxicity of the final product. Silicone-based esters (**Figure** 2.10) usually have better physical and chemical properties than other types of esters and mineral oils. Their outstanding advantages are the high VI, remarkably good thermal-oxidative stability, low vapor pressure, and exceptionally low PP, although they have a disadvantage associated with their immiscibility with most of the lubricants [108]. It should be noted that silicate esters have limitations in hydraulic applications due to their relatively low hydraulic stability. For instance, contact of the fluid with moisture would lead to hydrolysis of the esters and gel formation. In this regard, the products of the four-alkyl orthosilicates containing the tertiary alkyl groups are the most durable materials and are therefore generally favored [109].



a b

Figure 2.10: (a) Dimethyl polysiloxane, (b) tetraethylorthosilicate (n range from 90 to 410) [110,111].

As another type of esters, perfluoropolyalkylether, fluoroalkylether, and perfluoroalkylether represent excellent lubricating qualities, low PP, excellent fire resistance properties, biological inertness, and adaptability with most utmost plastics, elastomers, and metals [8]. These fluids are distinguished by radiation resistance, extreme chemical inertness, and a high degree of thermo-oxidative stability. Owing to their desirable and unique characteristics as discussed above, these fluorinated media have found many specialized applications in the chemical and aerospace industries [8]. Nevertheless, despite their advantages in enhancing the properties of HPHF (such as thermal and oxidative stability and reduced flammability), fluorinated fluids suffer from drawbacks including high cost, relatively low bulk modulus, poor solubility of additives, and immiscibility with other fluids [112,113]. It is noteworthy to highlight that although the mentioned additives are suitable for biobased HFs, comprehensive testing is crucial to verify compatibility and enhance the performance of biobased HFs when integrating these additives.

As a summary, **Table** 2.8 presents a comparison of various types of esters applicable as HFs for industrial applications with respect to advantages and disadvantages.

Table 2.8: Comparison of various types of esters applicable as HFs for industrial applications.

Type of esters	Examples	Advantages	Disadvantages
Diesters	Adipate ester	Low-temperature fluidity, inherent biodegradability, High thermal and oxidative stability, high VI	Poor hydraulic stability, volatile
Triesters	Trimethylolpropane ester Pentaerythritol ester Neopenthylglycol ester	Better compatibility with elastomers, excellent thermal and oxidative stability, higher hydrolytic stability, and higher VI	Poor low-temperature performance
Phosphate esters	Phosphate ester Dithiophosphate ester Thiophosphate ester	Fire-resistant, good thermal stability, excellent boundary lubrication properties, low volatility, and fair hydrolytic stability	Low VI, poor hydrolytic stability
Silicone-based esters	Dimethyl polysiloxane Tetraethylorthosilicate	High VI, excellent thermal-oxidative stability, low vapor pressure, and low PP	Immiscible with most lubricants
Fluoroalkyl ester groups	Perfluoropolyalkylether Fluoroalkylether Perfluoroalkylether	High lubricity, low PP, excellent fire resistance, biological inertness, and adaptability with most utmost plastics, elastomers, and metals	High cost, poor solubility with additives, and immiscibility with other fluids

2.5.1 Chemical modifications of vegetable oil-based esters

Vegetable oils are characterized by their fatty acid content, with notable variations in the composition of multiple unsaturated fatty acids, as demonstrated in **Tabl**e 2.9. This variance presents opportunities for chemical alterations at key sites within vegetable oils, such as acyl

(C=O) and double bonds (C=C) [114]. These modifications aim to enhance the properties of bio-based lubricants, including improved lubricity and heightened thermal-oxidative stability [115].

Table 2.9: Fatty acid composition of various vegetable oils.

Vegetable oils	Palmitic acid (16:0)	Stearic acid (18:0)	Oleic acid (18:1)	Linoleic acid (18:2)	Linolenic acid (18:3)	Erucic acid (22:0)	Ref.
Calabash oil	16.32	7.86	36.23	1.74	-	-	[116]
Palm oil	39.32	4.36	42.52	11.35	-	-	[117]
WCO	28.91	0.93	26.51	27.44	4.60	-	[118]
Moringa oil	5.50	5.70	73.20	1.00	-	-	[119]
Sunflower oil	6.31	3.55	21.39	63.35	1.46	-	[120]
Safflower oil	6.40	2.50	17.90	73.20	-	-	[121]
Soybean oil	11.07	3.72	22.61	51.33	5.63	-	[120]
Rapeseed oil	4.04	2.10	57.26	20.69	8.08	-	[120]
Canola oil	3.90	1.10	64.40	20.40	9.60	-	[122]
Mustard oil	1.74	1.04	9.56	13.31	11.10	42.16	[123]
Olive oil	10.08	2.90	67.80	9.70	-	-	[124]
Carinata	7.74	19.9	11.3	10.5		48	[125]
Cottonseed	2.8	1	13	58	-	-	[126]
Terminalia belerica	32.8	6.4	31.6	28.8	-	-	[127]
Rubber seed	10.2	8.7	24.6	39.6	16.3	-	[128]

Chemical modification of crude vegetable oils aims to increase the thermal stability and oxidation of the products and thus can be used as bio-based lubricants in a wide range of operating conditions in the industry [129,130]. Base oils containing saturated esters can withstand oxidation better than unsaturated esters as they help in the formation of tribofilms [18]. The presence of polyunsaturated molecules poses many problems in the oxidation stability of vegetable oils when used as HFs or as other lubricants. Therefore, the percentage of polyunsaturated fatty acids in base oil should not be higher than 5% [131]. Considering the general structure of vegetable oils, as illustrated in **Figure** 2.11, there are two sites that are susceptible to chemical modifications. For monounsaturated double bonds, the H atoms next to the double bonds in the fatty acid chain can be more easily attacked by free radicals and eventually replaced by a peroxide. On the other hand, polyunsaturated fatty acids contain multiple double bonds, which can be either allylic (-CH=CH-) or bis-allylic (-CH_2-CH=CH-CH_2-CH=CH-CH_2-). The presence of these allylic and bis-allylic sites makes the fatty acid chain more reactive compared to those with only allylic sites. This increased reactivity is due to the presence of additional double bonds, which provide more sites for chemical reactions to occur, such as oxidation or polymerization. Therefore, the fatty acid chain containing both allylic and bis-allylic sites is indeed more reactive than one containing only allylic sites [18]. In the following section, two types of chemical modification that lead to the production of suitable base oils with fewer double bonds for HFs are discussed: estolide esters and epoxidized vegetable oils.

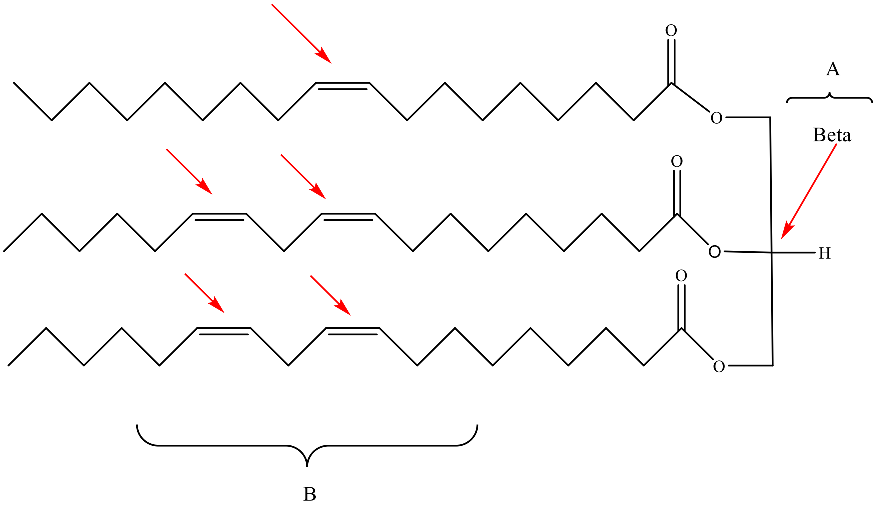
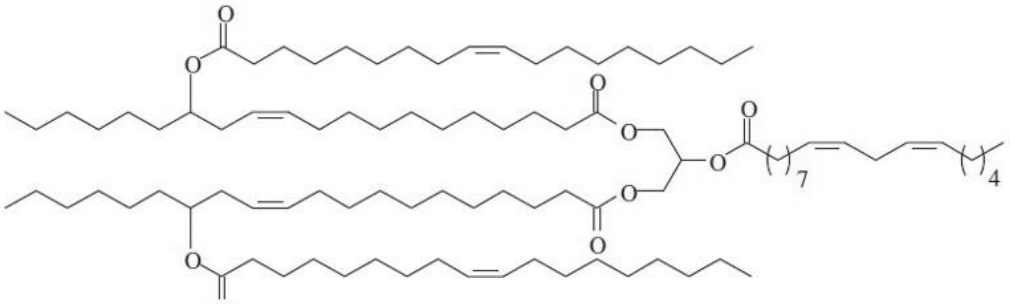


Figure 2.11: susceptible positions in triglycerides structure to chemical modifications. A) The ester moieties, especially the critical β-hydrogen in triglycerides; and (B) the double bonds in fatty acid chains [132].

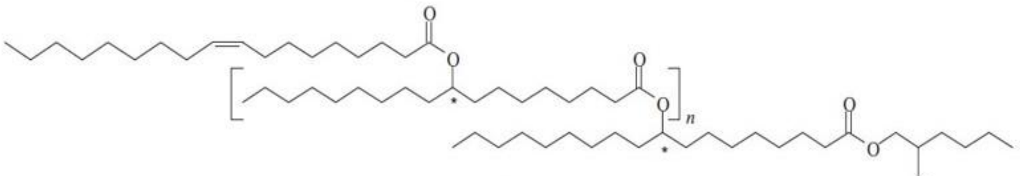
2.5.2 Estolide esters from vegetable oils

Estolides are in three different categories, namely (1) free acid estolides, (2) estolide esters, and (3) triglyceride estolides [133], among which triglyceride estolides, obtained from vegetable oils that are high in hydroxy fatty acids (e.g., Lesquerella oil, castor oil), have potential use as lubricants in many industrial applications [134]. Free acid estolides and estolide esters are oligomeric esters, formed through the condensation of a fatty acid/ester across the site of unsaturation of another fatty acid (e.g., oleic acid) under catalysis of H_2SO_4, $HClO_4$, P-Toluenesulfunic, or montmorillonite clays [133-135]. Molecular structures of some examples of estolides: triglyceride estolides, oleic-based estolide 2-ethylhexyl (2-EH) esters, and saturated-capped estolide 2-EH esters are illustrated in **Figure** 2.12 [133].

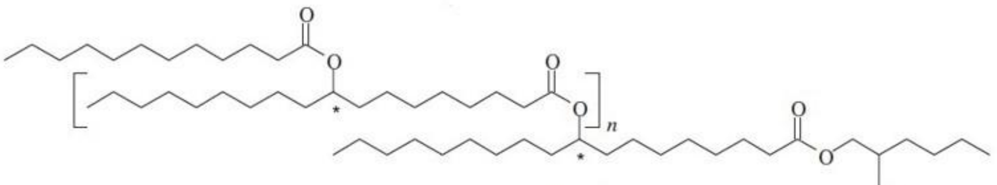
Estolides are a category of unique biolubricants which have found a wide application in industry. Their oligomeric structure comprises the secondary ester linkages on the alkyl backbone of the molecule which makes the molecule more resistant to water hydrolysis [136-139]. These ester linkages also give better biodegradability properties to the estolide molecule. The estolides derived from vegetable oils exhibit excellent lubrication performance. They demonstrate lower evaporation rates (lower volatility) during lubrication operations compared with their mineral oils counterparts, due to their high molecular weight, which also leads to an increase in flash and fire points [140]. Another attractive advantage of the estolides as HFs is that their properties (e.g., viscosity) could be tuned by varying the type of carboxylic acid used or controlling the degree of oligomerization [141]. High VI estolides would form a thicker film, hence have better protection against abrasion in high-temperature operating conditions. Thus, estolides can be a new class of base stocks for HFs as they meet most required properties such as oxidative stability, hydrolytic stability, volatility, biodegradability, stability in high-temperature operation, miscibility with various types of base stocks, and solubility for a wide range of additives [32].



Triglyceride–based estolide



Oleic–based estolide 2-EH esters



Saturated–capped estolide 2-EH esters

Figure 2.12: Molecular structures of triglyceride estolides, oleic-based estolide 2-ethylhexyl (2-EH) esters, and saturated-capped estolide 2-EH esters [133]. Copyright 2020 AOCS, Reprint permission obtained.

2.5.3 Epoxidized vegetable oils (EVOs)

Some vegetable oils, such as Soybean, Sunflower, Lesquerella, and those that have a double bond along their fatty acid chains show relatively poor oxidative stability due to the rapid reaction that occurs in unsaturated sites. An innovative method to improve the stability of unsaturated esters against oxidative attack is the epoxidation of double bond sites [142,143], including homogeneous and heterogeneous catalytic epoxidation, chemoenzymatic epoxidation, and epoxidation in the presence of polyoxometalates [144]. For heterogeneous catalytic epoxidation, the conversion and selectivity are affected by the surface area, pore diameter, and hydrophobic nature of the catalyst. Higher surface area and larger pore diameter of catalysts were found to be beneficial for high conversion, as these would facilitate the triglyceride molecules enter into the catalyst's inner pores and surfaces where more active sites are present [145].

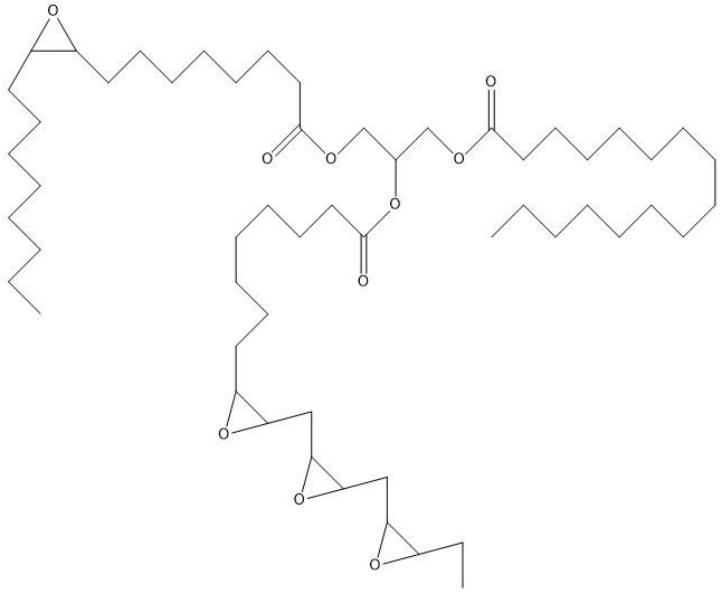


Figure 2.13: Structure of an epoxidized natural triglyceride with three different fatty acids [146].

As can be seen in **Figure** 2.13, in the structure of this vegetable oil linolenic acid is a polyunsaturated fatty acid, which leads to reduced thermo-oxidative stability [32,147]. The epoxidized soybean oil (ESBO) exhibited an acceptable response to antioxidant additives at low concentrations, suitable thermo-oxidative behavior, low coefficient of friction, increased viscosity, higher PP, and improved lubricity [148]. Since the oxirane groups can be easily functionalized by reacting with different nucleophilic reagents, epoxidized vegetable oils have been used as intermediate products in a wide range of biodegradable lubricant formulations [32,149]. In another study, diester derivatives of epoxidized vegetable oils (EVOs) were obtained with one- or two-step reaction [150]. These diester derivatives of EVOs were reported to have good oxidative stability and low-temperature performance properties suitable for many industrial applications, especially as hydraulic fluids, lubricants, and metal working fluids [151].

Therefore, epoxidation improves the thermal-oxidative stability of vegetable oils, and further chemical modifications of EVOs (e.g., oxirane ring opening process) can further enhance their properties more suitable for industrial applications as HPHFs.

2.6 Current challenges and future perspectives of bio-based hydraulic fluids/lubricants

Recently, growing concerns about the environment and resources have led to an increase in the demand for environmentally friendly bio-based lubricants. Vegetable oils have higher FP, HVI, good lubrication, and lower volatility than mineral oils. In addition, the renewability, biodegradability, and non-toxicity as well as a lower risk to soil, water, and flora and fauna in the events of equipment break-down, careless disposal, or accidental leakage, have made them and their derivatives a viable alternative to mineral-based HFs/lubricants [152,153]. Vegetable oils and chemically modified vegetable oil esters are superior to petroleum-based oils, PAO, PEG, PAG, and synthetic esters as base oils because they are renewable and more environmentally friendly [154,155]. However, bio-based HFs derived from vegetable oils have significant challenges that limit their widespread use as a base stock for HFs. The major challenges are related to (1) costs, (2) accessibility of vegetable oils and competition with food (if using edible vegetable oils), (3) service life, (4) operating conditions, (5) performance concerns and physicochemical properties (thermal/oxidative/hydraulic stability), (6) compatibility issues, and (6) regulatory support and market incentives.

Bio-lubricants are usually 30 to 40 percent more expensive than mineral oil lubricants [156,157]. Therefore, at present, these lubricants (biodegradable) are used for the special needs of the industry or in special cases. Moreover, certain nations lack the capacity to produce sufficient quantities of vegetable oils to fulfill demands for both food and industrial purposes. Consequently, the production of a substantial volume of bio-based HPHFs encounters hurdles related to accessing suitable feedstocks and contends with competition from food production. Therefore, governments, industries, and research institutions need to collaborate to drive down production costs through technological advancements, economies of scale, and policy support, making biobased fluids more economically viable [107,158].

On the other hand, BHFs must meet or exceed the performance standards of their petroleum-based counterparts to gain wider acceptance in various applications. For instance, the poor cold flow characteristics of vegetable oils prevent the use of vegetable oils-based HFs as industrial lubricants. In addition, bio-based triglycerides have poorer thermal stability due to the weakness of beta hydrocarbons in the glycerol backbone, and hence can thermally decompose more readily than the petroleum-based synthetic esters based on TMP, NPG, and PET. Most HPHFs derived from vegetable oils have C18 structure mainly unsaturated. Therefore, their oxidative stability depends on the degree of unsaturation of the fatty acid chain. Vegetable oils with a higher content of oleic acid could be obtained through plant hybridization, genetic modification, and oil physicochemical processing, thereby improving their oxidative stability [159,160]. Hence, research and development efforts should focus on improving the properties of biobased fluids, such as oxidative stability, lubricity, and temperature resistance, through formulation optimization, additive technology, and genetic engineering of feedstock crops.

In addition, over time with industrial application of hydraulic fluids, the base oils and additives will decompose, causing the hydraulic stability issue. Furthermore, the presence of water or moisture in the system can cause the molecules of biolubricants to break down by hydrolysis to form acids, recombine bonds, and change the compounds in the fluid. Therefore, special attention should be paid to the acid value of biolubricants at different time intervals. Moreover, the use of vegetable oils with higher oleic acid content, and more importantly, the use of appropriate additives or chemical modifications can significantly extend the service life of HFs within a suitable temperature range and thus improve their properties.

In terms of compatibility, biobased hydraulic fluids need to be compatible with existing equipment and infrastructure to facilitate seamless adoption. Standardization efforts, industry guidelines, and compatibility testing protocols should be developed to ensure the interoperability of biobased fluids with different hydraulic systems, seals, and materials.

Besides the above-mentioned challenges for biolubricants, choosing the right hydraulic fluid in accordance with the performance of the hydraulic system used requires special attention. The hydraulic system is a complex fluid-based system, and successful hydraulic operation requires a careful selection of hydraulic oils to meet the needs of the system. Particle contamination, water pollution (causing hydrolysis), air contamination (aeration or cavitation in hydraulic systems), clogged filters, high/low temperatures operation as well as an incorrect selection of hydraulic fluid can lead to poor performance or failure of a hydraulic system.

Finally, governments can play a crucial role in promoting the use of biobased hydraulic fluids through supportive policies, incentives, and regulatory frameworks. This includes tax incentives, subsidies, renewable energy mandates, and environmental regulations that encourage the adoption of sustainable alternatives and penalize the use of environmentally harmful fluids.

Figure 2.14 summarizes knowledge gaps in the manufacture and applications of bio-based HFs/lubricants, among which the most important one is the absence of biodegradable additives for different applications, e.g., anti-wear (AW), extreme pressure (EP) operation, robust and oxidation inhibitors (R&O), biocides, etc. Today, many manufacturers continue to use non-environmentally friendly additives in the production of HFs. Another important knowledge gap that limits the manufacture of biolubricants from non-edible vegetable oils is the lack of knowledge about the quality, quantity, and physicochemical properties of different non-edible vegetable oils. Due to the fierce competition in the lubricant market, it is necessary to conduct research on widely available and inexpensive primary vegetable oil feedstocks for the manufacture of biolubricants. In addition, fire resistance hydraulic (FRH) oils are widely used in industry, and as a result, the production of fire resistance bio-based HPHFs and the study of their toxicological and environmental behavior is of great importance. Additional endeavors ought to be pursued to develop economical procedures for synthesizing bio-based HFs/lubricants, such as exploring diverse chemical modifications, enzymatic methodologies, and other viable approaches.

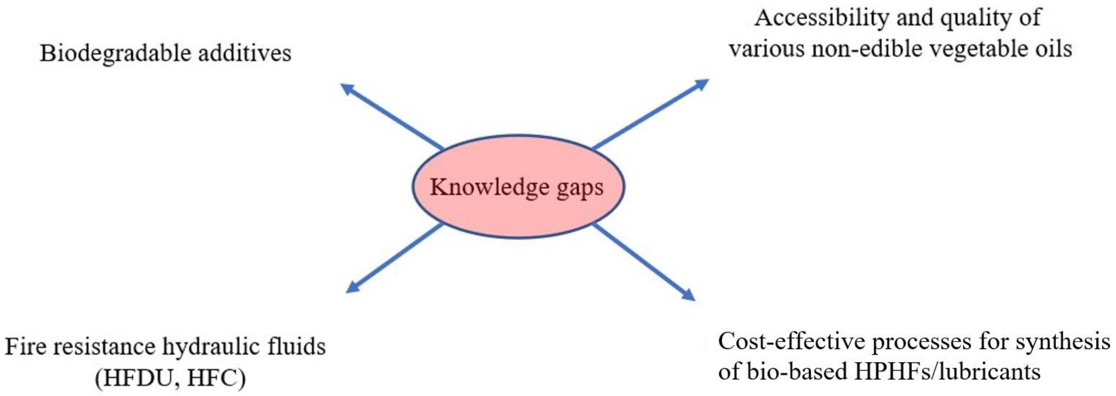


Figure 2.14: Knowledge gaps in manufacture and applications of bio-based HFs/lubricants.

The future perspectives of biobased HPHFs are promising, with ongoing advancements in technology and increasing environmental consciousness driving their adoption. Several key factors that shape the outlook for these fluids are (1) environmental sustainability, (2) performance enhancements, (3) technological innovations, (4) cost competitiveness, and (5) market expansion.

BHFs offer significant environmental benefits, including renewable sourcing, biodegradability, and reduced carbon footprint compared to conventional petroleum-based fluids. As environmental regulations tighten and sustainability becomes a priority, the demand for biobased fluids is expected to rise. In addition, continued research and development efforts are focused on improving the performance characteristics of BHFs. This includes enhancing their oxidative stability, thermal stability, lubricity, and compatibility with hydraulic system components. As these fluids approach or exceed the performance of petroleum-based alternatives, their adoption in high-performance applications is likely to increase. Furthermore, advances in biobased fluid formulation, processing techniques, and additive technologies are driving innovation in the field of HPHFs. New bio-based additives and modifiers are being developed to tailor the properties of biobased fluids to specific application requirements, expanding their versatility and applicability across various industries [45,159].

While biobased fluids may initially be more expensive than petroleum-based alternatives it is expected that economies of scale, technological advancements, and supportive policies drive down production costs. As biobased fluids become more cost-competitive, they will become increasingly attractive to end-users seeking sustainable and economically viable solutions. Moreover, the global market for biobased lubricants, including hydraulic fluids, is projected to expand significantly in the coming years. Growing awareness of environmental issues, coupled with regulatory initiatives promoting sustainable practices, will drive the adoption of biobased fluids across diverse industries such as automotive, construction, agriculture, and marine.

Overall, the future of biobased high-performance hydraulic fluids is characterized by their growing importance in addressing environmental concerns, advancing technology, improving performance, and expanding market opportunities. Consequently, further research and development (R&D) work needs to be done to fill the knowledge gaps and overcome the limitations in the manufacture and applications of bio-based HFs/lubricants, as discussed above. Meanwhile, special bio-based HFs/lubricants that have high thermo-oxidative stability and can maintain a long service life in a wide temperature range are required. As sustainability continues to drive innovation and decision-making across industries, biobased fluids are poised to play a central role in the future of hydraulic systems.

2.7 Conclusions

(1) Bio-based HFs/lubricants derived from vegetable oils have higher biodegradability and non- or less toxicity than petroleum-based lubricants owing to their straight-chain aliphatic compounds and the non-aromatic structure.

(2) The ester derivatives obtained from the chemical modification of vegetable oils, e.g., estolide esters and epoxidized vegetable oils, show excellent performance in high and low-pressure hydraulic systems. Although the use of bio-based HPHFs/lubricants still has high costs, their high price can be justified by the advantages such as a positive effect on the efficiency of the hydraulic system, improved protection of hydraulic components, and longer service life of the equipment. In addition, the use of natural esters is expected to have less environmental impacts (renewable feedstock, lower toxicity, and biodegradability) in particular when free environmental safety rules become more stringent, which makes them attractive for use in hydraulic systems.

(3) Polyol esters, for instance, are suitable as a base stock for lubricating hydraulic systems at high temperatures due to their higher thermal-oxidative stability. The high PP of these esters can be

remedied using various methods such as genetic modification, direct addition of additives, and chemical modification.

(4) Bio-based HFs derived from vegetable oils however have significant challenges that limit their widespread use as a base stock for lubricants and HFs, and the major challenges are related to: (1) costs, (2) accessibility of vegetable oils and competition with food (if using edible vegetable oils), (3) service life, (4) operating conditions, and (5) properties (thermal/oxidative/hydraulic stability).

(5) Further R&D work needs to be done to overcome the limitation in the manufacture and applications of bio-based HFs/lubricants, i.e., the absence of biodegradable additives for different applications, lack of knowledge about the quality, quantity, and physicochemical properties of different non-edible vegetable oils, the production of fire resistance bio-based HPHFs and cost-effective processes for the synthesis of bio-based HFs/lubricants. Vegetable oil esters with satisfactory performance are expected to be introduced as the main lubricants of hydraulic systems in the future.

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Chapter 3

3 Synthesis of TMP esters as a biolubricant from canola oil via a two-step transesterification-transesterification process

Abstract

Trimethylolpropane esters were synthesized from canola oil by a two-step transesterification-transesterification process. In the first step, canola oil reacted with ethanol to produce canola oil ethyl ester, while in the second step, canola oil trimethylolpropane ester was obtained by reacting the canola oil ethyl ester and trimethylolpropane using K_2CO_3 as a catalyst. In the first step, under the optimal reaction conditions (70°C, 2h, ethanol-to-canola oil molar ratio: 10:1, and 0.25 wt.% catalyst loading), canola oil ethyl ester was successfully synthesized with a yield of 95.7 wt.%. In the second step, the final product with the maximum total concentration of canola oil trimethylolpropane ester (82%) and the maximum conversion of canola oil ethyl ester (85%) was obtained at 130°C for 3h with a canola oil ethyl ester to trimethylolpropane molar ratio of 3.1:1, and 1 wt.% loading of K_2CO_3 catalyst. The produced polyol esters can be a promising biolubricant with excellent lubricant characteristics, quenching performance, biodegradability, and rheological/tribological properties.

3.1 Introduction

Nowadays, fossil resource is still the dominant source of fuels and chemicals, but it is recognized as an unsustainable resource due to its non-renewability [1,2]. Furthermore, the oil extraction, transportation, and industrial processes for oil refining lead to many environmental problems such as oil spills, low degradability of waste, toxic effluents, and accumulation of carbon dioxide in the atmosphere [3]. Industrial lubricant helps to reduce friction between surfaces in metal-based machinery, ultimately reducing the heat generated when the surfaces move. Currently, lubricating industries are searching for new, less costly, and renewable raw materials to produce lubricating oils and greases with good biodegradability, low aquatic toxicity, and low environmental impacts [4]. The world market for finished lubricants is around 35 million tonnes per year, while by far biolubricants account for only about 1% of the total production capacity [5]. However, the biolubricants market has shown an average growth of 10% per year over the past 10 years [6].

Vegetable oils are a vital and suitable source for the production of biolubricants, including fatty acid esters, which are considered as "green products" for the use of biolubricants, with excellent biodegradability [7] that avoids environmental pollution from possible spills and product disposal. Vegetable oils, with structural similarity to long-chain hydrocarbons in mineral oils, have been widely used as an environmentally friendly alternative source to petroleum for the production of lubricants [8,9]. Nevertheless, the direct use of vegetable oils as lubricants has some disadvantages such as their poor performance at low temperatures, and oxidative instability, which are undesired characteristics for lubricants [10]. These inferior properties can be improved to an acceptable extent by using chemical modifications and converting vegetable oils into complex esters. However, in order to significantly increase oxidation stability, more chemical modifications such as epoxidation or hydrogenation are needed [11].

One of the most effective chemical modifications of vegetable oils, in order to produce complex esters, is the transesterification of vegetable oils (triglyceride) with methanol into methyl esters of fatty acids (FAMEs), followed by the transesterification of FAMEs with polyols such as trimethylolpropane (TMP), pentaerythritol (PET), and neopentyl glycol (NPG) [12-15]. TMP is a colorless triol (three hydroxyl groups) with the formula of $CH_3CH_2C(CH_2OH)_3$, which is more economically attractive to produce complex esters on an industrial scale as it has a lower melting point than PET and NPG and is less expensive.

Polyol esters have a high viscosity index, satisfactory pour point, and high thermal-oxidative stability compared to simple esters of similar fatty acids [16]. In addition, the final physicochemical properties of a lubricant depend on the type of polyol used, the aliphatic fatty acid chain length, and the number and position of unsaturated bonds in the fatty acid chain [17]. It should be noted that saturated fatty acids have a remarkably higher melting point than unsaturated ones and, in a mixture, they will crystallize at a higher temperature [18].

Significant research has been performed on the exploration of new modification methods and the development of more efficient catalysts for the modification and conversion of vegetable oils into esters and complex esters [4,19]. Nie et al. [20] developed a reverse-addition reaction method for TMP-based biolubricant production by synthesizing FAMEs of six different vegetable oils and TMP using K_2CO_3 as a catalyst. They observed that the reverse-addition reaction was more efficacious than the one-pot reaction in polyester synthesis and the conversion was 96.4%. Yunes et al. [21] synthesized palm oil polyol esters using the transesterification of fractionated palm oil methyl esters with TMP using sodium methoxide as a catalyst. They obtained a high conversion of palm oil methyl esters to palm TMP triesters (98% w/w), and the final product has a pour point (PP) of −32ºC. In another study, Arbain & Salimon [22] synthesized trimethylolpropane esters through the esterification of fatty acids (FA) of Jatropha curcas oil with TMP using different catalysts. The yield and PP of the obtained TMP triesters were 70% and −23ºC, respectively. Furthermore, Wang et al. [23] investigated the production of TMP esters through transesterification of rapeseed oil methyl esters with TMP at TMP-to-fatty acid esters molar ratio of 1:9 with zinc oxide catalyst at 0.45 wt. % loading, achieving 91.3% conversion of FAME and 82.5% yield of TMP triester. There is little information about the production of complex esters with fatty acid ethyl esters (FAEEs), as well as the investigation of their physicochemical properties in terms of tribological and rheological aspects. Therefore, those gaps need to be addressed to further advance technology.

In this study, canola oil, a vegetable oil with a high percentage of oleic acid (C18:1, 64%) [24] was used as a bio-feedstock for the synthesis of trimethylolpropane esters as a biolubricant. A lubricant with a higher oleic content has better oxidation stability and film strength, which typically leads to longer-life products and better four-ball wear results, respectively. Canola is an oil crop plant with two physiologic periods as winter and summer. Canada, China, and India are the largest producers of canola oil, led by Canada with 36% of the total production [25]. It is important to note that canola oil while possessing lubricating properties, is not typically used directly as a lubricant due to several limitations. Its relatively high viscosity, susceptibility to oxidation and degradation, potential compatibility issues with machinery materials, and performance shortcomings in demanding industrial applications hinder its effectiveness as a lubricant. However, through modification processes such as transesterification or esterification, canola oil can be converted into biodiesel or biocomplex esters, which can enhance its lubricating properties, stability, and compatibility with machinery and equipment. Furthermore, according to Market Data Forecast, the canola oil market size was anticipated at $ 31.8 million in 2022 and is estimated to reach an extent of $ 44.5 million by 2027. Therefore, the high price of canola oil compared to mineral oils can be justified for lubricant manufacturers due to its high oleic acid content, availability, biodegradability, and environmental friendliness.

Additionally, ethanol as a renewable alcohol was used as a substitute for methanol for transesterification reactions. Since most of the vegetable oil transesterification reactions have been done with methanol and in industrial applications, the use of methanol can bring major corrosive problems in tubes and pumps. Using ethanol instead of methanol in the transesterification reaction of vegetable oil offers several advantages. Ethanol is less toxic than methanol, enhancing safety for workers and reducing health risks associated with exposure. Additionally, ethanol is typically derived from renewable biomass sources, aligning better with sustainable practices and reducing greenhouse gas emissions. Its compatibility with existing infrastructure simplifies production processes and reduces the need for equipment modifications. Furthermore, byproducts generated from ethanol production, such as distillers grains, can be utilized, providing additional economic and environmental benefits.

The motivation of this study was to develop a process to produce biolubricant complex esters with improved thermal and oxidative stability from vegetable oils (in particular canola oil, abundantly produced in Canada) for non-internal combustion engine applications, by converting vegetable oil triglyceride into TMP esters via the 2-step transesterification-transesterification process. Reaction conditions, including catalyst loading, fatty acid ethyl ester (FAEE)-to-TMP molar ratio, reaction temperature, and reaction time in both steps were investigated. The final canola oil TMP (COTMP) esters were analyzed using GC-FID, FTIR, and ^{1}H NMR. Furthermore, the physicochemical, biodegradability, tribological, and rheological properties of the final product were characterized for biolubricant application.

3.2 Materials and Methods

3.2.1 Materials

Analytical grade n-heptane, hydroxide potassium pellets (KOH, purity 85%), anhydrous sodium sulfate (Na_2SO_4, purity >99%), absolute ethanol, pure glycerol, analytical grade ethyl acetate (GC grade), N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) (98%), sodium chloride solution, and potassium carbonate (K_2CO_3) were obtained from Sigma-Aldrich and used as received. Commercial-grade Canola oil was purchased from a local grocery store. 2-ethyl-2-hydroxymethyl-1,3-propanediol (TMP) (assay > 98%) was supplied by Progressive Industrial Fluid Ltd. For the gas chromatography (GC-MS) analysis, ethyl heptadecanoate (C19:0 FAEE) as an internal standard, was purchased from Sigma-Aldrich. In this study, in the 1st step, canola oil was converted to FAEEs or canola oil ethyl esters (COEE) using the ethanol transesterification process, followed by several purification steps as similarly described elsewhere [26]. The FAEE or COEE was used as feedstock to synthesize TMP ester in the 2nd step process by transesterification with TMP. The influence of various reaction parameters on the conversion of canola oil to FAEE in the 1st step and FAEE to TMP ester in the 2nd step was examined in order to assess the best reaction conditions. Thermogravimetric analysis (TGA) plots of crude canola oil, COEE, and COTMP ester were collected on a Perkim-Elmer TGA system by heating the samples in 50 mL/min nitrogen at 10°C/min.

The viscosity and viscosity index (VI) of the biolubricant (COTMP ester obtained at the best conditions) were measured using ASTM methods D445 and D2270, respectively. The Pour point was determined by ASTM method D97 with an accuracy of ±3°C using a Pour Point Tester manufactured by HK Petroleum Co., China. The Flash point (open cup) of the products was specified using the HK petroleum Co. apparatus according to ASTM D 92-18 method. Quench test measurements were performed according to ISO 9950 method.

3.2.2 Methodology

3.2.2.1 The 1st step transesterification

The 1st step transesterification experiments were carried out in a 500 mL three-neck round bottom flask equipped with a thermometer, magnetic stirrer, and a refluxing condenser at atmospheric pressure. The reactor was preheated to 65°C to eliminate moisture and then 50 g of vegetable oil was added. When the reactor reached the desired temperature for the experiment, a mixture of alkali (KOH) ethanol solution as a catalyst was added in the amount established for each experiment. Then, the magnetic stirrer was turned on and this was set as time zero of the reaction. The reaction mixture was stirred at 1200 rpm and refluxed for the required reaction time. The effects of 4 reaction parameters were investigated by using the one-variable-at-a-time (OVAT) method: catalyst loading (0.25 wt.% - 1 wt.% of the vegetable oil mass), ethanol-to-oil molar ratio (7-12), reaction time (1.5 h-3.5 h), and reaction temperature (45°C - 80°C).

After the completion of the reaction, a separatory funnel was used in order to phase separation between ethyl ester and glycerol. It should be noted that due to the formation of strong emulsion, the separation of glycerol was difficult. To overcome this difficulty, pure glycerol (~ 10 g) was added to the mixture in the separatory funnel, shaken vigorously, and separated two phases from each other after 1-2 h (**Figure** 3.1). The addition of pure glycerol to the mixture could also remove the residual catalyst and the soap that formed during the transesterification reaction. After phase separation, the ethyl esters of the canola oil phase were washed twice with 50 cm^3 of 50 °C warm distilled water in the separatory funnel until a neutral pH. Finally, this product was evaporated under reduced pressure at 80°C in a rotary evaporator to remove the unreacted ethanol from the product mixture, followed by drying at 105°C in an oven to remove traces of water. All experiments were performed in triplicate and the results are presented as the average value with the respective standard deviation. The obtained esters product was denoted as COEE in this work and analyzed by GC-MS, FTIR, and ^{1}H NMR for chemical compositions, and confirmation of the functional groups and structure. The reaction between triglyceride (vegetable oil) and ethanol is shown in **Figure** 3.2.

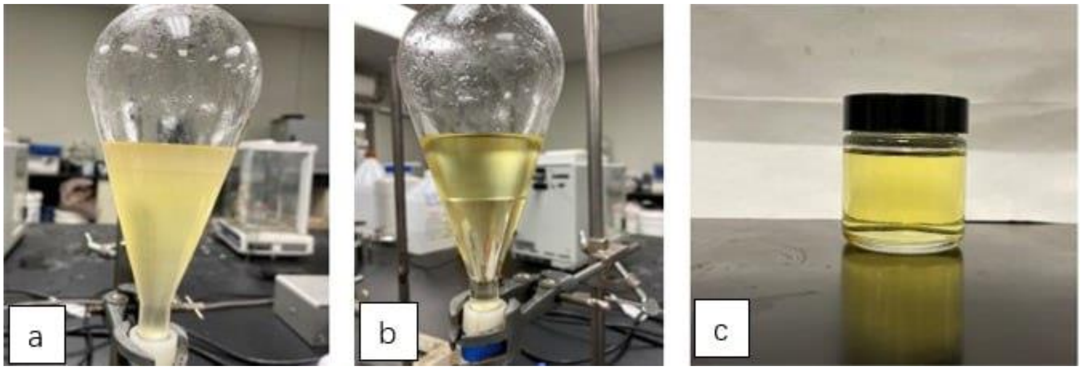


Figure 3.1: (a) The crude COEE product, (b) phase separation to remove glycerol, and (c) the obtained COEE.

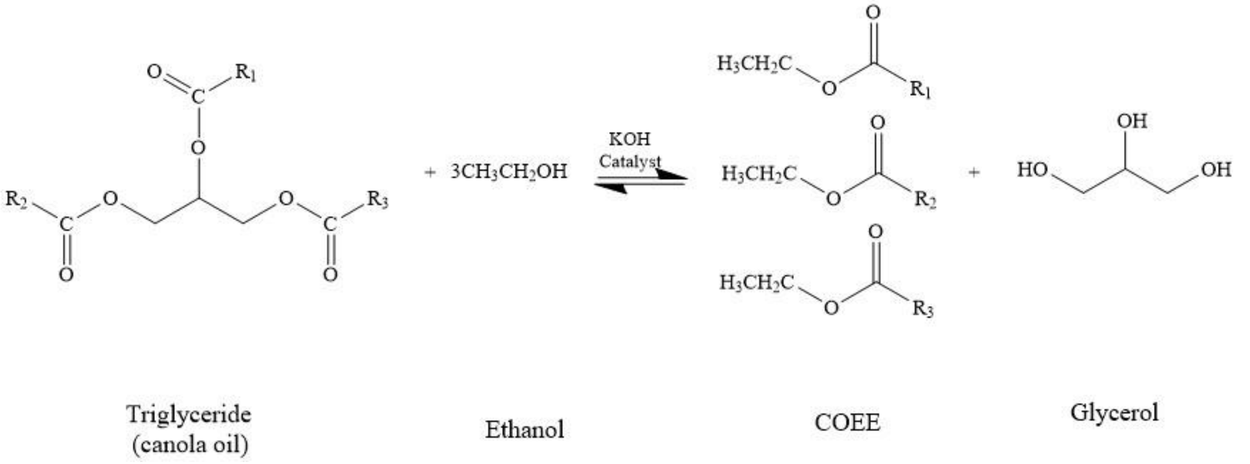


Figure 3.2: The 1st step transesterification reaction. Note: R_1, R_2, and R_3 are mixed vegetable oil fatty acids in canola oil: oleic acid (C18:1), linoleic acid (C18:2), and α-linolenic acid (C18:3).

3.2.2.2 The 2nd step transesterification

A representative reaction between COEE and TMP is shown in **Figure** 3.3. The reactor was carried out in a 500 mL three-neck round bottom flask reactor, equipped with a reflux condenser, thermometer, and magnetic stirrer. A vacuum pump equipped with an air relief valve was connected to the top of the condenser to adjust the vacuum level. A predetermined amount of TMP was added to the reactor, heated up to 80°C with continuous stirring at 1000 rpm under a 15 mbar vacuum inside a silicone oil bath. The temperature was maintained at 90°C for about 10 min to remove moisture in the hygroscopic TMP. A calculated amount of COEE according to the TMP/COEE molar ratio was then introduced into the reactor and the reaction mixture was heated to the desired temperature. After reaching the desired reaction temperature, the required amount of catalyst was charged to the reactor and the vacuum was turned on to avoid spilling over the reaction. The reaction conditions were varied based on the studied parameters, i.e. reaction time and temperature, catalyst loading, and TMP/COEE molar ratio. Referring to the optimal reaction conditions shown by Aziz et al. [27], the reaction parameters were varied in the following ranges: the temperature from 120°C to 160°C, the reaction time from 2 h to 7 h, the COEE/TMP molar ratio from 3.1:1 to 5:1, and the catalyst loading from 0.5% wt.% to 3% wt.%. Once the reaction was completed, the product solution was extracted using ethyl acetate and dried using anhydrous sodium sulfate. In order to remove the solvent, the final solution was dried by a rotary evaporator under reduced pressure at 80°C. All experiments were performed in triplicate and the results are presented as the average value with the respective standard deviation. The obtained COTMP ester product was dried using a vacuum rotary evaporator at 80°C and analyzed by GC-FID, FTIR, and ^{1}H NMR for chemical compositions, and confirmation of the functional groups and structure.

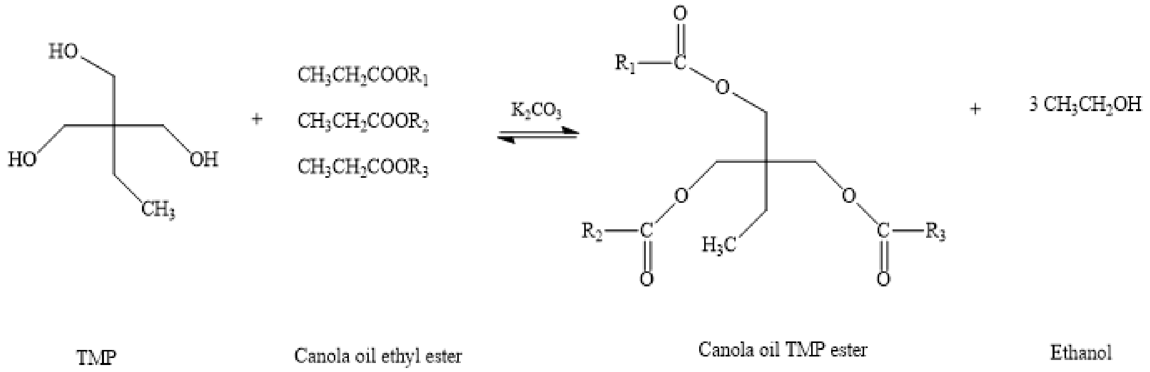


Figure 3.3: A representative reaction of the 2nd step transesterification reaction for the conversion of COEE to TMP ester. R_1, R_2, and R_3 are mixed vegetable oil fatty acids in canola oil: oleic acid (C18:1), linoleic acid (C18:2), and α-linolenic acid (C18:3).

3.2.3 Analysis

3.2.3.1 The 1st step transesterification reaction product analysis

The concentrations of COEE in the products from the 1st step transesterification experiments were quantified with a gas chromatography-mass spectrometry (GC–MS) system (Agilent 7890A GC/MSD-5977), equipped with a HP−5MS column (30 m × 0.25 mm × 0.25 μm), using pure helium as carrier gas at a flow rate of 1 mL/min. The temperature program involved holding the temperature at 50°C for 5 min, then heating it to 250°C at 10°C/min, and then finally holding at this temperature for 2 min. The GC-MS analysis of the obtained COEE products confirmed that there are no diglycerides and triglyceride present in the product, indicating complete conversion of the vegetable oil to FAEE. An internal standard method was implemented for the final product quantification using ethyl heptadecanoate, C19:0, as the internal standard [28]. Approximately 1 μL sample was injected into the GC. The injection was performed in split mode (1:1). The FAEE content (wt.%) was calculated using the following equation:

$$C\ (wt.\%) = \frac{[(\sum A) - A_{ei}]}{A_{ei}} \times \frac{C_{ei} \times V_{ei}}{m} \times 100\% \qquad (1)$$

where ΣA is the total peak area of all ethyl esters in the sample injected to GC-MS, A_{ei} is the peak area of the internal standard (C19:0) in the sample, C_{ei} is the concentration (mg/mL) of internal standard solution, V_{ei} is the volume (mL) of internal standard solution, and m is the mass (in mg) of the sample. In fact, the FAEE or COEE yield at the best condition (ethanol-to-oil molar ratio 10:1, 70°C, 2 h, catalyst loading 0.25% w/w) determined by the GC measurement or simply by mass recovery was 94.5% and 95.7%, respectively, hence very close. Therefore, for simplicity, in this part of work (the 1st step transesterification), the COEE yields reported in the figures were determined by mass recovery based on the experimental data, as defined by the following equation:

$$COEE\ yield\ (wt.\%) = \frac{Mass\ of\ ethyl\ esters\ produced}{Mass\ of\ vegetable\ oil\ used} \times 100\ wt.\% \qquad (2)$$

3.2.3.2 The 2nd step transesterification reaction product analysis

The compositions of COTMP ester products from the 2nd step transesterification reaction were analyzed by GC-FID (Shimadzu GC-2010 gas chromatograph) employing a method similar to that reported by Yunus et al. [29] Approximately 0.03 ± 0.005 mL of sample was taken in a 2 mL autosampler vial and diluted with 1 mL of ethyl acetate and then swirled to prevent sample degradation and reverse reactions. All samples were then derivatized using 0.5 mL of N,O-BSTFA to convert the polar -OH groups to more volatile silyl groups to facilitate elution and prevent column precipitation. HT5-SGE GC capillary column (12 m × 0.53 × 0.15 μm) was used for separation in the GC system. Before injecting the sample into the GC column, the prepared samples were heated for 10 minutes at a temperature of 50°C. The temperature program involved holding the temperature at 80°C for 3 min, then heating it to 380°C at 6°C/min, and then finally holding it at this temperature for 6 min. The detector and injector temperatures were set at 360°C and 300°C, respectively. The carrier gas used was helium with a flow rate of 26.7 mL/min, and the split ratio was 10:1. The run-time for each analysis was 53 min to ensure proper elution of esters. The esterification between COEE and TMP can produce three groups of esters, namely, monoester (ME), diester (DE), triester (TE), and ethanol as a by-product. Since the standards for TMP-based ME, DE, and TE were not available commercially, in this study, the COEE and TMP-based esters concentrations (wt.%) in the COTMP ester samples were calculated approximately based on the peak area percentages. It should be noted that no TMP was detected in all samples, suggesting complete conversion of TMP in the experiments. The formula for calculating the concentration percentage of COEE, ME, DE, and TE is as below:

$$Concentration\ (wt.\%) = \frac{Peak\ area\ of\ each\ component}{Total\ peak\ area} \qquad (3)$$

3.2.3.3 Fourball analysis

Four-ball wear tests were performed to investigate the performance of the obtained COTMP ester with different percentages of prophos900 and Zinc dialkyldithiophosphate (ZDDP) additives compared with a commercial lubricant oil (synthetic polymeric ester) in accordance with the ASTM D4172 method [30]. Four-ball wear tests are also called the wear preventive tests (hydrodynamic tests), in which Three balls are kept stationary in a ball pot, while the fourth ball rotates through a rotating spindle on these three balls. The lubricant oil sample volume used in each test was 10 ml. The test according to ASTM D4172 conditions were 40 kg load, an operating temperature of 75 ± 2°C, a rotational speed of 1200 rpm, and an operation time of 60 min.

3.2.3.4 Quench analysis

This test is based on the determination of lubricant cooling rate using ASTM D6600. According to this standard, the cooling property of the lubricant was done in a 2L beaker without stirring. In this test, the nickel alloy probe was heated inside a furnace to a temperature of 850 ± 2°C. Then the probe was transferred into a heat-treating oil. The temperature inside the probe assembly and the cooling times were recorded by the software at selected time intervals (60 s) to establish a cooling temperature versus time curve.

3.2.3.5 Biodegradability analysis

The biodegradability of COTMP ester is evaluated based on the oil remaining in the culture medium after the incubation of oil-degrading bacteria. In short, 1 wt.% of COTMP ester is loaded into minimal salt medium M9 (6 g/L Na_2HPO_4, 3 g/L KH_2PO_4, 5 g/L $(NH_4)_2SO_4$, 0.5 g/L NaCl) as sole carbon source and petroleum-based lubricant is used for comparison [31,32]. For degradation, a newly screened and isolated active oil-degrading bacterium was prepared in the laboratory. The oil-degrading bacteria are inoculated at the 1:100 ratios and the culture medium is incubated in a shaker at pH 7, 35°C, and 220 rpm. After the incubation, the medium is taken out from the incubator and centrifuged to remove the cell. The remaining oil in the culture medium is extracted with an equal volume of chloroform and quantified by the weight remaining after chloroform evaporation. The evaluation of the remaining oil is based on the initial amount of oil and the extracted oil with the following equation.

$$Remaining\ oil\ (\%) = \frac{m(extracted)}{m(initial)} \times 100 \qquad (4)$$

Where m(extracted) is the mass of the extracted oil from the culture medium and m(initial) is the mass of oil loaded into the culture medium at the beginning.

3.3 Results and Discussion

3.3.1 Results of the 1st step transesterification reaction

3.3.1.1 Effects of the ethanol-to-oil molar ratio

Five transesterification experiments were carried out by varying the ethanol-to-oil molar ratio between 7:1 and 12:1, while fixing the temperature and catalyst loading at 65°C and 1% by weight, respectively. **Figure** 3.4 shows the variation of COEE yield with ethanol-to-oil molar ratio and the reaction time. At all molar ratios, the COEE yield increased with time but leveled off at 2.5 h, suggesting equilibrium of the transesterification reaction at the time. At 7:1 molar ratio, the COEE yield was about 79 wt.% after 2.5 h reaction. The ester yield increased with increasing the ethanol-to-oil molar ratio but peaked at approximately 90% yield with the molar ratio of 10:1. A further increase in the molar ratio to 12:1 did not result in an increase in the ester yield, but a slightly reduced yield (89 wt.%). The reduction in COEE yield at a highly excessive ethanol-to-oil molar ratio (12:1) might be due to the separation difficulty of glycerol in the reaction system in the presence of a large amount of ethanol. Although an excess of alcohol for the vegetable oil transesterification reaction could thermodynamically or kinetically favor the conversion of tri-/di-glycerides to monoglycerides, the reverse reaction of esters and glycerol could also take place if the glycerol was not effectively removed from the reaction system, hence lowing the final esters yield [26,33]. Based on the results in **Figure** 3.4, the best alcohol-to-oil molar ratio and reaction time at 65°C appear to be at 10:1 and 2.5 h, respectively. As such, our further experiments were carried out under such conditions.

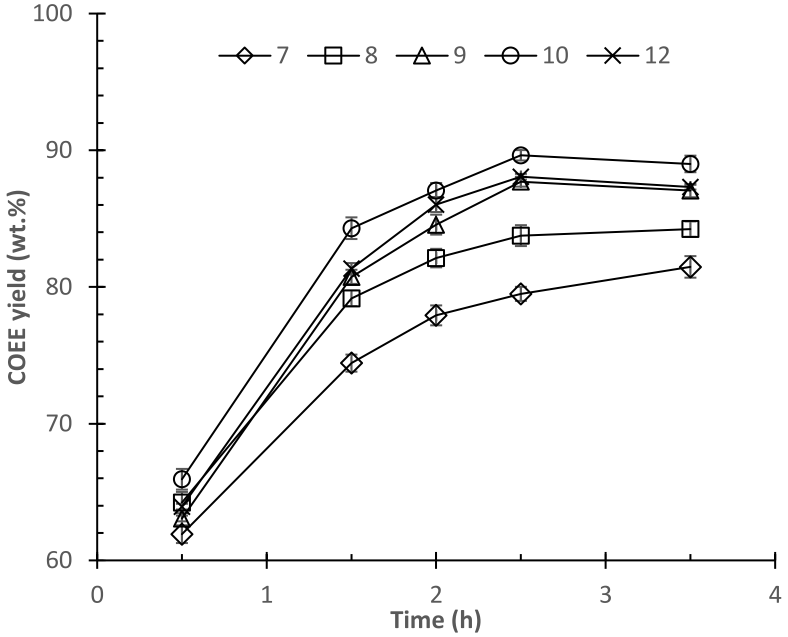


Figure 3.4: Effects of ethanol-to-oil molar ratio on COEE yield at different time intervals (Other conditions: KOH loading 1 wt.%; reaction temperature: 65°C).

3.3.1.2 Effects of the temperature

Although the transesterification reaction is an exothermic reaction (thermodynamically favorable at a lower temperature), an increase in temperature leads to an increase in the reaction rate constant, as confirmed in many other studies [34-37]. In this series of experiments, the effects of reaction temperature were investigated by changing the temperature from 40°C to 80°C, while the ethanol-to-oil molar ratio and reaction time were fixed at 10:1 and 2.5 h, respectively, and the catalyst loading was fixed at 1 wt.%, and the obtained COEE yield vs. reaction temperature was presented in **Figure** 3.5. As clearly shown, the COEE yield increased with increasing temperatures up to 70°C where the highest ester yield (90%) was obtained. The COEE yield decreased at temperatures higher than 70°C, which was likely due to the equilibrium shift of the transesterification reaction (slightly exothermic), thermodynamically unfavorable at higher temperatures. In addition, this reduced COEE yield at >70°C could also be due to the boiling of ethanol which led to an adverse effect on the reaction process [38]. Therefore, 70°C appears to be the best temperature for the transesterification of canola oil with ethanol.

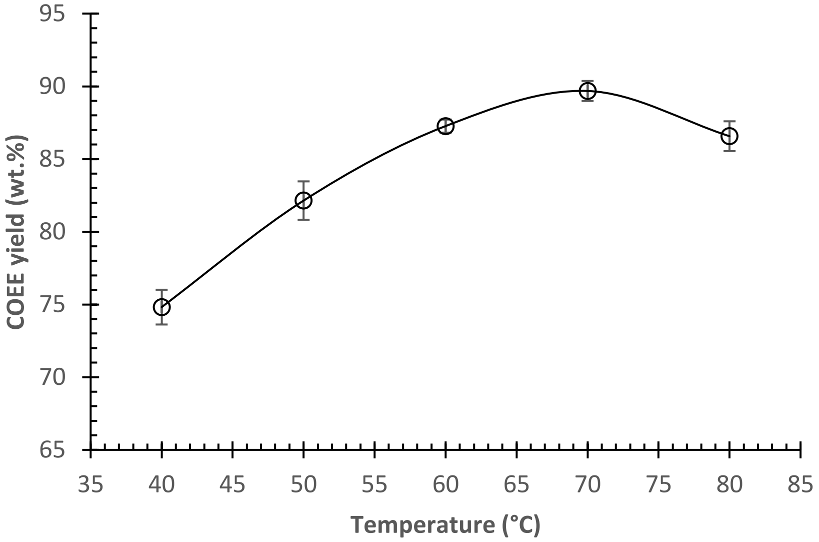


Figure 3.5: Effects of reaction temperature on COEE yield (Other conditions: KOH loading 1 wt.%; ethanol-to-oil molar ratio 10:1; reaction time: 2.5 h).

3.3.1.3 Effects of the catalyst loading

Catalyst loading is another critical reaction parameter for transesterification reactions: On one hand, the addition of more catalyst (commonly alkaline catalyst) compensates for the acidity caused by the free fatty acids and avoids catalyst deactivation, generally promoting the transesterification reaction [39,40]. However, an excess amount of KOH catalyst would lead to a lower biodiesel yield and quality due to undesirable saponification reactions, resulting in increased viscosity and the formation of gels [41]. These issues would hinder the glycerol separation and, hence, reduce the ester yield. On the other hand, an insufficient amount of catalyst resulted in the incomplete conversion of triglycerides into esters [42]. In this study, four different loadings of the KOH catalyst (0.2%, 0.25%, 0.5%, and 1 wt.%) were tested at a fixed ethanol-to-oil molar ratio of 10:1 and 70°C, but for a varying length of reaction time (1 h, 2 h, 3 h, and 4 h). As shown in **Figure** 3.6, the COEE yield increased markedly when increasing the KOH loading from 0.2 wt.% to 0.25% wt.%, but the yield remained almost no change when further increasing the catalyst loading to above 0.25 wt.%. The maximum COEE yield, 95.7%, was obtained with the catalyst loading of 0.25 wt.%, ethanol-to-oil molar ratio of 10:1, at 70°C for 2 h.

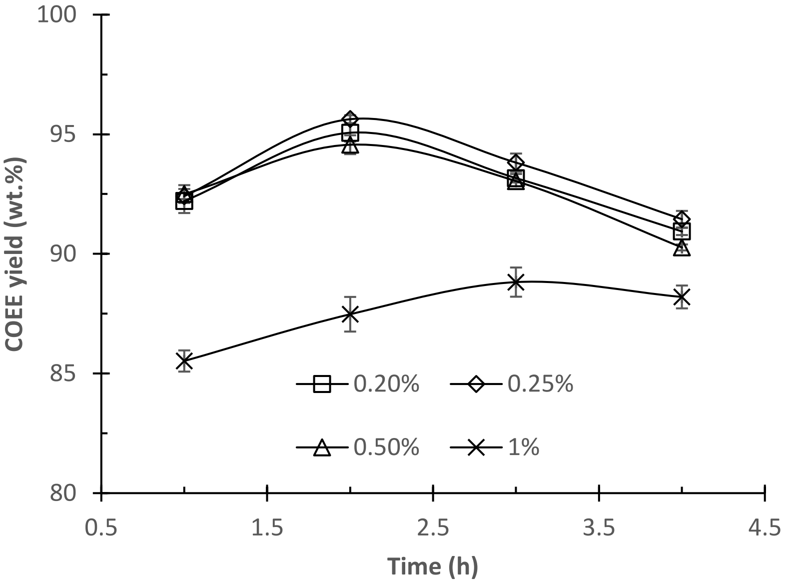


Figure 3.6: Effects of catalyst (KOH) loading on COEE yield (Other conditions: ethanol-to-oil molar ratio 10:1; reaction temperature: 70°C).

3.3.2 Results of the 2^{nd} step transesterification reaction

3.3.2.1 Effects of the temperature

As was discussed previously in Section 3.1.2 (**Figure** 3.5), reaction temperature could have mixed effects on the product yield of transesterification reaction due to its exothermic heat effect [43]. On one hand, increasing the reaction temperature would enhance the transesterification reaction rate, hence favoring the formation of ester [44]. In addition, a higher temperature led to a reduction of system viscosity, hence promoting the reaction by improving the mass transfer in the reaction system [45]. On the other hand, an increased temperature would also shift the reaction equilibrium to the reactants side, hence leading to a lower product yield. Moreover, the synthesis of TMP ester has commonly been performed below 160°C to avoid sublimation of TMP.

In this work, the effects of temperature on COTMP product yield/composition in the transesterification of COEE with TMP were examined at various temperatures: 120°C, 130°C, 140°C, and 150°C, all below 160°C, while fixing the other parameters as follows: COEE/TMP molar ratio of 3.9:1, K_2CO_3 catalyst loading of 1 wt.%, and the reaction time of 5 h, and the results are illustrated in **Figure** 3.7. The COTMP triester (TE) concentration was 38.5, 53.6, 44.8, and 36.9 wt.%, and the total concentration of TE/DE/ME esters was 50.4, 73.8, 53.4, and 49.3 wt.% at

120, 130, 140, and 150°C, respectively (**Figure** 3.7a). These results indicated that the yield of TE as well as the total yield of TE/DE/ME esters, increased with temperature up to 130°C, reaching the maximum values, then declined at a higher temperature, which was apparently due to the equilibrium shift of the transesterification of COEE with TMP reaction (exothermic) at higher temperatures, thermodynamically favoring the backward reactions that reverse the COTMP ester back to the COEE. These results are in good agreement with similar findings reported by Yunus et al. [46] in the transesterification of FA with TMP. Additionally, TMP would sublimate and COEE could also evaporate at high temperatures, resulting in an equilibrium shift to the reverse reaction and hence a reduced yield of COTMP esters product. Notably, a higher reaction temperature lead to discoloring of the COTMP ester product likely due to the impurities generated in the reaction (**Figure** 3.7b). Therefore, in further experiments, the reaction temperature was fixed at 130°C.

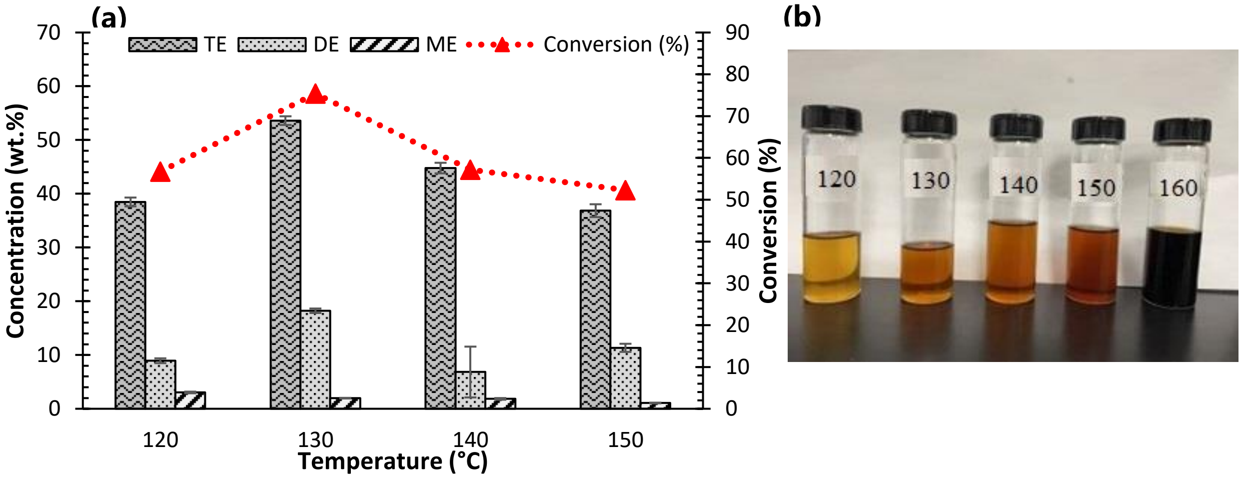


Figure 3.7: Transesterification of COEE with TMP at different reaction temperatures. (a) influence of reaction temperature on esters concentration in the final products. (b) Picture of the final product. (Other reaction parameters: molar ratio of COEE to TMP: 3.9:1; catalyst concentration: 1 wt.%; reaction time: 5h).

3.3.2.2 Effects of the catalyst loading

Alkali catalysts such as sodium methoxide, potassium hydroxide, and sodium hydroxide are more commonly used for transesterification reactions due to their ability to complete the transesterification reaction at a higher rate as well as high conversion efficiency [26,46-48]. In this work, potassium carbonate (K_2CO_3) was used as the catalyst for the 2nd step transesterification of

COEE with TMP, and the effects of the catalyst loading (wt.% of COEE-TMP reaction mixture) on the reaction were investigated by varying the mass ratio of K_2CO_3 to the COEE-TMP reaction mixture in the range of 0.5−3% w/w for a reaction time ranging from 2 h to 7 h, while other parameters such as temperature and COEE/TMP molar ratio were fixed at 130°C and 3.9:1, respectively. The concentrations of TMP triester (TE), TMP diester (DE), TMP monoester (ME), and total concentration of the COTMP esters in the final product are illustrated in **Figure** 3.8. As shown in **Figure** 3.8, at all catalyst loadings, the yield of TE and the total yield of TE/DE/ME esters increased with time, but peaked at around 4-6 h, then decreased after 6 h. It is also apparent that 1 wt.% catalyst loading led to the maximum concentration of TE in the final COTMP product (57 wt.%) and the maximum total concentration of all TE/DE/ME esters (81 wt.%).

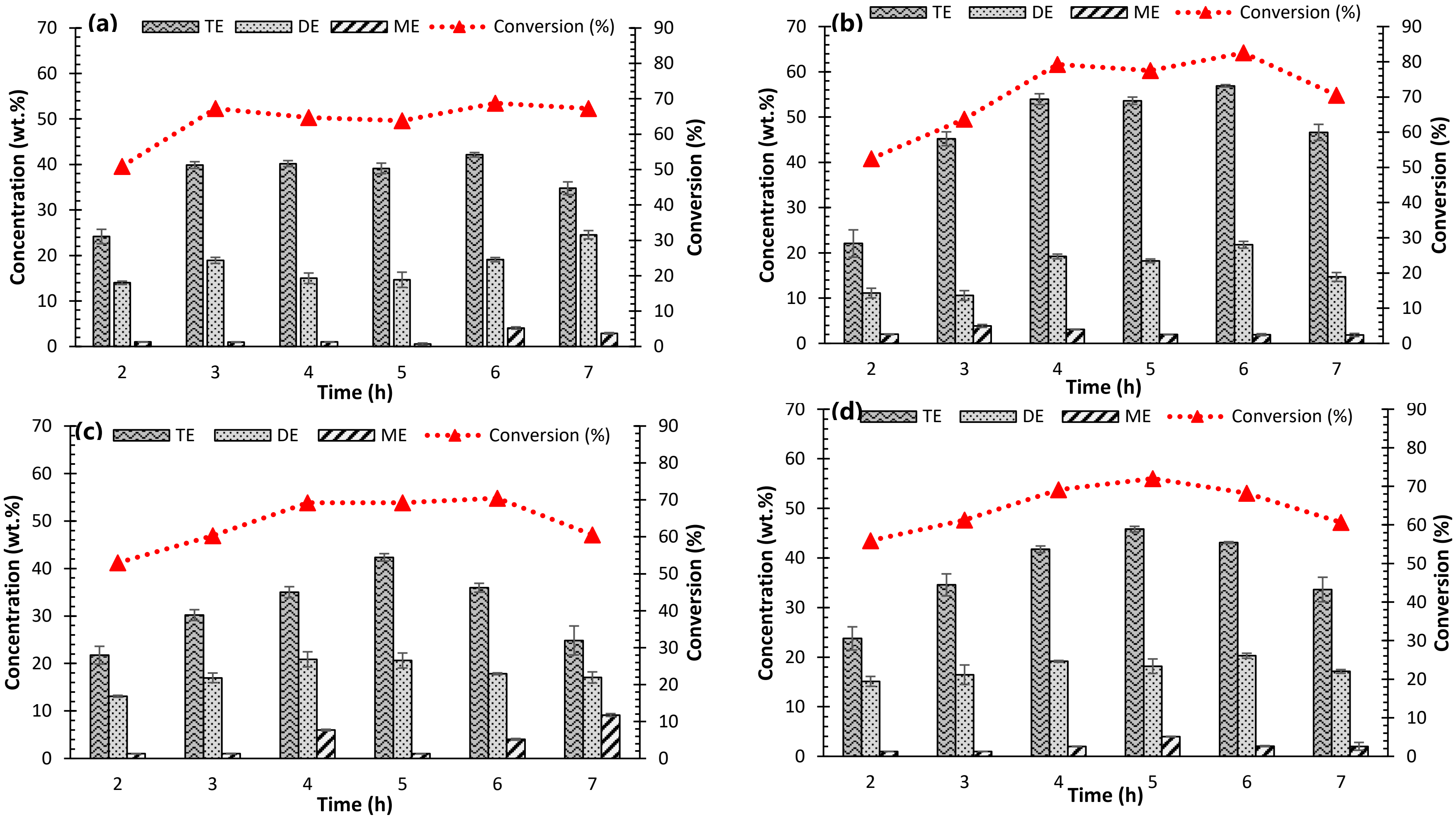


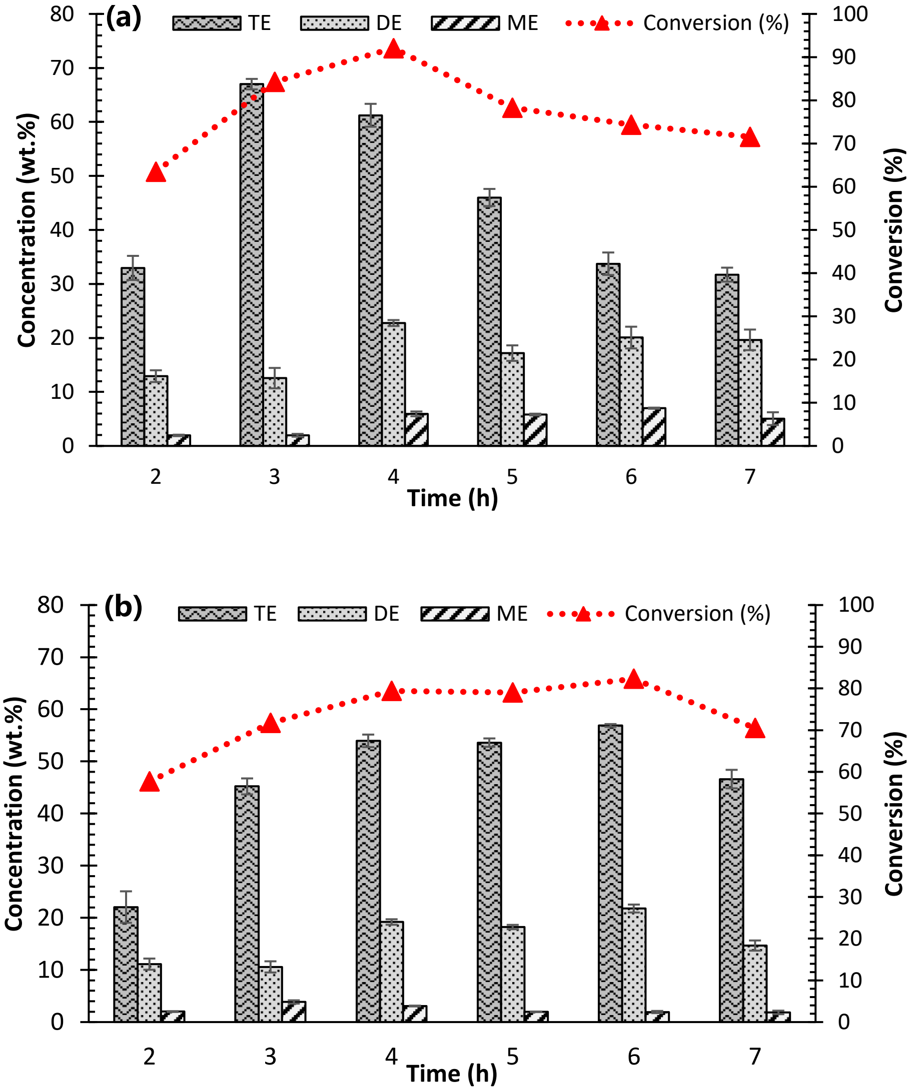
Figure 3.8: Influence of catalyst loading on transesterification of COEE with TMP: (a) 0.5 wt.%, (b) 1.0 wt.%, (c) 2.0 wt.%, and (d) 3.0 wt.% catalyst loadings (Other reaction parameters: COEE/TMP molar ratio: 3.9:1; reaction temperature: 130°C).

3.3.2.3 Effects of the canola oil ethyl ester-to-trimethylolpropane molar ratio and time

As transesterification reactions are reversible, it is expected that using one of the reactants in excess will promote the forward reaction. The stoichiometric molar ratio between the COEE and TMP is 3:1, as shown in **Figure** 3.3. To ensure complete TMP conversion, in this work, the effects of COEE/TMP molar ratio were investigated by reacting COEE with TMP at 130°C, 20 mbar vacuum, and 1 wt.% K_2CO_3 catalyst loading, with various COEE/TMP molar ratios: 3.1:1, 3.9:1, and 5:1, for a reaction time ranging from 2 h to 7 h. The concentrations of TE, DE, ME, and their total concentration in the produced COTMP product are presented in **Figure** 3.9. A higher COEE/TMP molar ratio produced a COTMP product with lower concentrations of TMP esters (TE, DE, and ME) which was expected owing to the presence of an increased amount of unreacted COEE in the final COTMP products, as evidenced by the higher concentration of COEE in the final product obtained at a higher COEE/TMP molar ratio, simply calculated by (100% – total concentration of TE/DE/ME). The concentration of the unreacted COEE in the final COTMP products was as high as 30-60 wt.% in the experiments at a COEE/TMP molar ratios of 3.9:1 or 5:1, compared with that (6-50 wt.%) in the product obtained with COEE/TMP molar ratio of 3.1:1. Therefore, the best COEE/TMP molar ratio was considered as 3.1:1.

The effects of reaction time (ranging from 2 h to 7 h) on the COTMP ester product compositions can also be observed in **Figure** 3.8 and **Figure** 3.9. Generally, the concentrations of TE, DE, and ME as well as their total concentration increased with time, but peaked at around 3-6 h, then decreased when further prolonging the reaction time. From **Figure** 3.9, the concentration of TE reached the maximum value of 67 wt.% after reacting for 3 h, while the total concentration peaked at 90 wt.% after the 4 h reaction. The concentration of TE decreased rapidly with a further increase in the reaction time to 4–7 h, possibly due to conversion of TE to DE/ME for a longer reaction time. A longer reaction time might also lead to a decrease in the total concentration of

TE/DE/ME due to side reactions such as polymerization, which was evidenced by the observation of the change of color of the final product from light yellow (short reaction time) to dark brown (longer reaction time). These results match well with those obtained by Li et al., [49] where the effects of the reaction time (1–5 h) on the yield of the TMP triester over the $[PyBS]_3PW_{12}O_{40}$ solid catalyst were investigated, and the TMP conversion and the yield of TMP triester reached the highest values of 95% and 88%, respectively, after reacting for 3 h.



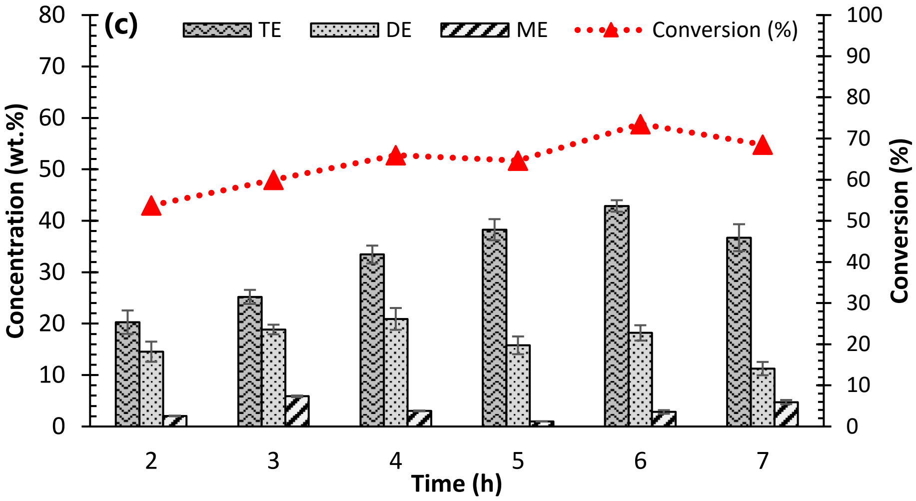


Figure 3.9: Influences of the COEE/TMP molar ratio and reaction time on transesterification of COEE with TMP: (a) 3.1:1, (b) 3.9:1, (c) 5:1 COEE/TMP molar ratio (Other reaction parameters: K_2CO_3 catalyst loading: 1 wt.%; reaction temperature: 130°C).

In this work, the maximum concentration of TMP triester (67 wt.%) in the final COTMP ester product was obtained with COEE/TMP molar ratio of 3.1:1 and 1 wt.% K_2CO_3 catalyst loading, at 130°C for 3 h, where the total concentration of TE/DE/ME esters was 82 wt.%. Based on the mass of COTMP ester product (12.75 g) obtained in this experiment under the best conditions, the remaining COEE concentration in the final product (18 wt.%) and the COEE mass (15 g) before the reaction, the COEE conversion in this experiment can be calculated to be around 85% using the following equation:

$$\text{COEE conversion } (\%) = \frac{M_{COEE} - (M_{COTMP} \times C_{COEE})}{M_{COEE}} \times 100 \qquad (5)$$

Where M_{COEE} is the mass of COEE before reaction (g), M_{COTMP} is the mass of COTMP ester product (g), and C_{COEE} is the remaining COEE concentration in the final product (wt.%).

It should be considered that the second transesterification reaction includes 3 reversible steps. In the first step, COEE will convert to TMP monoesters, then TMP monoester to TMP diesters, and finally to TMP triesters. For instance, as it can be seen in **Figure**

3.9a, the maximum concentration of TMP ester (including ME, DE, and TE) is about 90 wt.% after 4 h compared to 3 h reaction time which is 82 wt.%. However, because of the high concentration of DE (23 wt.%) in 4 h reaction time, the best condition is considered at 3 h reaction time which gave a higher concentration of TMP triester (~67 wt.%) and lower concentration of TMP diester (~13 wt.%). Therefore, finding the best conditions to obtain the high concentration of the TMP triester (not TMP monoester or TMP diester) was the main purpose of this study.

3.3.3 Characterizations of the reaction products

3.3.3.1 FTIR spectroscopy

Figure 3.10 shows the FTIR spectra of the COTMP ester product obtained at the best conditions (i.e., COEE/TMP molar ration: 3.1:1; temperature: 130°C; time: 3h; K_2CO_3 catalyst loading: 1 wt.%), TMP, crude canola oil, and COEE. The broad peak around 3250 cm^{-1} is attributable to the –OH stretch of TMP, while 2920 cm^{-1} and 2852 cm^{-1} bands indicate the presence of –CH stretch in all samples. The strong IR absorption peaks at around 1736 cm^{-1} and around 1165 cm^{-1} indicate the C=O ester group and C-O stretching, respectively, in the crude canola oil and the COEE and COTMP esters. The medium IR absorption peaks around 1370 and 1463 cm^{-1} indicate the presence of C-H bond in all samples. In addition, the strong peak around 722 cm^{-1} indicates the presence of double bond C=C in the crude canola oil, the COEE and COTMP ester, originated from the crude canola oil [50]. The peak around 1653 cm^{-1} is related to double bond C=C and is more evident in the COTMP ester than that in the crude canola oil or the COEE, possibly due to de-hydrogenation reaction creating new C=C bonds in the final product.

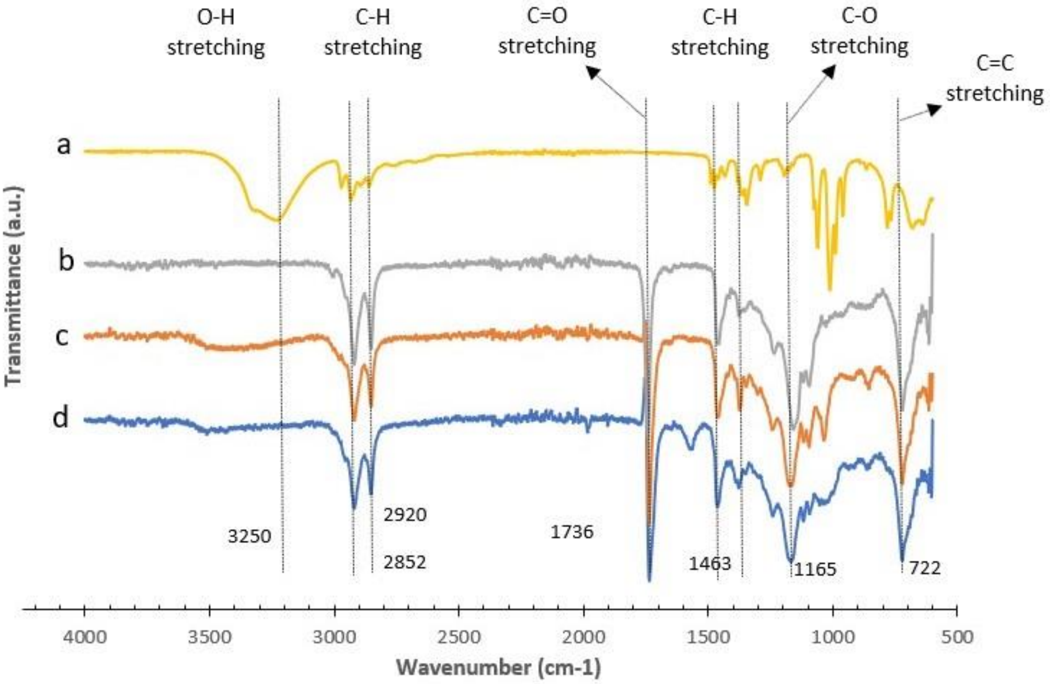


Figure 3.10: FTIR spectra of (a) TMP, (b) crude canola oil, (c) COEE, and (d) Canola oil TMP (COTMP) ester obtained at the best conditions.

3.3.3.2 ^{1}H NMR

^{1}H NMR spectrum was also used to confirm the structure of COTMP esters. A typical ^{1}H-NMR spectrum of the COTMP ester obtained at the best conditions (i.e., COEE/TMP molar ratio of 3.1:1, reaction time: 3 h, reaction temperature: 130°C, and catalyst loading: 1 wt.%) is shown in **Figure** 3.11. The ^{1}H-NMR spectrum shows peaks of olefinic hydrogens at 5.32 ppm, and a triplet of α-CH_2 protons at 2.27 ppm as well as a signal at 1.99 ppm related to methylene protons of the olefinic carbon chain, and a signal at 1.25 ppm from the β-carbonyl methylene protons, which are the characteristic peaks for the confirmation of olefinic structure present in the TMP ester. Another observed peak is at 0.85 ppm of terminal methyl protons in TMP ester backbone. However, when the hydroxyl group of TMP is attached to a fatty acid ethyl ester (COEE), the electron density around the protons in the TMP-CH_2 group was decreased. Therefore, the protons in that TMP-CH_2 group would shift to 4.00 ppm once TMP DE and TE formed. Hence, the ^{1}H-NMR spectrum characteristic peaks well confirm the structure of COTMP ester obtained from the transesterification of COEE with TMP.

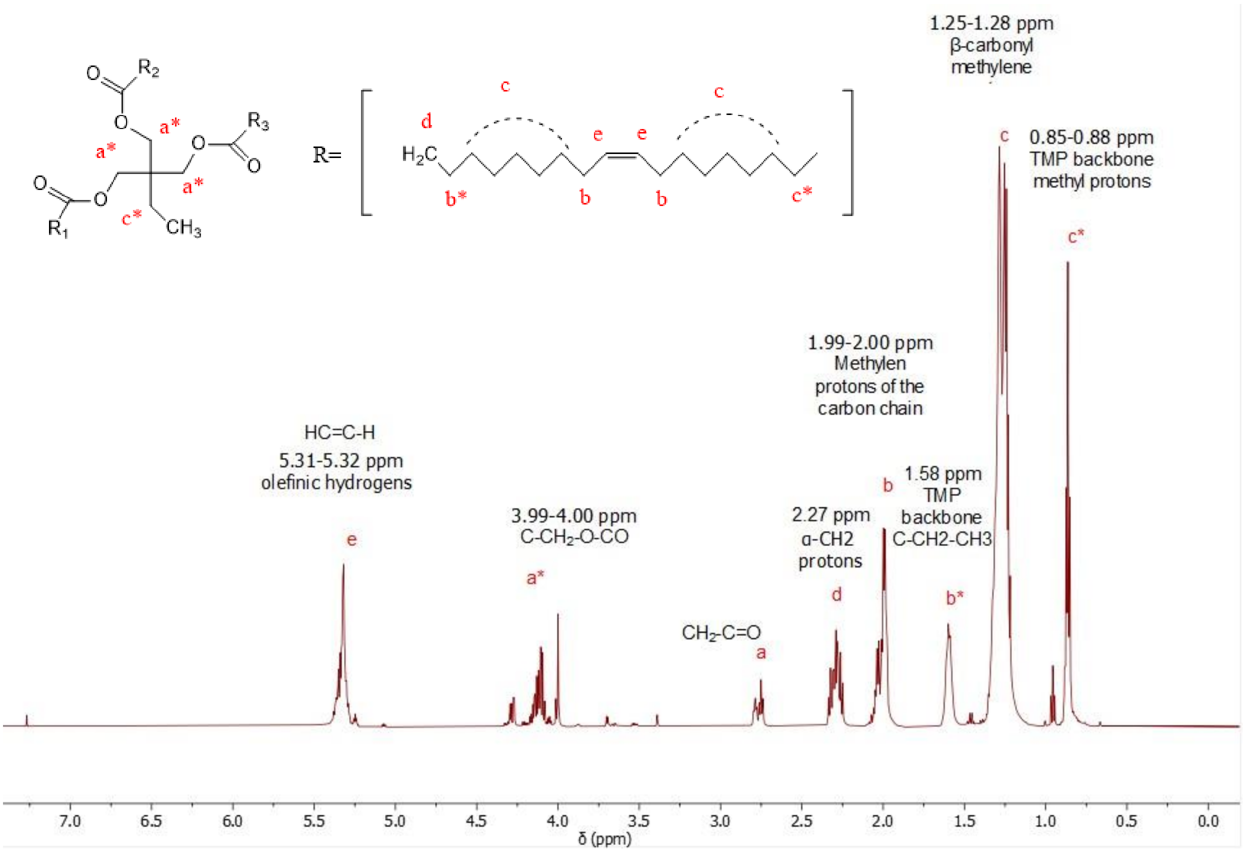


Figure 3.11: ^{1}H NMR spectrum of the COTMP ester obtained at the best reaction conditions. Note: R can be oleic acid, linoleic acid, and linolenic acid.

3.3.3.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted to record the weight loss of the crude canola oil, COEE, and COTMP ester when being heated to high temperatures due to dehydration and decomposition reactions, and the results are illustrated in **Figure** 3.12. As shown, the crude canola oil and COEE started to vaporize at approximately 300°C and 200°C, respectively, and both oils ended vaporization at approx. 500°C. For both COEE and COTMP ester samples, the mass started to decrease at approximately 200°C due to the vaporization, and the second weight-loss step started at approx. 370°C, which might be due to the presence of some unesterified residual canola oil in these ester samples. The COTMP ester started to vaporize at 200°C, same as the COEE ester, which should be due to the residual COEE in the final COTMP product (**Figures** 3.8 and 3.9), while its vaporization ending point was at approximately 700°C. compared with 500°C for the COEE ester, suggesting that the COTMP ester has a higher thermal stability than the COEE and the crude canola oil.

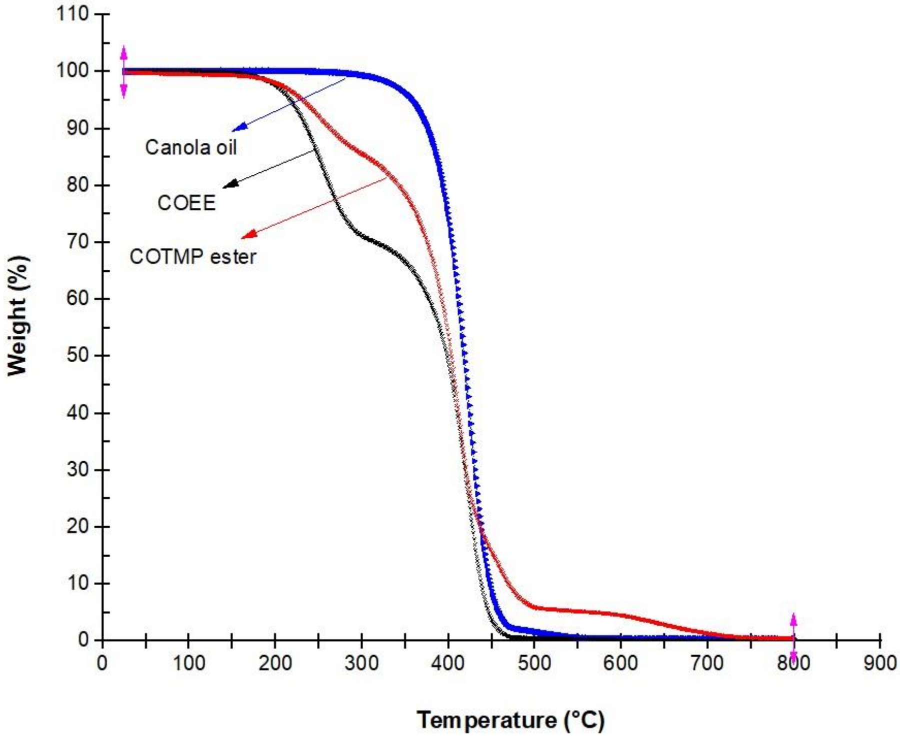


Figure 3.12: Overlay of TGA curves of the crude canola oil, COEE, and COTMP ester.

3.3.3.4 Physical properties

The average values with standard deviations of physical properties of the crude canola oil, COEE, and COTMP ester are compared with those of other lubricants in **Table** 3.1. Compared with the crude canola oil and COEE, the obtained COTMP ester product has a higher pour point (–9°C) and flash point (309°C), and a medium/acceptable viscosity index. The pour point of COTMP ester was –9°C which is better than that (2°C) of the palm kernel oil methyl ester-based TMP triester as obtained by Yunus et al. [46]. In addition, compared with a commercial lubricant oil (Lubricit TMP THCFA), the COTMP ester has better VI, which means it can operate in a wider temperature range.

It should be noted that the pour point of a lubricant could be greatly improved (up to –30°C) by adding pour point depressant (PPD) additives. Overall, considering the viscosity at 40°C (30.13 cSt), the obtained COTMP ester product can be an excellent ISO VG 32 hydraulic oil for industrial applications.

Table 3.1: Physical properties of the crude canola oil, COEE, and COTMP ester, compared with those of other lubricants.

Propertiy	**ASTM**	**Canola oil**	**COEE**	**COTMP ester**	**TMP triester**[a]	**Commercial lubricant**[b]
Viscosity @40°C (cSt)	D445	35.9± 0.11	19± 0.14	30.13 ± 0.12	39.7	37
Viscosity @100°C (cSt)	D445	8.2± 0.08	4.4± 0.06	6.27± 0.07	7.7	7
VI	D2270	216.8± 4.1	153± 3.8	167± 3.9	167	155
Pour point (°C)	D97	−18	−12	−9	2	-15
Flash point (°C)	D92-18	205± 1	270± 1	309± 1	310	300

a Yunus et al. (2003)
b Lubricit TMP THCFA

3.3.4 Lubricant testing

3.3.4.1 Fourball wear test

The wear scar diameter (WSD) and the friction force measurement results of the COTMP ester-based biolubricants with different additives (zinc additive, prophos 900, and ZDDP) are compared with those of a commercial lubricant oil (a synthetic polymeric ester) in **Table** 3.2 and **Figure** 3.13. The comparisons clearly indicate that the wear-preventive performance of the COTMP ester-based biolubricant is much better than that of the commercial lubricant oil**.** The above results suggest that the presence of long fatty acid carbon chains in the COTMP ester (C16-C18) could help to reduce the friction between the ball surfaces [51]. The results also show that the COTMP biolubricants with 2 wt.% of prophos900 or 1 wt.% of ZDDP exhibited the best performance in terms of the wear preventive properties.

Table 3.2: Wear preventive properties of the COTMP-based biolubricants and a

commercial lubricant oil.

Samples	Average WSD (mm)	Average Friction (N)	Coefficient of friction
COTMP ester	0.8 ±0.023	3.71± 0.2	0.023 ± 0.002
COTMP ester with 1% high zinc additive	0.79 ± 0.021	3.6 ± 0.3	0.023 ± 0.003
COTMP ester with 1% prophos900	0.79 ± 0.018	3.58 ± 0.15	0.023 ± 0.002
COTMP ester with 2% prophos900	0.42 ± 0.018	0.77 ± 0.2	0.005 ±0.001
COTMP ester with 3% prophos900	0.68 ± 0.019	1.63 ± 0.2	0.01 ± 0.002
COTMP ester with 0.5% ZDDP	0.76 ± 0.021	3.39 ± 0.1	0.021 ± 0.002
COTMP ester with 1% ZDDP	0.68 ± 0.017	1.26 ± 0.2	0.008 ± 0.001
COTMP ester with 2% ZDDP	0.73 ± 0.018	2.24 ± 0.2	0.014 ± 0.002
Commercial lubricant oil	1.24 ± 0.026	5.49 ± 0.3	0.034 ± 0.003

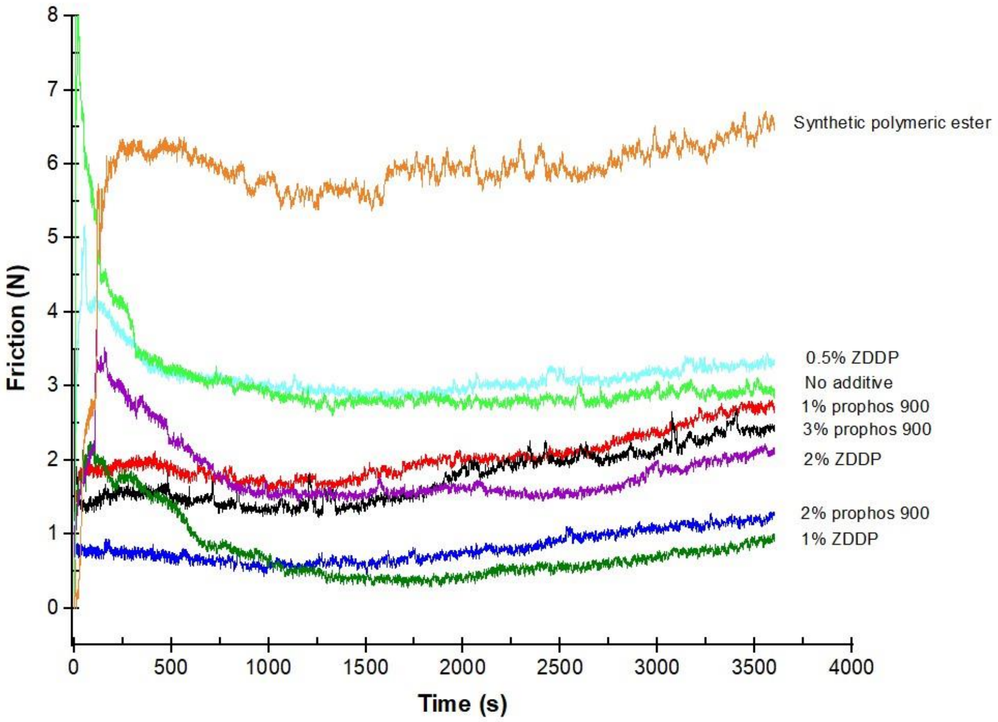
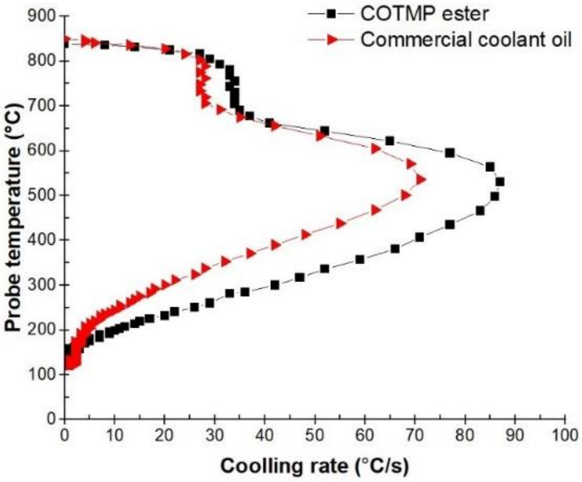


Figure 3.13: Fourball testing results of the COTMP ester-based biolubricants with different percentages of prophos 900 and ZDDP additives, compared with those of a commercial lubricant oil.

3.3.4.2 Quench test

Quench test measurements were performed for the COTMP ester and a commercial coolant oil (mixture of mineral oil with heat transfer additive). The typical cooling rate curves and some basic parameters derived from the curves for the two lubricant oils are shown in **Figure** 3.14. For both lubricants, the maximum cooling rate occurred at around 550°C. The results clearly show that the rate of cooling for the COTMP ester is higher than that of the commercial coolant oil almost in the entire temperature range tested. Thus, this result suggests that the COTMP ester can be a suitable candidate for coolant oils in industrial metalworking applications.



Basic parameters derived from the cooling curve.

	Unit	COTMP ester	Commercial coolant oil
T600	s	9.4	10.1
T400	s	12.6	13.3
T200	s	20.9	27.6
Vmax	°C/s	87	72
Tvmax	°C	553	543
V300	°C/s	42	20

Note: T600: time to 600°C; T400: time to 400°C; T200: time to 200°C; Vmax: maximum cooling rate; Tvmax: the temperature at maximum cooling rate; V300: the cooling rate at 300°C.

Figure 3.14: Typical cooling rate curves and basic parameters derived from the cooling curves for the COTMP ester and a commercial coolant oil according to ISO 9950. (Note: Commercial coolant oil is a mixture of mineral oil and heat transfer additive).

As a comparison with other studies, it is obvious in the figure that the time to reach 200°C for the COTMP ester is 20.9 s, which is lower than soybean oil (24 s) and Palm Oil (24 s) according to Komatsu et al. [52], and hydrogen-winterized soybean oil (27.5 s) according to Totten et al. [53] In another study, Otero et al. [54] investigated the quenching performance of different bioquenchants at 60°C bath temperature. The rate of cooling at 300°C in their study is between 8.18 to 19.31°C/s which is lower than the rate of cooling with the COTMP ester (42°C/s). These results indicate that the COTMP ester produced can be a good substitute for coolant oils in metalworking industries.

3.3.4.3 Variation of viscosity with temperature

The variations in dynamic viscosity with temperature for three different lubricants: adipate ester, a petroleum-based gear oil, and the COTMP ester using a Thermo

Scientific MARS iQ Air rheometer equipped with the P25 parallel plate in CR mode, are shown in **Figure** 3.15. With increasing the temperature, the dynamic viscosity decreases monotonically and this behavior of the variation of viscosity with temperature for all three lubricants obeys Reynolds' equation using the curve fitting method [55] given by Eq. (6).

$$\mu_0 = be^{-aT_A} \qquad (6)$$

where μ_0 is the dynamic viscosity at atmospheric pressure (Pa.s), a and b are constants, and T_A is the absolute temperature (°C).

The petroleum-based gear oil has the highest coefficient of viscosity (0.8 Pa.s at 20°C). In fact, it has the largest negative gradient values with temperature, indicating that it is more susceptible to temperature variations. Adipate ester and the COTMP ester have smaller values of dynamic viscosity because of their synthetic origin, and better stability than the petroleum-based gear oil as evidenced by their smaller values of negative temperature gradient of dynamic viscosity (less susceptible to temperature variations). It should be noted that the use of adipate ester is not ideal at temperatures above 140°C because evaporation of the lubricant occurs. Therefore, the COTMP ester has more promising properties than the other two lubricants tested here.

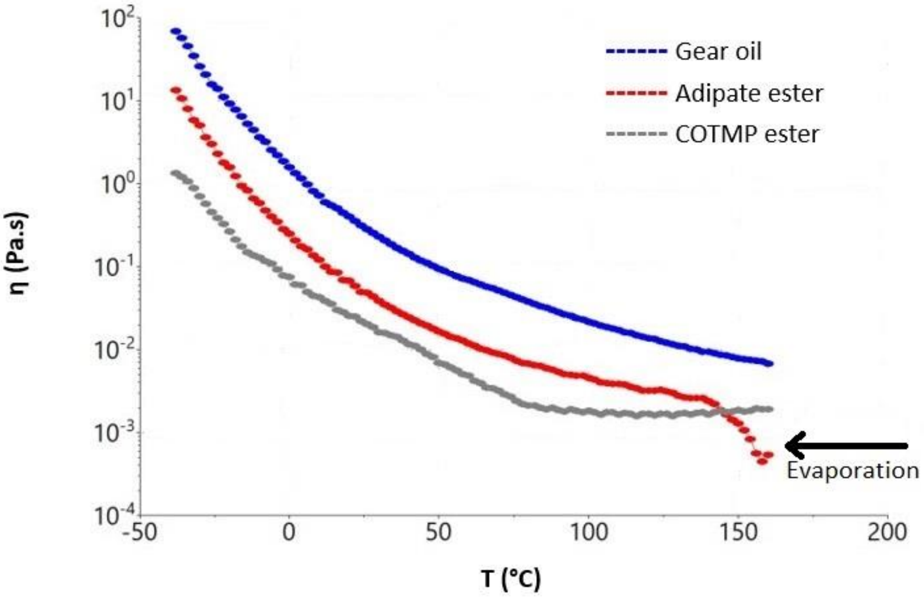


Figure 3.15: Variation of dynamic viscosity with temperature for adipate ester, a

petroleum-based gear oil, and the COTMP ester.

3.3.4.4 Variation of viscosity with shear rate

The variations of viscosity with the shear rate at 40°C and 100°C are shown in **Figure** 3.16. The dashed outline on the plot indicates the measuring range of the MARS iQ Air rheometer equipped with the P60 parallel plate. The valid data collected within the measuring range of the instrument indicate Newtonian behaviour across the examined shear rate range, which is expected for most pure lubricant oils. At a higher shear rate, there is no significant variation, and the dynamic viscosity is almost constant over the entire range of shear rates. The petroleum-based gear oil shows the largest variation of viscosity with shear rate and adipate ester and COTMP ester show the same smallest values which could be attributed to their synthetic origin. The lower the viscosity of the sample, the higher the shear rate that must be applied in order to overcome the low torque limit of the instrument. In addition, since these three lubricants have orders of magnitude differences in viscosity, the starting shear rate was adjusted to accommodate these differences. In essence, the petroleum-based gear oil @ 40°C can be measured with a starting shear rate of 0.1 s^{-1}, while the low viscosity of the COTM ester @ 100°C limits the starting shear rate to ~10 s^{-1}.

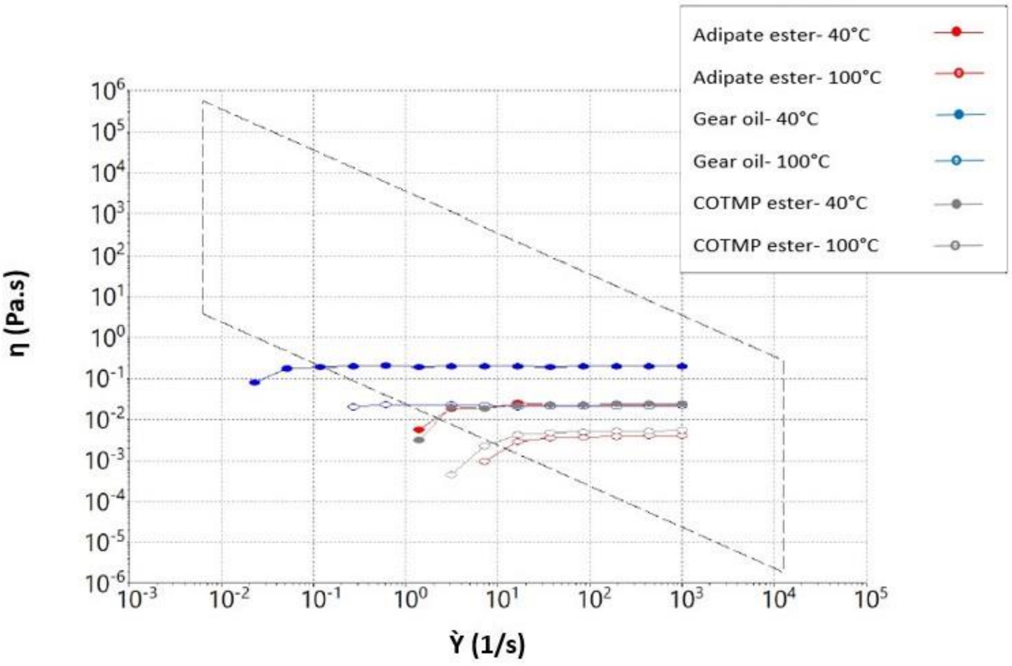


Figure 3.16: Variation of viscosity with the shear rate for adipate ester, a petroleum-based gear oil, and the COTMP ester.

3.3.4.5 Stribeck curve

Stribeck curves are given in **Figure** 3.17, which depicts the coefficient of friction as a function of sliding velocity at 40°C and 100°C for adipate ester, a petroleum-based gear oil, and the COTMP ester. At low speeds, there is a gradual increase in the frictional resistance of the system with increasing sliding velocity. In the static region, the system is susceptible to wear and high frictional resistance due to direct contact between the surfaces and poor lubrication. The value of the friction coefficient at the breakaway point indicates the amount of resistance from the contact to reach the set sliding velocity. In principle, up until the breakaway point, there is no macroscopic motion at the contact, and in this static regime, the sliding velocity as depicted in this Figure is due to the elastic deformation of the system. After the breakaway point at around 8 mm/s when increasing the sliding velocity the boundary layer gets thinner, leading to decreasing frictional resistance, as shown in **Figure** 3.17. The sudden increase and fall of friction coefficient close to 300 mm/s at 100°C were likely due to the stick-slip events caused by the spontaneous jerking motion. Therefore, the COTMP ester with smaller resistance to the initiation of motion demonstrated superior performance than adipate ester (diester) and the petroleum-based gear oil.

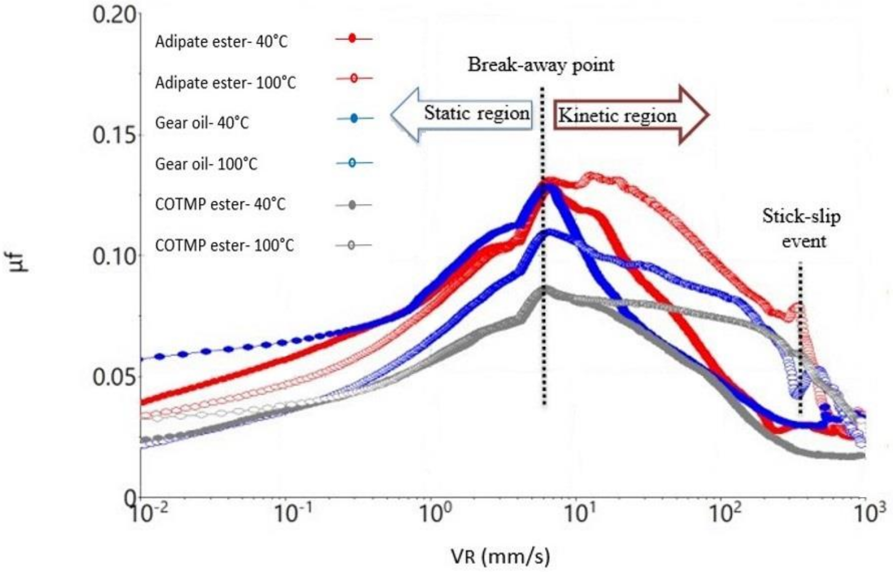


Figure 3.17: Stribeck curves depicting the coefficient of friction as a function of sliding velocity at 40 °C and 100 °C for adipate ester, a petroleum-based gear oil, and the COTMP ester.

3.3.5 Biodegradability testing

Biodegradation is the decomposition of organic matter by microorganisms such as bacteria and fungi [56]. Various *Citrobacter* sp. have shown their outstanding ability in degrading various light and heavy oils. Ibrahim shows that *Citrobacter freundii* HM-2 isolated from oil-contaminated soil can degrade more than 20% of used engine oil within 6 days [57]. Similarly, Morales-Guzmán et al. reported that *Citrobacter freundii* CCC4DS3 can degrade almost 20% of diesel within 48 h [58]. Moreover, Wang et al. indicate that *Citrobacter sp.* is one of the major contributors to their lipid-degrading microbe consortium, which can rapidly and effectively degrade more than 93% of waste kitchen oil within 5 days [59]. Besides its outstanding lipid hydrolysis activity, *Citrobacter* sp. WTB1 can produce biosurfactants which can further assist the suspension and degradation of the oil in liquid medium [60].

In our study, the biodegradability of the COTMP ester was evaluated based on the oil remaining percentage in the culture medium after incubating of oil-degrading bacteria for different lengths of time, compared with that of a petroleum-based lubricant oil (gear oil). For this purpose, the oil-degrading bacterium *Citrobacter* sp. WTB1 is isolated from a contaminated industrial lubricant sample. The LB-overnight cultured *Citrobacter* sp. WTB1 is inoculated into the above medium at the ratio of 1% (v/v %) and incubated in a shaking incubation at 35°C with a rotation speed of 220 rpm. The remaining oil is sampled every 24 h by centrifuging the medium at 4000 rpm to remove the bacterium from the medium and extracted by equal volume of chloroform for 2 mins. After the extraction, the chloroform was separated from the water phase and evaporated. The remaining oil is quantified by the weight remaining after chloroform evaporation.

As one can see in **Figure** 3.18, after 48 hours, nearly 44 wt.% of the COTMP ester was degraded, compared to only 6 wt.% degradation for the gear oil. The remaining percentage of the COTMP ester decreased significantly to 10 wt.% after 144 h incubation, compared with 84 wt.% oil remaining for the gear oil at the same time. The results indicate that the COTMP ester has excellent biodegradability in a short time, which makes it a promising biolubricant.

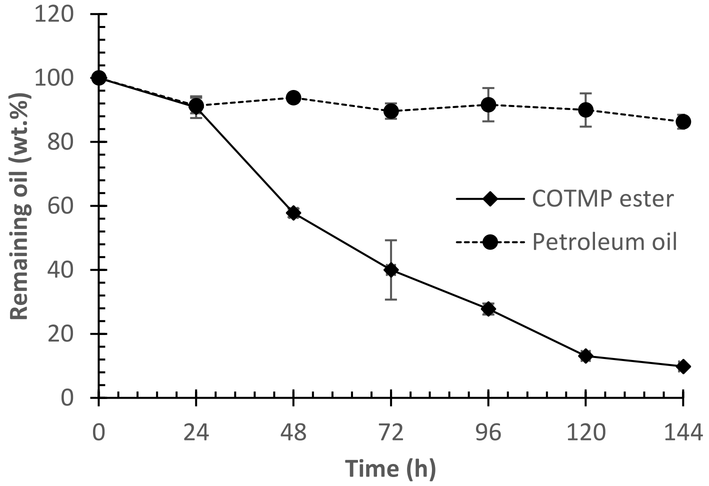


Figure 3.18: The remaining oil percentage vs. incubation time in the culture medium.

The turbidity (OD600) of the culture medium can be used to estimate cell growth according to Martinez & Déziel [61]. It is noteworthy that the emulsion of the oil could affect the measurement of the OD600, hence the OD600 might not strictly represent the growth of the bacteria population. However, the emulsion of the oil and the turbidity of the medium are usually caused by the enzymes and other emulsifiers secreted by the bacteria, thus the OD600 value can still be considered a result of cell growth and metabolism. **Figure** 3.19 indicates that the OD600 of the culture medium in the presence of the COTMP ester increased to about 2 after 144 h incubation, while it remained almost constantly at < 0.2 for the gear oil.

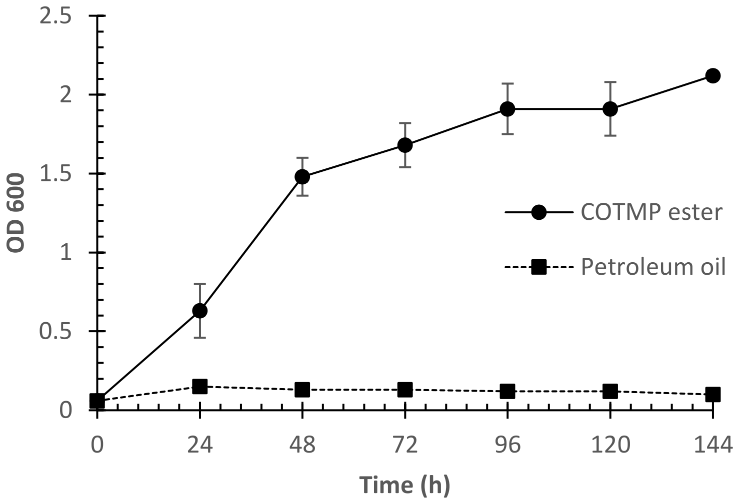


Figure 3.19: The OD600 (turbidity) of the culture medium vs. incubation time.

3.4 Conclusions

The present work demonstrated the synthesis of bio-based canola oil TMP (COTMP) ester through a two-step transesterification-transesterification process using ethanol (KOH catalyst) and TMP (K_2CO_3 catalyst), respectively. Effects of various parameters in both steps were studied parametrically, and the best reaction conditions (temperature, the reactants molar ratio, time, and catalyst loading) were determined to be 70°C, 10:1, 2 h, 0.25 wt.% and 130°C, 3.1:1, 3 h, 1 wt.% for the 1st step transesterification and the 2nd step transesterification reaction, respectively. The final COTMP ester product obtained at the best conditions contains 67 wt.% TMP triester and 82 wt.% total concentration of TE/DE/ME and has a Pour point at –9°C, a Flash point at 309°C, and kinematic viscosities of 30.13 cSt @ 40°C and 6.27 cSt @ 100°C. In addition, the obtained COTMP ester product with 2 wt.% of prophos900 as additive exhibits perfect wear preventive performance than other samples with WSD of 0.42 mm. Moreover, the additive-free COTMP ester exhibits complete quenching performance, superior rheological and tribological properties over a commercial lubricating oil, as well as excellent biodegradability (90 wt.%) after 144 h.

3.5 References

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Chapter 4

4 Preparing vegetable oils-based metalworking fluids by a hydrolysis-esterification two-step process

Abstract

Oil-soluble esters of free fatty acids were synthesized with a 2-step process including the first step of reacting vegetable oil with water in the presence of sulfuric acid and p-Toluenesulfonic acid as a catalyst, followed by removing water and glycerol, and the second step of reacting the obtained free fatty acids with various polyhydric and fatty alcohols. The best conditions were 190°C, 6 h, 30 to 1 water to oil molar ratio, 5 wt.% PTSA catalyst loading in the hydrolysis reaction (the 1st step), and 150°C, 10 h, 4 to 1 fatty acid to trimethylolpropane molar ratio, 1 wt.% PTSA catalyst loading in the esterification reaction (the 2nd step). Under the best conditions, the process achieved the final product with the 87% yield of free fatty acid trimethylolpropane ester and 82 wt.% conversion of free fatty acid, respectively. Different esters were made concurring to the aforementioned conditions with distinctive polyhydric and fatty alcohols. Hydrolysis reactions facilitated by catalysts offer an alternative approach to traditional hydrolysis in supercritical conditions, enabling efficient substrate conversion under milder operating conditions. Furthermore, the inclusion of the obtained esters mixed with base oil and additives produced bio-based metalworking fluids with exceptionally lubricant performance in wear resistance, with a wear scar diameter of 0.33 mm.

4.1 Introduction

Lubricity and anti-wear properties, along with coolant performance, stand as pivotal considerations for numerous industries, particularly metalworking companies [1-4]. Currently, the prevalent approach within the lubrication sector involves blending various additives like triarylphosphates, zinc dialkyldithiophosphate (ZDDP), or zinc di-thiophosphate (ZDTP) with a base oil to mitigate wear characteristics. Nevertheless, as per technical data sheets of lubricants, wear scar diameters, per ASTM D4172 standards, often exceed 0.45 mm at best. [5]. Moreover, due to the adverse environmental impact of ZDDP, the quest for lubricants with reduced wear scar diameter, without ZDDP/ZDTP, while delivering equivalent or superior protection to metalworking systems is imperative [6].

Synthetic esters have long found applications in various lubrication fields, encompassing hydraulic fluids, fire-resistant hydraulic fluids, maintenance oil, metalworking fluids, drill oils, compressor oils, automotive lubricants, industrial gear lubricants, turbine lubricants, industrial chain lubricants, and various greases. These esters offer an array of benefits, including low volatility, high viscosity indices, high flash points, low pour points, excellent thermo-oxidative stability, remarkable lubricity, and biodegradability, making them environmentally conscientious and resource-efficient choices [7-11].

Esters exhibit inherent dipole properties due to the electronegativity of oxygen, which enables positively charged sites on metal surfaces to bind with negatively charged oxygen. Therefore, esters have the natural affinity to provide partial protection against friction and wear in mixed or boundary lubrication conditions [12,13]. Consequently, esters can be viewed as friction enhancers capable of reducing wear and the coefficient of friction, particularly under moderate load conditions [14,15].

Various processes are currently employed to produce diverse esters suitable for a range of applications [16]. The utilization of methanol or ethanol in the transesterification reaction is a widely adopted approach for ester production [17]. However, the common practice of utilizing methanol or ethanol in an industrial-scale ester synthesis via transesterification reactions has certain drawbacks, such as corrosion issues in industrial equipment (using methanol) and the challenging separation of glycerol from ethyl esters [18,19]. Additionally, methyl/ethyl esters derived from vegetable oils tend to exhibit poor thermo-oxidative stability, a crucial consideration in metalworking systems [19,20].

Considerable research effort has been dedicated to exploring methods for ester production. Notably, U.S. Pat. No. 5908946 has explored the production of linear monocarboxylic esters through transesterification of vegetable oils or animal fats with low molecular weight monoalcohols, catalyzed by substances like zinc oxide (ZnO), mixtures of ZnO and aluminum oxide (Al_2O_3), and zinc aluminate ($ZnAl_2O_4$). This process is a continuous/discontinuous transesterification of the vegetable oils with alcohols on a fixed bed/autoclave at temperatures ranging from 170 to 240°C and reactor pressures below 100 bar which results in 80-95 % of conversion rates [21]. Meanwhile, U.S. Pat. No. 9,850,444 B2 has described the synthesis of unsaturated polyol esters via transesterification, highlighting the necessity for industrial lubricants that enhance lubrication and reduce wear properties. It indicated wear scar diameters of 0.74, 0.55, 0.67, and 0.54 mm under conditions of 40 kg load, 60 min time, 1200 rpm rotation speed, and a temperature of 75±1°C for 5 PE- 9DDAME, high oleic canola oil, commercial TMP oleate (Synative® ES 2964), and Afton Actralube 8330, respectively [22].

Another avenue for ester preparation involves the hydrolysis-esterification of vegetable oils and animal fats. The hydrolysis of vegetable oils, though feasible, becomes cost-prohibitive on an industrial scale due to high-temperature reactions. To address this, researchers have explored the hydrolysis of vegetable oils to free fatty acids (FFAs) in the presence of solid acid catalysts, necessitating further chemical modification to enhance thermal stability and lubricity [23-25].

For instance, free fatty acids (FFAs) can be obtained through the hydrolysis of vegetable oils in sub- and supercritical water at temperatures above 220°C and the corresponding water vapor pressure [26,27]. However, this process is not economical on an industrial scale due to high-temperature reactions (up to 350°C). Satyarthi et al. [28] discussed the hydrolysis of vegetable oils and fats to free fatty acids (FFAs) in the presence of solid acid catalysts like Fe-Zn DMC, sulfated zirconia, AmberlystTM70 (macroporous polymeric resin), zeolite H-Y (SiO_2/Al_2O_3 = 5), zeolite H-β (SiO_2/Al_2O_3 = 28), $MoOx/Al_2O_3$(supported oxide), and zeolite SAPO-11. This process is a batch process in a Teflon-lined stainless-steel reactor with a reactor temperature in the range of 180-200°C, oil: water molar ratio of 1: 20, 5 wt.% catalyst loading, and 8 h reaction time which results in 98 % conversion rate with the DMC catalyst. However, the DMC catalyst is rather expensive and not feasible for industrial-scale applications [29]. In addition, the FFAs obtained from the hydrolysis of vegetable oils still need further chemical modification to achieve high thermal and oxidative stability, excellent lubricity, and cooling performance. This entails esterification of FFAs with polyol alcohols, such as neopentyl glycol (NPG), trimethylolpropane (TMP), or pentaerythritol (PET) [30,31].

Motivated by these considerations, this study seeks to develop an enhanced anti-wear biolubricant through a low-temperature hydrolysis reaction, followed by the conversion of FFAs into complex esters using polyhydric or fatty alcohols. Canola oil is selected as the base, given its abundance, high oleic acid content, and potential to enhance anti-wear properties [19,32]. Additionally, PTSA, an organic compound with low health hazards, is selected as a catalyst [33,34].

This research aimed to synthesize biodegradable esters, compatible with mineral or synthetic oils, and their combination with base oils and appropriate additives demonstrates exceptional wear and friction properties, bolstering the performance of anti-wear and coolant operations in metalworking systems. The study meticulously explored the reaction conditions, including catalyst loading, reactant molar ratio, reaction temperature, and reaction time in both hydrolysis-esterification steps. The analysis of the ultimate complex esters encompassed GC-FID, FTIR, and ^{1}H NMR techniques. Additionally, comprehensive evaluation of the physicochemical attributes, rheological and tribological behavior, as well as the four-ball of the final product, was conducted to ascertain its suitability for biolubricant applications.

4.2 Materials and Methods

4.2.1 Materials

Analytical grade n-heptane, toluene, isopropyl alcohol, pyridine, glycerin, concentrated sulfuric acid (98%), PTSA, anhydrous sodium sulfate (Na_2SO_4, purity >99%), N-methyl-N-trimethylsilyltrifluoracetamide (MSTFA) (GC grade), pentaerythritol (PTE), polyethylene glycol (PEG, MW: 300), isotridecanol, adipic acid, Monoolein (1-Mono [cis-9-octadecenoyl]-racglycerol), diolein (1,3-Di [cis-octadecenoyl]glycerol), and triolein (1,2,3-Tri [cis-octadecenoyl]glycerol) were obtained from Sigma-Aldrich and used as received. Commercial-grade Canola oil was purchased from a local grocery store. 2-ethyl-2-hydroxymethyl-1,3-propanediol (TMP) (assay > 98%) was supplied by Progressive Industrial Fluid Ltd. For the gas chromatography (GC-FID) analysis, 1,2,4-Butanetriol and tricaprin as internal standards, were purchased from Sigma-Aldrich.

In this study, the first step involved the converting of vegetable oil into FFAs using the hydrolysis process, followed by several purification steps to achieve pure FFAs [28]. The obtained pure FFAs were reacted with TMP to synthesize TMP ester in the 2nd step through the esterification reaction. The influence of various reaction parameters on the conversion of canola oil to FFAs in the 1st step hydrolysis reaction and FFAs to TMP ester in the 2nd step esterification reaction was evaluated to determine the best reaction conditions.

Thermogravimetric analysis (TGA) of samples including crude canola oil, FFAs, and TMP ester was recorded on a Perkim-Elmer TGA system by heating the samples in 50 mL/min nitrogen at 10°C/min [35].

The viscosity, viscosity index (VI), pour point, flash point (open cup method), and Fourball of the final TMP ester were measured using ASTM methods D445, D2270, D97 (Pour Point Tester manufactured by HK Petroleum Co., China), D 92-18 (Flash Point Tester manufactured by the HK Petroleum Co., China), and D4172, respectively [36-38].

The ^{1}H NMR spectra of the crude canola oil, FFAs, and TMP ester were collected using a Bruker® spectrometer, model Ultrashield (300 Hz). Chemical shifts present on each spectrum were referenced in parts per million (ppm) relative to the signal for tetra-methyl silane (TMS). All samples were dissolved in deuterated chloroform ($CDCl_3$) by directly transferring an aliquot of approximately 200 µl of each sample into 5-mm NMR tubes and the volume was completed to 600 µl with $CDCl_3$ containing 0.05% TMS [39].

Four-ball wear tests were performed to investigate the performance of the obtained lubricants by blending various esters obtained by esterification of FFAs with polyhydric/fatty alcohols, a mineral base oil, and suitable additives and compared with a commercial lubricant oil in accordance with the ASTM D4172 method [40]. The Fourball test measures the wear caused by the rotation of the upper ball on three fixed balls inside the cup. The test conditions in the Fourball test are a 40 kg load, an operating temperature of 75 ± 2°C, a rotational speed of 1200 rpm, and an operation time of 60 min. The lubricant oil sample volume used in each test was 10 ml [41].

Rheology analysis of the COTMP ester was done using a Thermo Scientific MARS iQ Air rheometer equipped with the P25 parallel plate for investigation of the behavior of dynamic viscosity against shear rate and temperature ramp in CR mode [18,42].

4.2.2 Methods

4.2.2.1 The 1st step hydrolysis reaction

Hydrolysis of vegetable oils or fat, of which the reaction scheme is illustrated in **Figure** 4.1, was carried out in a 25 ml Teflon-lined stainless-steel reactor (**Figure** 4.2) by taking a known quantity of vegetable oil (5–20 g), with a water-to-oil molar ratio of (10~50): 1 in the presence of sulfuric acid or PTSA as a catalyst. The reaction was conducted at 160–210°C and an autogenous pressure for a specific period of time (5–10 h). Upon completion of the reaction, the reactor was cooled to 25°C. The reaction product consists of two layers, an upper oily layer of fatty acids and mono-, di, and triglycerides, and a lower, aqueous layer of water and glycerol. These layers were separated by decantation. Any trace of water in the upper layer was removed by distillation. On an industrial scale, the product can transfer into a conical tank lifted from the ground which acts as a separatory funnel. Allowing for the separation of the mixture of glycerol and water from free fatty acids. Thereafter, by using heat or a special centrifuge, for example, a Disc Stack Centrifuge, the pure product free fatty acids from vegetable oil can be obtained [43]. All experiments were performed in triplicate and the results are presented as the average value with the respective standard deviation. The product was analyzed by GC-FID, titration, FTIR, and ^{1}H NMR spectroscopy for chemical compositions and confirmation of the functional groups and structure.

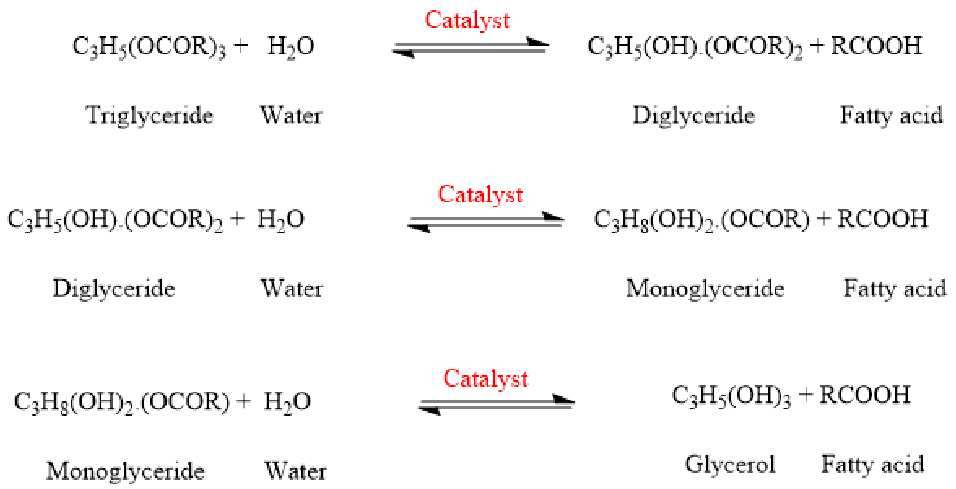


Figure 4.1: The first step hydrolysis reaction between triglyceride and water. R is mixed fatty acids in canola oil: oleic acid (C18:1), linoleic acid (C18:2), and α-linolenic acid (C18:3).

Figure 4.2: Schematic of the reactor used for the hydrolysis reaction.

4.2.2.2 The 2nd step esterification reaction

The 2nd step esterification experiments were conducted according to the methodology outlined by Rani et al. [44] with some modifications. FFAs (obtained from the 1st step hydrolysis of canola oil) were mixed with TMP at a molar ratio of (3-5):1 in a three-neck round bottom flask, equipped with a thermometer and Dean-Stark apparatus to facilitate the in-situ removal of water under vacuum. PTSA catalyst and toluene solvent were added to the mixture, which was then heated at 120-160°C for 4-13 h with continuous stirring. The product, canola oil TMP (COTMP) ester, was neutralized with 5% sodium bicarbonate ($NaHCO_3$) solution, and sodium chloride solution (26%) and extracted with ethyl acetate. The ethyl acetate-extracted product was kept overnight by adding anhydrous sodium sulfate to absorb residual water. The product was then filtered by Whatman No 1 filter paper and the solvent used was removed by rotary evaporator under reduced pressure at 80°C. All experiments were performed in triplicate and the results are presented as the average value with the respective standard deviation. The COTMP ester was analyzed using GC-FID, FTIR, and ^{1}H NMR. The reaction between obtained FFAs from canola oil and TMP is shown in **Figure** 4.3.

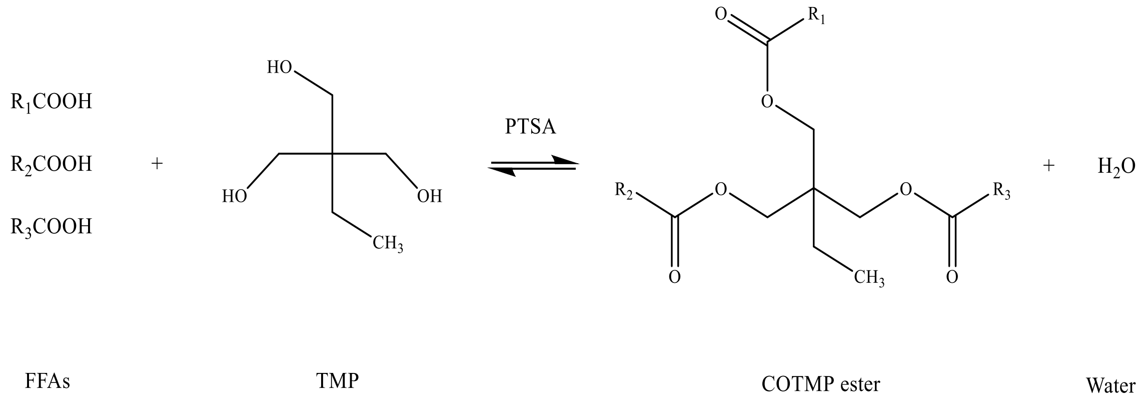
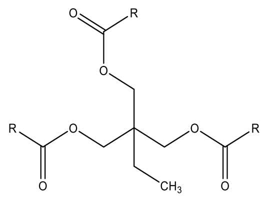
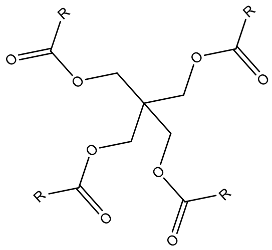
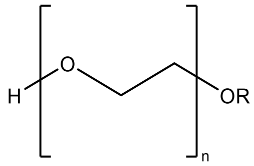
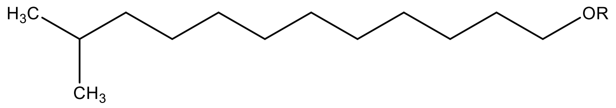
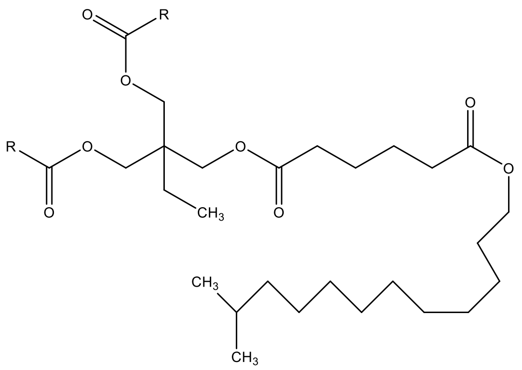


Figure 4.3: The second step esterification reaction to produce canola oil trimethylolpropane (COTMP) ester by reacting FFAs of hydrolyzed canola oil and trimethylolpropane (TMP). R_1, R_2, and R_3 are mixed vegetable oil fatty acids in canola oil: oleic acid (C18:1), linoleic acid (C18:2), and α-linolenic acid (C18:3).

The process of esterification of FFAs with other polyhydric and fatty alcohols such as pentaerythritol (PTE), polyethylene glycol (PEG, MW:300 g/mol), and isotridecanol (Exxal 13) was also conducted and a comparison was made between these esters and commercial metalworking fluids. **Table** 4.1 illustrates the structure of different esters obtained from the esterification of FFAs with polyhydric and fatty alcohols.

Table 4.1: The chemical structure of esters and complex esters obtained by reacting hydrolyzed FFAs of canola oil and different polyhydric/fatty alcohols.

Type of ester	Chemical structure
TMP ester	
PET ester	
Polyethylene glycol ester	
Isotridecyl alcohol ester	
Complex ester (a mixture of TMP, ADA, Exxal 13, and FFAs)	

R is FFAs in canola oil: oleic acid (C18:1), linoleic acid (C18:2), and α-linolenic acid (C18:3).

4.2.2.3 Analyses of mono-, di- and triglycerides, free fatty acids (FFAs), and canola oil trimethylolpropane (COTMP) ester analysis by GC-FID

The quantitative analysis of mono-, di- and triglycerides and free fatty acids (FFAs), was conducted using gas chromatography equipped with a flame ionization detector (Shimadzu GC-2010) and HT5- SGE GC capillary column (12 m × 0.53 mm × 0.15 µm). The oven temperature was programmed according to Srisanong et al. [45] as follows: initially set at 150°C and held for 3 min, then increased at a rate of 10°C /min to 300°C and held for 20 min. The injector and detector temperatures were set at 250°C and 300°C, respectively. The carrier gas (linear velocity) used was helium with a flow rate of 8.55 mL/min, a split ratio of 20:1, and a purge flow of 3 ml/min, respectively. Prior to injection into the GC system, samples were diluted with MSTFA to enhance the volatility of mono- and di-glycerides, as they are polar and high-boiling components. For the quantification, 100 mg of the sample (±0.003 mg) was derivatized with MSTFA (0.5 ml, 15 min at room temperature) and diluted in 5 ml of heptane [46], and a 1.5 ml aliquot of this solution was then transferred to a vial. Finally, 1 µl of the sample was injected into the GC-FID system. Equation 1 was used in order to calculate the concentration percentage of FFAs, ME, DE, and TE. 1,2,4-butanetriol (internal standard 1) for glycerine and tricaprin (internal standard 2) for mono-, di- and triglycerides were used for calibration according to ASTM D6584-17. The concentration of FFAs including mono-, di-, and triglycerides were obtained through Eq. (1).

$$C\ (wt.\%) = \frac{A_s}{A_{IS}} \times C_{IS} \times \frac{V_{IS}}{m} \times 100\% \tag{1}$$

where A_s is the peak area of related FFA in the sample injected to GC-FID, A_{IS} is the peak area of the related internal standard in the sample, C_{IS} is the concentration (mg/mL) of related internal standard solution, V_{IS} is the volume (mL) of related internal standard solution, and m is the mass (in mg) of the sample.

The analysis of COTMP ester was also conducted by GC-FID (Shimadzu GC-2010) according to the procedure described elsewhere [19,47]. Eq. (2) was used to calculate the concentration of samples.

$$Concentration\ (wt.\%) = \frac{Peak\ area\ of\ each\ component}{Total\ peak\ area} \times 100\% \tag{2}$$

4.2.2.4 Fatty Acid and acid value (AV) determination by titration

An official method proposed by the American Oil Chemist Society (Ca 5a-40) was used to determine the percentage of fatty acid in the collected samples. This method can be applied to all crude and refined vegetable oils. The procedure is described briefly as follows: 0.1 g of the sample was weighed into a conical flask and 50 ml titration solvent (100 ml toluene, 99 ml isopropyl alcohol, and 1 ml deionized water) was added to ensure a definite and sharp titration endpoint. A phenolphthalein indicator was then added (1 ml). The mixture was titrated against sodium hydroxide (0.1 N) until a permanent pink color persisted for at least 30 s. The weight percentage of FFAs and AV was calculated on an oleic acid basis using Eq. (3) and Eq. (4), respectively, as follows. All samples were titrated in duplicate with a variance of < 0.5%.

$$Free\ fatty\ acids\ as\ oleic, \% = \frac{ml\ of\ alkali \times N\ (conc.of\ NaOH) \times 28.2}{wt.of\ sample} \tag{3}$$

$$Acid\ value\ \left(\frac{mgKOH}{g}\right) = 1.99\ \times FFA\% \tag{4}$$

4.3 Results and Discussion

4.3.1 The 1st step hydrolysis reaction

4.3.1.1 Effects of reaction time

The effect of reaction time was studied at fixed reaction temperature, catalyst loading, and water to canola oil molar ratio of 120°C, 5 wt.%, and 30:1, respectively. As shown in **Figure** 4.4, the maximum acid values (AV) were 185 and 194 mg KOH/g with sulfuric acid and PTSA as catalysts after 6 h, respectively. However, beyond this reaction time, the AV dropped from 185 to 146 mg KOH/g for sulfuric acid and from 194 to 155 mg KOH/g for PTSA. This can be attributed to potential reverse reactions, possibly leading to the reformation of FFAs from triglycerides (TG), diglycerides (DG), and monoglycerides (MG). Therefore, at longer reaction time there is more possibility that FFAs can convert back to reactants causing a lower reaction conversion rate. The maximum TG conversion achieved was 94 wt.% and 97 wt.% for the hydrolysis reaction using sulfuric acid and PTSA as catalysts, respectively. Hence, the reaction time of 6 h was selected to be an optimum level.

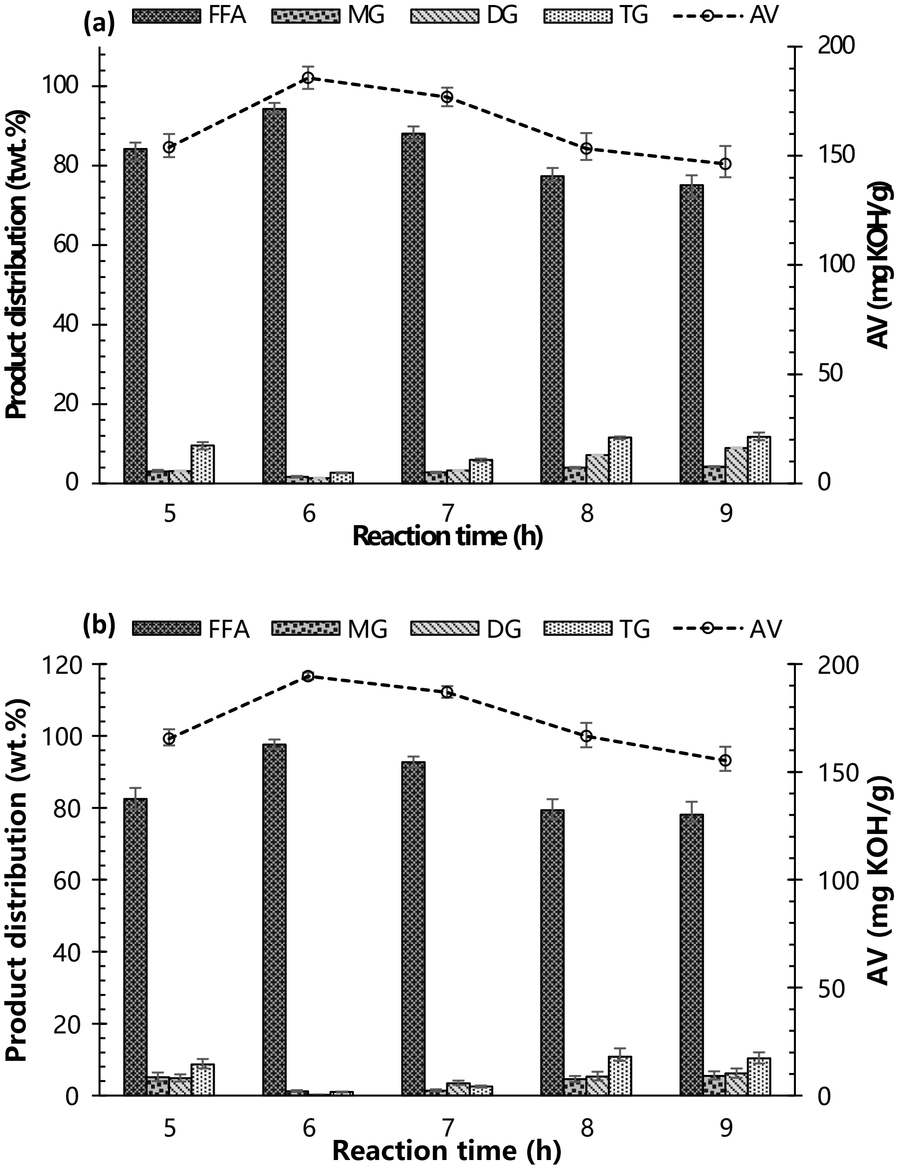
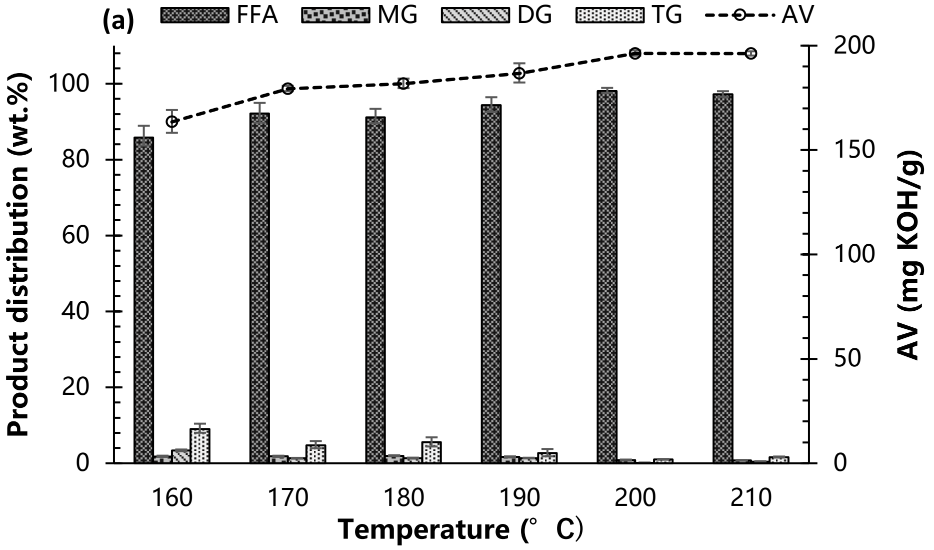


Figure 4.4: TG conversion and product distribution of hydrolysis reaction of canola oil at water to oil molar ratio: 30:1; Temperature: 190°C; Catalyst loading: 5 wt.%. ((a): conc. Sulfuric acid, (b) PTSA).

4.3.1.2 Effects of temperature

The effect of reaction temperature was studied at fixed reaction time, water to canola oil molar ratio, and catalyst loading of 6 h, 30:1, and 5 wt.%, respectively. As presented in **Figure** 4.5, the maximum AV was 196 mg KOH/g for sulfuric acid at 200ºC and 194 mg KOH/g for PTSA at 190ºC. At higher temperatures, there was an increased possibility for the byproduct mixture of water and glycerol to evaporate, facilitating a forward shift in the hydrolysis reaction and consequently leading to higher reaction conversion and AV. For this effect, a reaction temperature of 200ºC for sulfuric acid and 190ºC for PTSA was selected to be an optimum level.



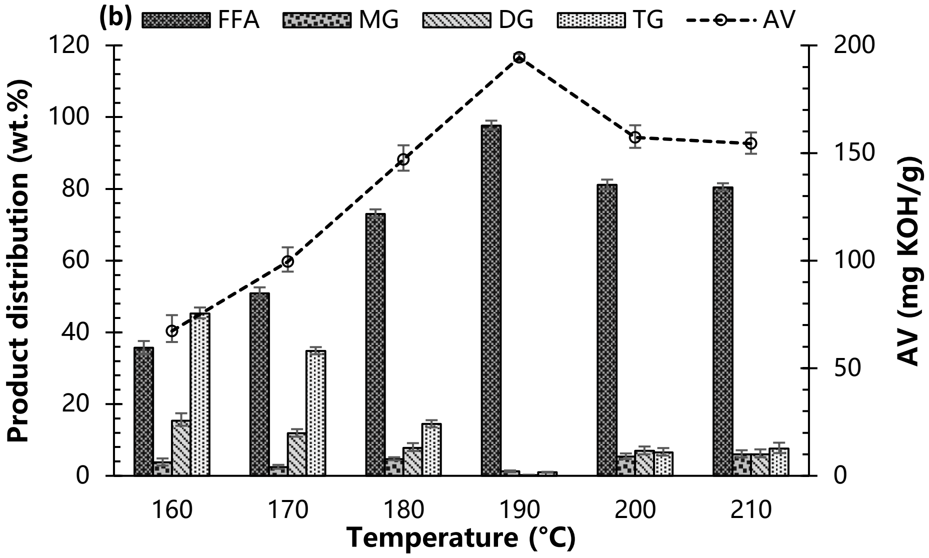


Figure 4.5: TG conversion and product distribution of hydrolysis reaction of canola oil at water to oil molar ratio: 30:1; time: 6h; catalyst loading: 5 wt.%. ((a): conc. Sulfuric acid, (b) PTSA).

4.3.1.3 Effects of molar ratio

The effect of reactant molar ratio was studied at fixed reaction temperature, time, and catalyst loading at 200ºC with sulfuric acid and 190ºC with PTSA, 6 h, and 5 wt.%, respectively. The hydrolysis of triglycerides is a three-step, consecutive, reversible reaction. Stoichiometrically, 1 mole of TG requires 3 moles of water (oil: water molar ratio = 1: 3) to produce 3 mole of fatty acids and 1 mole of glycerol (**Figure** 4.1). As an endothermic reaction, hydrolysis benefits from excess water, which drives the equilibrium towards the formation of final products – fatty acids and glycerol [48]. The maximum AVs were obtained at a molar ratio of 30:1 which were 196 and 194 mg KOH/g for sulfuric acid and PTSA, respectively (**Figure** 4.6). However, increasing the water/oil molar ratio beyond 30:1 did not further enhance the yield of free fatty acids (FFAs). In addition, GC-FID analysis indicated maximum TG conversion rates of 98 wt.% for both sulfuric acid and PTSA. Thus, the optimal water/oil molar ratio was chosen as 30:1.

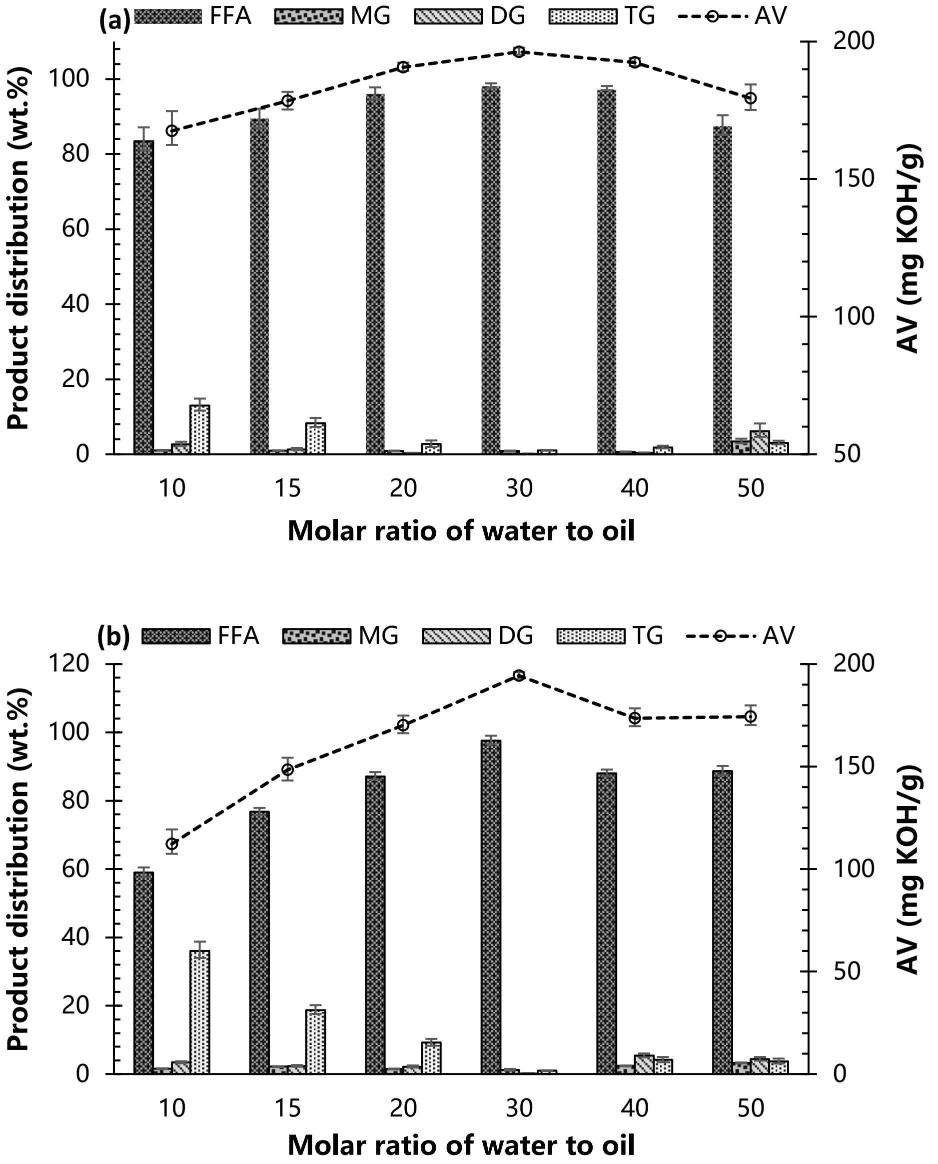


Figure 4.6: TG conversion and product selectivity of the hydrolysis reaction of canola oil at temperature: 200°C for Conc. H2SO4 and 190°C for PTSA; time: 6h, catalyst loading: 5 wt.%. ((a): conc. Sulfuric acid, (b) PTSA).

4.3.1.4 Effects of catalyst loading

High temperatures decrease the dielectric constant of water from 80 (200ºC) to 25 (250ºC) and make the dissolution properties of subcritical water similar to those of organic solvents, increasing the interactions of oil in water and the reaction rate [49]. Therefore, the use of a catalyst to carry out the reaction at lower temperatures is essential for industrial-scale applications. Catalysts such as sulfuric acid and PTSA exhibit relatively hydrophilic properties, allowing them to dissolve into the water layer. Because of their hydrophilic nature, their surface is covered with water molecules during the catalytic reaction thereby limiting access to the surface for oil molecules. As shown in **Figure** 4.7, the AV increased markedly from 142 to 196 mg KOH/g for sulfuric acid and from 77 to 194 mg KOH/g with PTSA upon reaching the hydrolysis equilibrium with an increase in the amount of catalyst up to 5 wt.%. It should be noted that increasing the catalyst loading over 5 wt.% causes mass transfer limitation in the reaction rate which has a major effect on reaction equilibrium [49]. Thereby, the optimal dosage of catalyst for both sulfuric acid and PTSA was determined to be 5 wt.%.

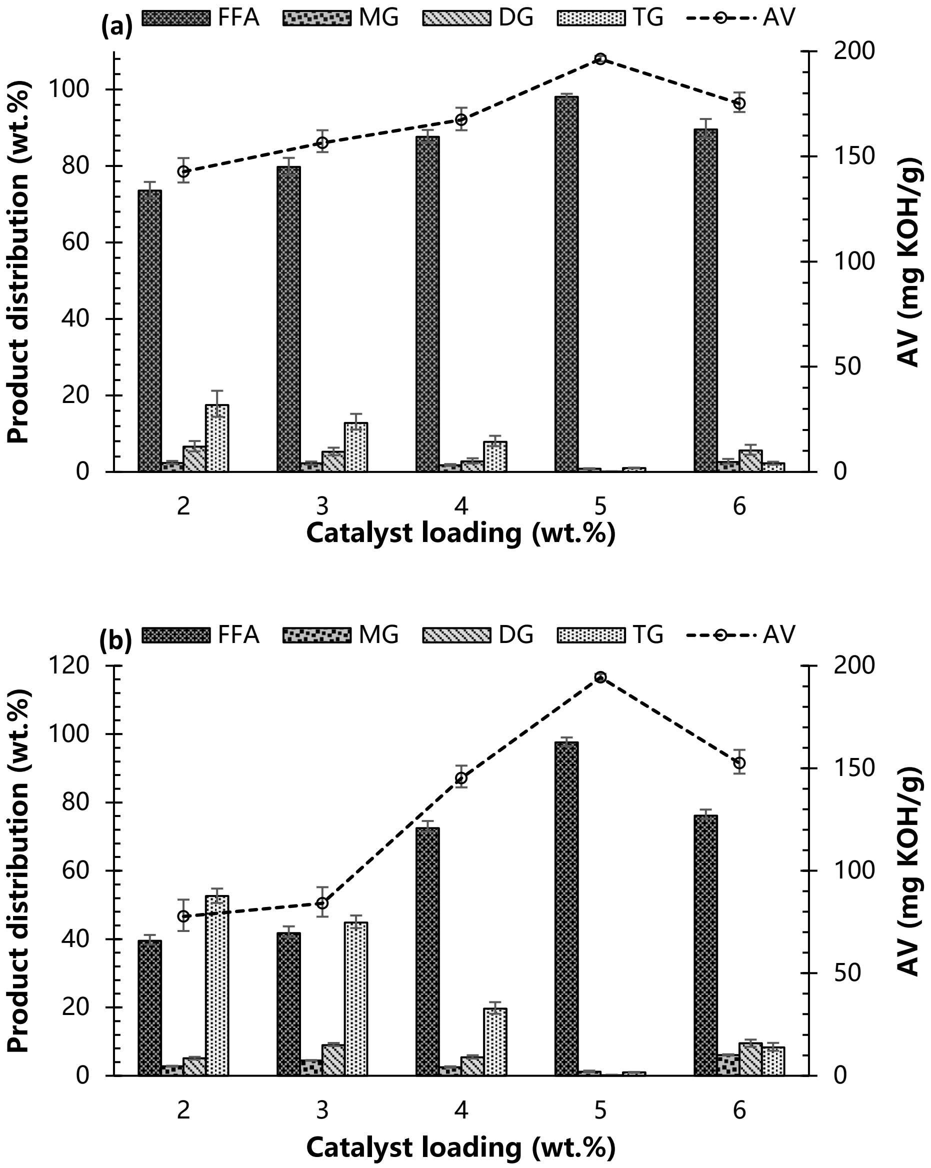


Figure 4.7: TG conversion and product distribution of hydrolysis reaction of canola oil at water to oil ratio: 30:1; time: 6h; temperature: 200°C for Conc. H2SO4 and 190°C for PTSA. ((a): conc. Sulfuric acid, (b) PTSA).

4.3.2 The 2nd step esterification reaction

4.3.2.1 Effects of reaction time

The reaction time is one of the most important parameters in the esterification of FFAs with TMP. As shown in **Figure** 4.8, at lower reaction times (2-8 h), no significant change in the conversion of FFAs was observed. However, the concentration of TE significantly increased (71.4 wt.%) with increasing time (up to 10 h). After 10 h, the concentration of TE decreased while the total concentration (ME, DE, and TE) remained almost constant, indicating that the reverse reactions were occurring. In addition, as one can be seen in **Figure** 4.8, the yield of the final product dramatically decreased after 10 h which is most probably due to the polymerization which can simply be notified from the change of color of the final product (**Figure** 4.9) from light brown (10 h reaction time) to dark brown (18 h reaction time). Hence 10 h was considered the best reaction time.

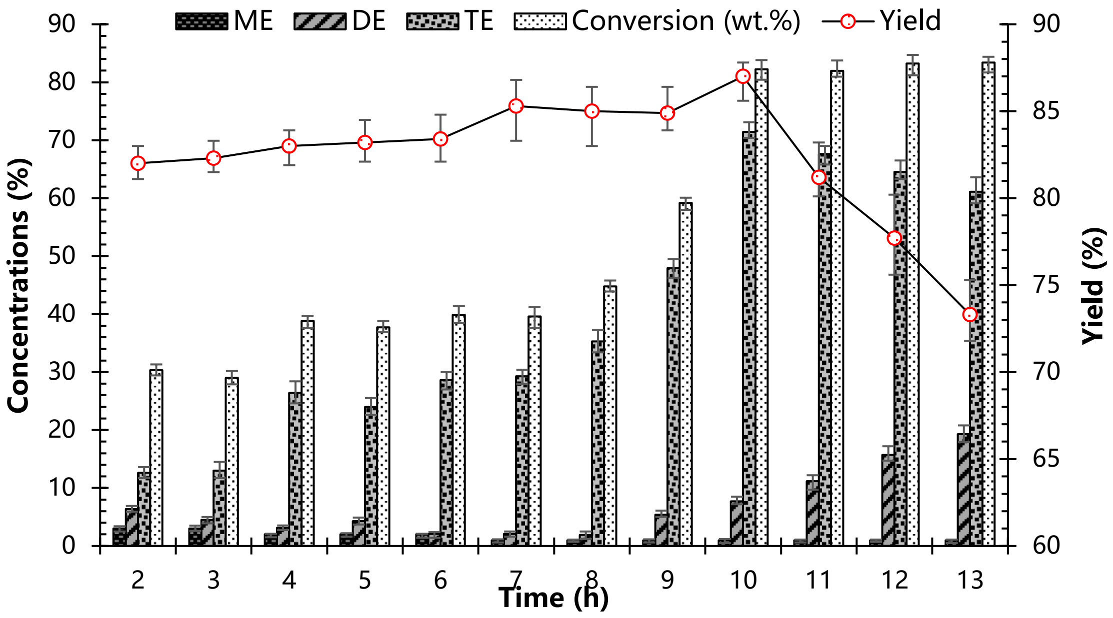


Figure 4.8: Investigation of conversion, yield, and Influences of the reaction time on esterification of free fatty acids (FFAs) with trimethylolpropane (TMP). Other reaction parameters: PTSA catalyst loading: 1 wt.%; temperature: 150°C). ME: monoester; DE: diester; TE: triester.

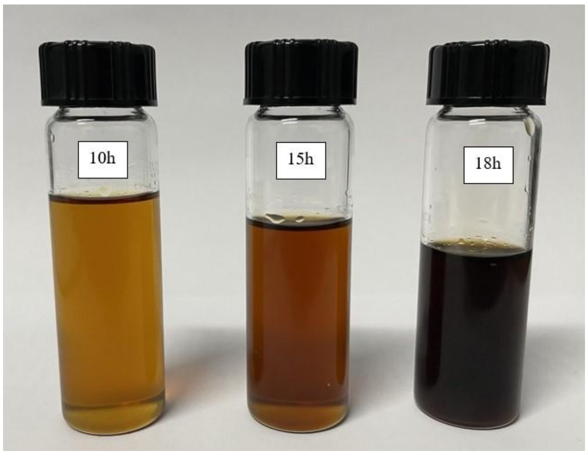


Figure 4.9: Impact of reaction time on the color of the final product.

4.3.2.2 Effects of temperature

In the esterification reaction, due to the exothermic nature of this reaction, the reaction rate constant increases as the reaction temperature increases [50]. In fact, increasing temperature would help the formation of esters in an esterification reaction [51]. In this step, the effect of reaction temperature was investigated between 130-190°C, and other reaction conditions were fixed at FFAs to TMP molar ratio of 4:1, 10 h reaction time, and 1 wt.% PTSA catalyst loading. As obviously illustrated in **Figure** 4.10, the concentration of TE as well as the total yield of the final product, demonstrated an upward trend with increasing temperature up to 150°C. Afterward, a further increase in temperature caused a reduction in the yield and TE concentration of COTMP ester due to the fact that higher temperatures can cause the equilibrium shift of the esterification of FFAs with TMP reaction and reverse COTMP ester back to FFAs. Furthermore, the yield of the ester markedly decreased after reaching 150°C due to polymerization. Thereby, 150°C was chosen for further experiments.

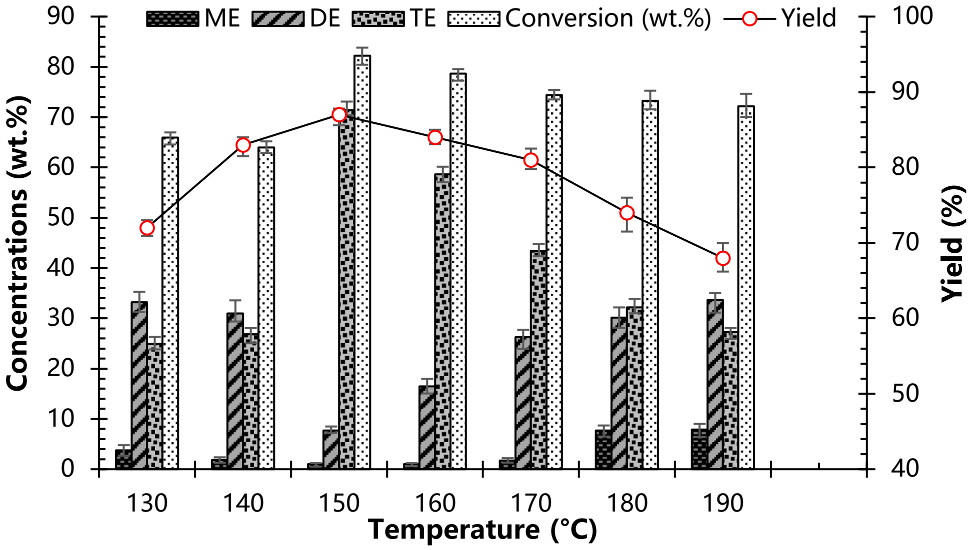


Figure 4.10: Investigation of conversion, yield, and Influences of the reaction temperature on esterification of FFAs with trimethylolpropane (TMP). Other reaction parameters: PTSA catalyst loading: 1 wt.%; time: 10 h, FFAs to TMP molar ratio: 4:1). ME: monoester; DE: diester; TE: triester.

4.3.2.3 Effects of catalyst loading

In this work, PTSA was used as the catalyst for the 2nd step esterification of FFAs with TMP, and the effects of the catalyst loading (wt.% of FFAs-TMP reaction mixture) on the reaction were investigated by varying the mass ratio of PTSA to FFAs-TMP reaction mixture in the range of 0.5−4 wt.% while other parameters such as reaction time, reaction temperature and FFAs/TMP molar ratio were fixed at 10 h, 150°C, and 4:1, respectively. The concentrations of TMP triester (TE), TMP diester (DE), TMP monoester (ME), yield, and the conversion of COTMP esters in the final product are illustrated in **Figure** 4.11. As shown in **Figure** 4.11, the maximum concentration of TE and total yield of TE/DE/ME esters increased, up to 1 wt.% PTSA catalyst loading and then considerably decreased. It is also evident that 1 wt.% catalyst loading led to the maximum conversion (82 wt.%) and yield (87%) of FFAs and COTMP ester products, respectively. It should be considered that an excess amount of PTSA (more than 1 wt.%) would reduce the yield and conversion of the final product. The most important reason is that the higher the amount of catalyst, the lower the amount of product after the purification steps due to the formation of salt with 5% sodium bicarbonate and sodium chloride solution. Hence, the catalyst loading of 1 wt.% was considered for the next steps.

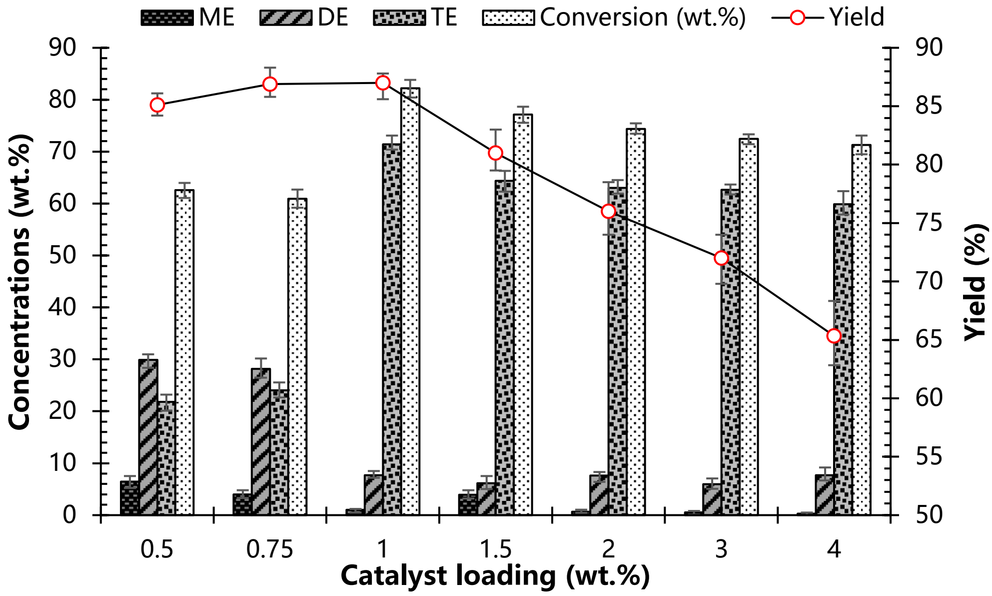


Figure 4.11: Investigation of conversion, yield, and Influences of catalyst loading on esterification of FFAs with trimethylolpropane (TMP). Other reaction parameters: temperature: 150°C; time: 10 h; FFAs to TMP molar ratio: 4:1). ME: monoester; DE: diester; TE: triester.

4.3.2.4 Effects of FFAs-to-TMP molar ratio

Due to the reversible nature of the esterification reaction, the increase or decrease of one of the reactants can have a direct effect on the yield of the final product [52]. The stoichiometric molar ratio between the FFAs and TMP is 3:1, as shown in **Figure** 4.1. In this work, the effect of various FFAs/TMP molar ratios (3.1:1, 3.5:1, 4:1, 4.5:1, and 5:1) on the esterification of FFAs with TMP was investigated in order to ensure the complete TMP conversion, while other parameters were fixed at 150°C, and 1 wt.% PTSA catalyst loading, and 10 h. The concentrations of TE, DE, and ME in the produced COTMP product as well as the conversion of FFAs and yield of the final ester are presented in **Figure** 4.12. Increasing the molar ratio would shift the equilibrium to the right-hand side of the reversible esterification reaction and increase the yield and conversion of the COTMP ester. However, a higher molar ratio of FFAs/TMP produces a COTMP product with lower conversion and concentrations of TMP esters (TE, DE, and ME), due to the increased presence of unreacted FFAs in the final COTMP products (as high as 40 wt.%). Therefore, the best FFAs/TMP molar ratio was considered as 4:1.

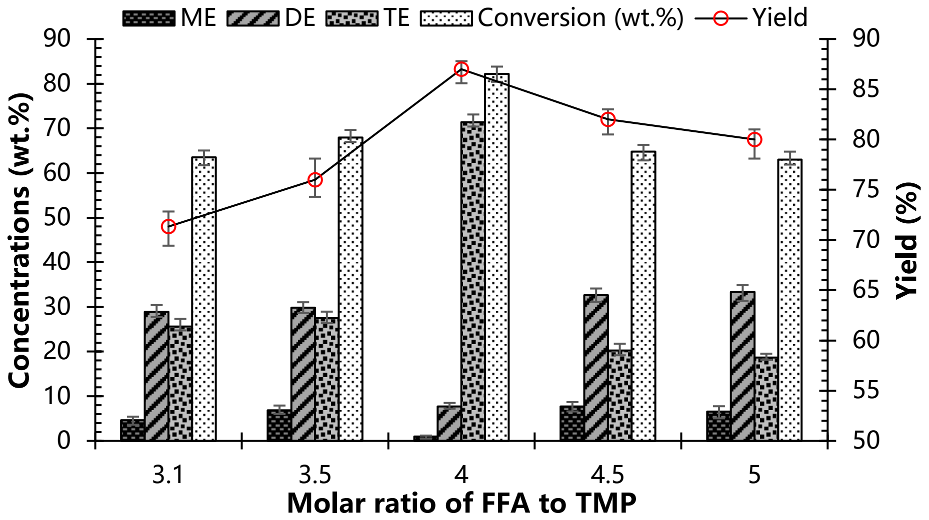


Figure 4.12: Investigation of conversion, yield, and Influences of FFAs to TMP molar ratio on esterification of FFAs with TMP. Other reaction parameters: temperature: 150°C; time: 10 h; catalyst loading: 1 wt.%). ME: monoester; DE: diester; TE: triester.

In summary, the maximum yield and conversion of esterification reaction of FFAs with TMP at the best conditions (150°C reaction temperature, 10 h reaction time, 1 wt.% catalyst loading, and FFAs to TMP molar ratio of 4:1) were 87% and 82 wt.%, respectively.

$$\text{FFAs conversion (wt.\%)} = \frac{M_{FFAs} - (M_{COTMP} \times C_{FFAs})}{M_{FFAs}} \times 100 \qquad (5)$$

$$Yield\ (\%) = \frac{M_{COTMP}}{M_{FFAs}} \times 100\% \qquad (6)$$

Where M_{FFAs} is the mass of FFAs before reaction (g), M_{COTMP} is the mass of COTMP ester product (g), and C_{FFAs} is the remaining FFAs concentration in the final product (wt.%).

4.3.3 Characterizations of the reaction products

4.3.3.1 FTIR spectroscopy

The FTIR spectra of the TMP, crude canola oil, FFAs, and obtained COTMP ester at the best conditions (i.e., FFAs/TMP molar ratio: 4:1; Temperature: 150°C; time: 10h; PTSA catalyst loading: 1 wt.%) is illustrated in **Figure** 4.13. The spectra of the TMP apparently showed a broad peak around 3250 cm^{-1} which is attributable to the –OH function groups of TMP. This peak almost disappeared in the final COTMP ester product, indicating that all the -OH functions of TMP have reacted with FFAs. The strong absorption peaks (2923 cm^{-1}, 2853 cm^{-1}, and 3007 cm^{-1}) and the medium IR absorption peaks at 1370 cm^{-1} 1463 cm^{-1} bands indicate the presence of –CH stretch in all samples. The peaks of C=O ester groups and C-O stretching bonds in the crude canola oil, FFAs, and COTMP ester appeared at peaks around 1742 cm^{-1} and 1161 cm^{-1}, respectively. In addition, since canola oil contains unsaturated FFAs (including oleic acid, linoleic acid, and linolenic acid), the clearly strong peak at around 723 cm^{-1} indicates C=C double bonds stretching in the crude canola oil, FFAs, and COTMP ester [53].

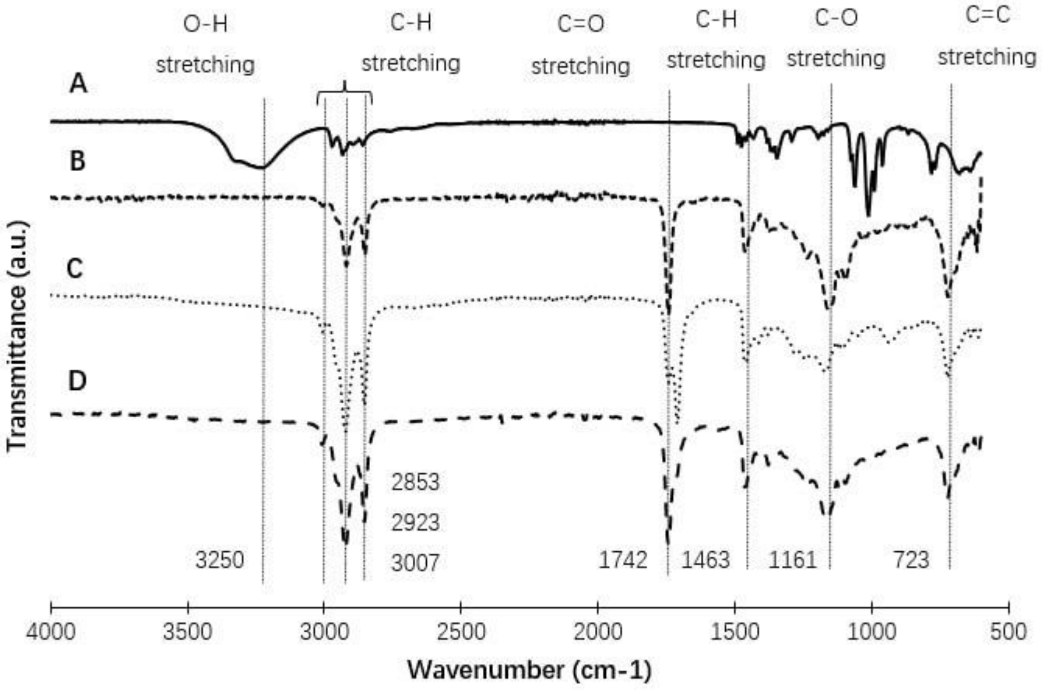


Figure 4.13: FTIR spectra of (A) trimethylolpropane (TMP), (B) crude canola oil, (C)

FFAs, and (D) canola oil trimethylolpropane (COTMP) ester obtained at the best conditions in esterification reaction.

4.3.3.2 ^{1}H NMR spectroscopy

In order to confirm the structure of the samples (crude canola oil, FFAs, and COTMP ester), ^{1}H NMR spectrum was performed which is indicated in **Figure** 4.14. The ^{1}H NMR for FFAs and COTMP ester was done at the best conditions which were canola oil/ water molar ratio of 1:30, reaction time: 6 h, reaction temperature: 190°C, PTSA catalyst loading: 5 wt.% and FFAs/TMP molar ratio of 4:1, reaction time: 10 h, reaction temperature: 150°C, and PTSA catalyst loading: 1 wt.%, respectively. **Figure** 4.14A, illustrates the ^{1}H NMR spectrum of crude canola oil and the peaks are as below:

a: Methyl protons, 0.85 ppm, (CH_3-C-), b: Methyl protons of linolenic acid, 0.92 ppm, (-HC=CH-), c: Methylene protons of fatty acid of triacylglycerol, 1.25 ppm, (-C-CH_2-C-), d: β-carboxylic protons, 1.57 ppm, (-CH_2-CH_2-C=O-), e: Allylic protons outside, 1.98 ppm, (-C-CH_2-C=C-), f: α-carboxylic protons, 2.27 ppm, (-O-CO-CH_2-), g: Internal allylic protons, 2.73 ppm, (-CH=CH-CH_2-CH=CH-), h & i: Methylenic protons of the glycerol, 4.12 and 4.27 ppm, (-C-CH_2-O-), j: H-2 proton of glycerol methylenic, 5.21 ppm, (-CH_2-CH-CH_2-), and k: olefinic protons, 5.32 ppm, (-HC=CH-) [54], [55]. Signals at around 4.12 and 4.27 ppm (small double doublets peaks), verified the presence of di- or monoacylglycerols in the structure of vegetable oil. **Figure** 4.14B indicates the ^{1}H NMR spectrum of FFAs. As one can be seen in this figure, according to the ^{1}H NMR spectroscopy, it can be concluded that the hydrolysis product at the end of 6 h contains mainly fatty acid (FA) with negligible amounts of glycerides. In addition, the appearance of peak (l) around 3.65 ppm (oleic acid), revealed that the hydrolysis reaction is done successfully [56]. In **Figure** 4.14C, which is related to the ^{1}H NMR spectrum of COTMP ester, a signal at 1.25 ppm from the β-carbonyl methylene protons is a confirmation of olefinic structure present in the COTMP ester. The peak around 0.85 ppm is attributed to the terminal methyl protons in the TMP ester backbone. However, when the hydroxyl group of TMP is attached to a free fatty acid, the electron density around the protons in the TMP-CH_2 group is reduced. Hence, the protons in that TMP-CH_2 group would shift to 4.00 ppm (peak m) once TMP DE and TE formed. Therefore, the structure of FFAs and COTM ester obtained from the hydrolysis-esterification reaction is well confirmed by the ^{1}H NMR spectroscopy instrument.

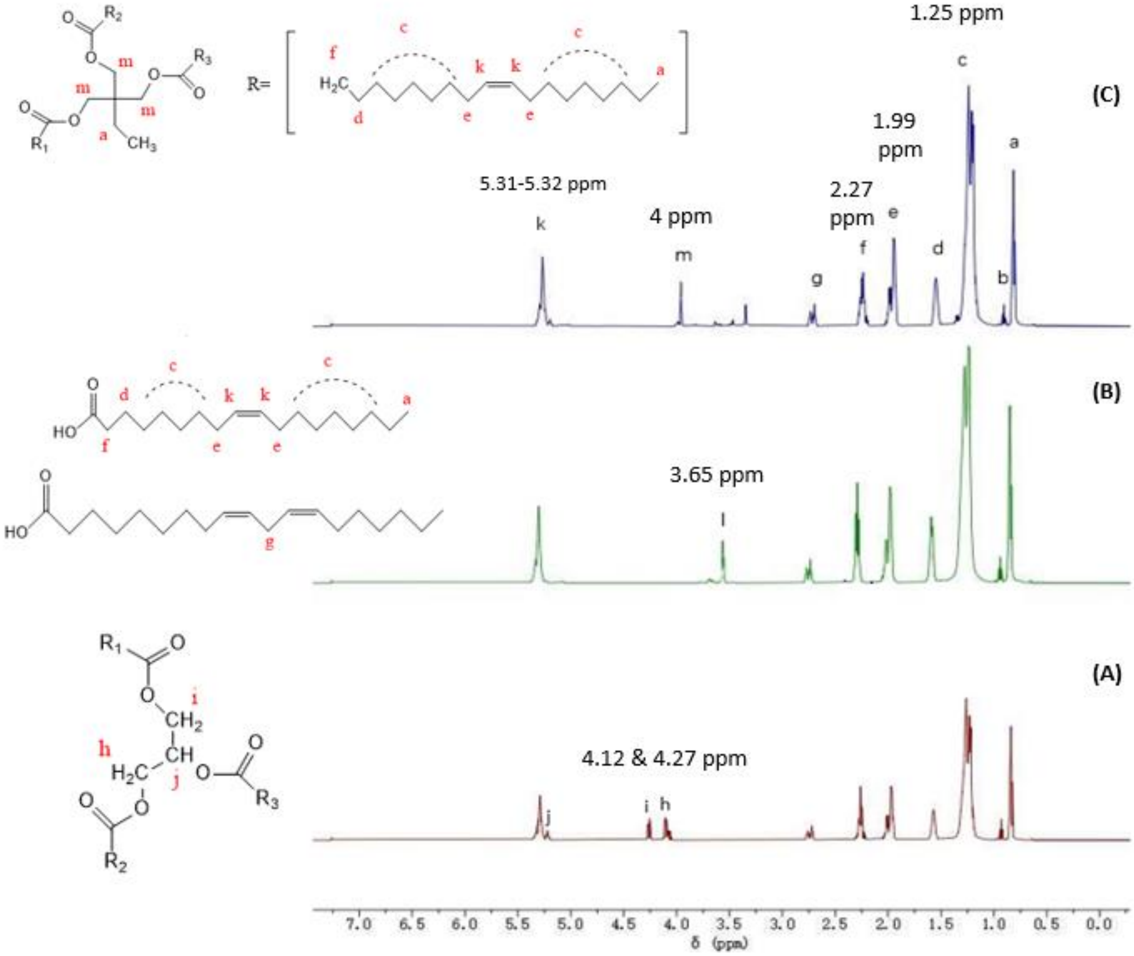


Figure 4.14: ^{1}H NMR spectrum of (A) canola oil, (B) FFAs, and (C) canola oil trimethylolpropane (COTMP) ester obtained at the best reaction conditions in the esterification reaction.

4.3.3.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was accomplished to determine the weight loss of the samples. In this method, samples were heated to about 800°C to see the impact of dehydration and decomposition reactions on crude canola oil, FFAs, and COTMP ester

(**Figure** 4.15). As illustrated, the crude canola oil and FFAs started to vaporize at approximately 300°C and 220°C, respectively. The vaporization of these two samples finished at approx. 500°C and 700°C, respectively. In the first step, both FFAs and COTMP ester samples started to vaporize at around 220°C and 250°C, while the second step of vaporization occurred at around 350°C and 450°C for FFAs and COTMP ester, respectively. It is noteworthy mentioning that, as one can be seen in the figure, COTMP ester lost about 5 wt.% of weight at around 230°C but this amount for FFAs is at around 180°C. However, complete weight loss occurred at around 720°C for both FFAs and COTMP ester. [18]. This suggests that the thermal stability of the final product (COTMP ester) has increased as expected for complex esters with polyol alcohols [57].

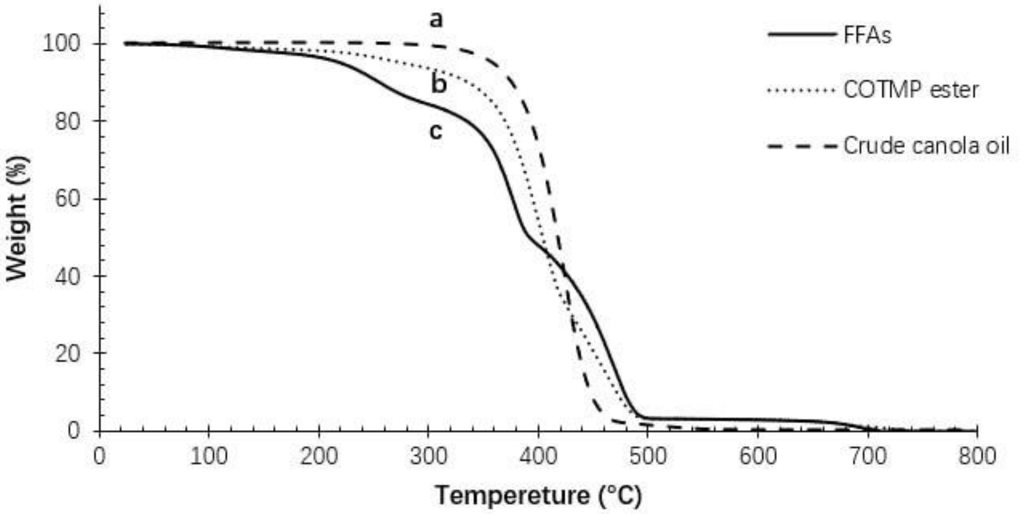


Figure 4.15: TGA curves of (a) crude canola oil, (b) FFAs, and (c) canola oil trimethylolpropane (COTMP) ester.

4.3.3.4 Physical properties and fourball test results

Table 4.2 shows the physical properties of the crude canola oil, FFAs, and the obtained esters by synthesizing FFAs of canola oil and polyol/fatty alcohols which were measured according to ASTM D445, D2270, D97, D 92-18, and D4172 for viscosity, viscosity index (VI), Pour point, Flash point (open cup method), and Fourball, respectively. As one can be seen, all obtained esters have a better Flash point and VI than crude canola oil and FFAs suggesting that these esters are able to perform in a wide range of temperatures. Among these esters, the best VI (315) belonged to PET ester. Moreover, compared to other esters, the complex ester including the mixture of TMP, adipic acid (ADA), FFAs, and isotridecanol showed better physical characteristics with WSD, coefficient of friction (COF), and flash point of 0.72 mm, 0.031, and 310 °C, respectively.

Table 4.2: Physical characteristics of crude canola oil, FFAs, and esters/complex esters obtained through the esterification of FFAs with related polyhydric/fatty alcohols.

Properties	Crude canola oil	FFAs	FFAs-TMP	FFA-PET	FFAs-PEG	FFAs-Isotridecanol	FFAs-ADA-TMP-Isotridecanol
V@40°C (cSt)	35.8±0.11	23.97±0.13	30.58±0.09	25.3±0.09	26.28±0.11	14.66±0.15	28.05±0.09
V@100°C (cSt)	8.2±0.07	7.04±0.05	8.67±0.05	7.89±0.08	7.77±0.05	4.79±0.07	7.87±0.03
VI	216.7±2.1	286.1±0.09	284.2±1.8	315±2.9	293.7±1.3	294±3.9	275±1.1
PP (°C)	-18	-9	-12	-12	-15	-12	-15
FP (°C)	205±1	214±1	306±1	302±1	281±1	277±1	310±1
WSD (mm)	0.97±0.07	0.91±0.11	0.83±0.09	0.91±0.10	0.95±0.08	0.77±0.08	0.72±0.09
COF	0.032±0.003	0.029±0.002	0.023±0.001	0.030±0.002	0.031±0.002	0.021±0.001	0.018±0.002

In order to improve the WSD and Pourpoint of the samples usable for metalworking systems, a mixture of these esters with a base oil (SN240) and suitable additives was made and a comparison was performed between these lubricants and commercial ones. All the samples were made according to ISO 46 (**Table** 4.3).

Table 4.3: Physical characteristics of new lubricants obtained from mixing esters/complex esters with a mineral base oil (SN240), and suitable additives.

Properties	Lub A	Lub B	Lub C	Lub D	Lub E	SN240
V@40 (cSt)	46.45±0.21	46.73±0.13	46.9±0.09	47.1±0.2	46.25±0.07	46.1±0.09
V@100 (cSt)	9.47±0.11	9.39±0.14	9.67±0.12	9.56±0.11	9.34±0.08	7.23±0.10
VI	194±2	190±3	198±3	193±3	191±2	117±4
PP (°C)	-36	-36	-30	-33	-33	-18
FP (°C)	245±1	245±1	245±1	245±1	245±1	245±1
WSD (mm)	0.33±0.1	0.4±0.1	0.44±0.1	0.33±0.2	0.46±0.1	0.55±0.2
COF	0.021±0.004	0.029±0.007	0.031±0.006	0.022±0.004	0.036±0.005	0.042±0.005
Friction (N)	3.34±0.3	4.66±0.2	4.88±0.2	3.89±0.2	6.6±0.3	6.5±0.3

Lub A: mixture of FFA-TMP with SN240 & additive, Lub B: mixture of FFA-PET with SN240 & additive, Lub C: mixture of FFA-Exxal 13 with SN240 & additive, Lub D: mixture of FFA-TMP-ADA-Exxal 13 with SN240 & additive, Lub E: mixture of FFA- PEG with SN240 & additive.

As evident from **Table** 4.3, the physical characteristics of the lubricants by adding esters improved outstandingly. The WSD of the new lubricants was reduced below 0.45 mm with the best result for Lub A (mixture of base oil, ester of FFAs-TMP, and additives) which was 0.33 mm. In addition, other lubricants had smaller WSD and COF than SN240. Furthermore, the pourpoint of new lubricants was decreased to -36°C. **Figure** 4.16 and **Figure** 4.17 indicate the fourball testing results and SEM images of scar morphologies for new lubricants, respectively. It is clear that the combination of SN240 and additives yields an average WSD of 0.44 mm, and the addition of a small percentage of, for example, TMP ester obtained through this research can significantly enhance the WSD to 0.33 mm consistently.

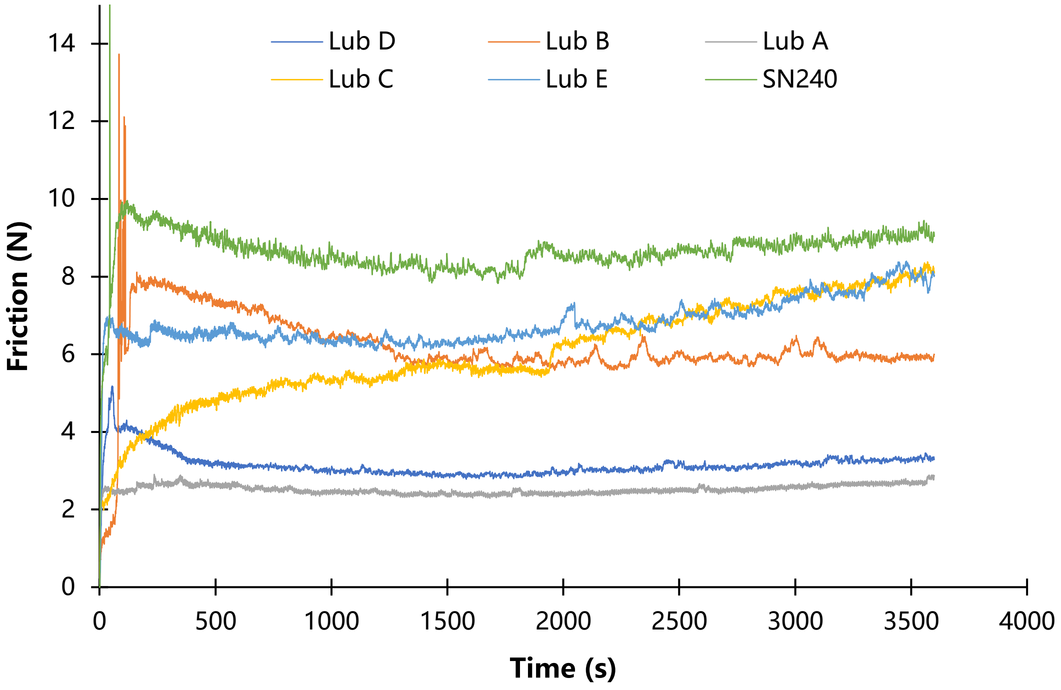


Figure 4.16: Fourball testing results of the new lubricants. (Lub A: mixture of FFA-TMP with SN240 & additive, Lub B: mixture of FFA-PET with SN240 & additive, Lub C: mixture of FFA-Exxal 13 with SN240 & additive, Lub D: mixture of FFA-TMP-ADA-Exxal 13 with SN240 & additive, Lub E: mixture of FFA- PEG with SN240 &

additive).

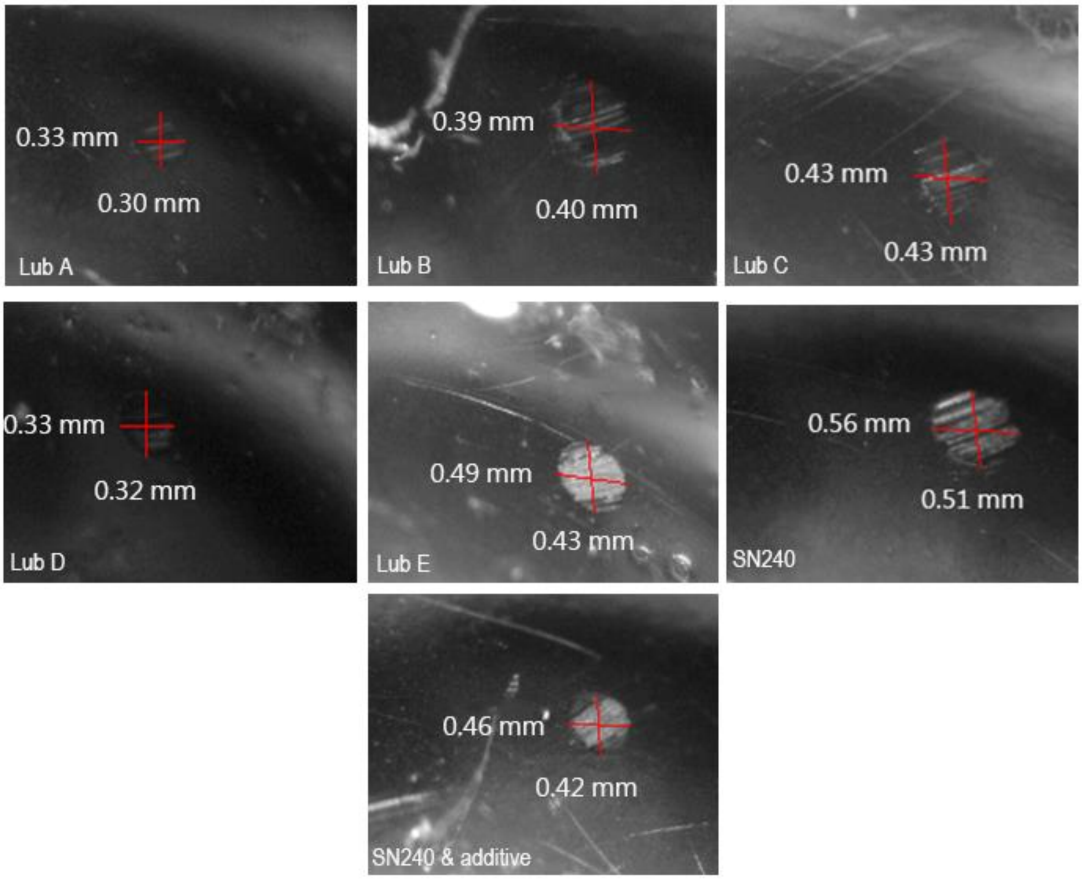


Figure 4.17: SEM images of scar morphologies for new lubricants. (Lub A: mixture of FFA-TMP with SN240 & additive, Lub B: mixture of FFA-PET with SN240 & additive, Lub C: mixture of FFA-Exxal 13 with SN240 & additive, Lub D: mixture of FFA-TMP-ADA-Exxal 13 with SN240 & additive, Lub E: mixture of FFA- PEG with SN240 & additive)

Table 4.4 shows the comparison between Lub A, Lub D, and Lub B, Additin® RC 2526, Castrol Magna Range, and PIL [58].

Table 4.4: The comparison between physical properties of Lub A, Lub B, Lub D, and commercial lubricants.

Properties	Lub A	Lub B	Lub D	Additin® RC 2526[c]	Castrol Magna Range[b]	MJO-PIL[a]
WSD (mm)	0.33±0.1	0.4±0.1	0.33±0.2	0.7	0.42	0.45
Force load	392	392	392	300	392	392

(N/h)

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[a] Kumar et al. [58]

[b], [c] Commercial EP additives

As one can be seen, the WSD of lub A, Lub D, are so far better than commercial ones and the PIL obtained by Kumar et al. [58] by mixing refined Jatropha oil-based (MJO) with 1 wt.% of [P66614][Phosphinate] (PIL) additive. In summary, the WSD of 0.33 mm belong to Lub A and Lub D suggests perfect friction in metal-metal contact and their excellent physical properties reveal that they are useful and applicable in many industrial applications, especially in metalworking industries.

4.3.4 Rheology

4.3.4.1 Variation of viscosity with shear rate

Figure 4.18 illustrates the variations in viscosity concerning shear rate at both 20 °C and 80°C. The delineated dashed outline on the graph represents the range within which the MARS iQ Air rheometer, equipped with the P25 parallel plate, can effectively measure. Within this instrument's measuring range, the data collected indicates a Newtonian behavior across the entire spectrum of shear rates, which aligns with the typical behavior of most pure lubricant oils.

As shear rates increase, there is no substantial change, and the dynamic viscosity remains nearly constant throughout the entire range. As it is obvious, COTMP ester exhibits the lowest fluctuations in dynamic viscosity with changing shear rates likely due to its synthetic origin. Additionally, given the vast differences in kinematic viscosity between these three lubricants, the initial shear rate is adjusted to accommodate these distinctions. For instance, the starting shear rate for measuring COTMP ester at 80°C is 10 s^{-1}, while the compound oil which has the highest viscosity requires a starting shear rate of approximately 1 s^{-1}.

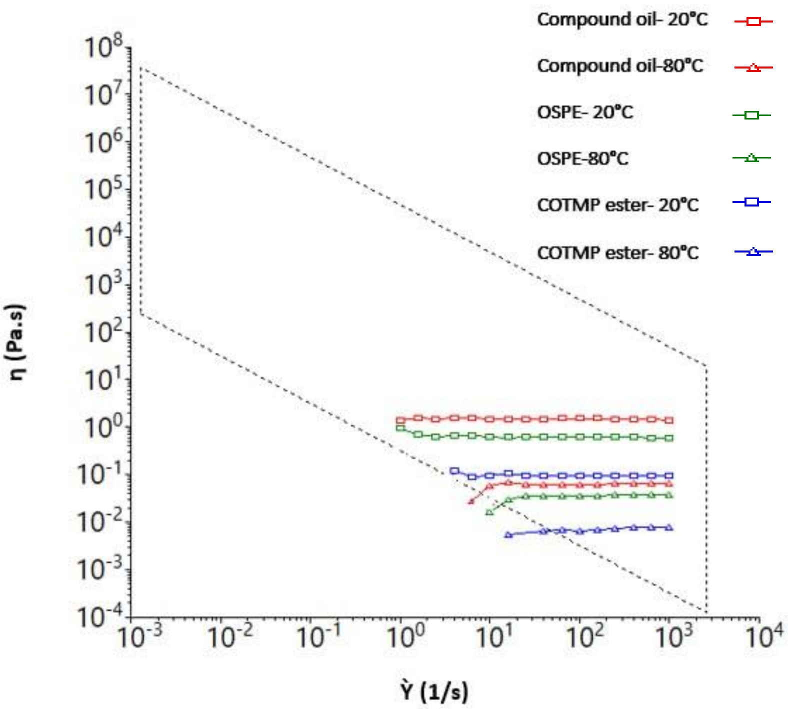

Figure 4.18: Variation of viscosity with the shear rate for compound oil, oil soluble phosphate ester (OSPE), and the canola oil trimethylolpropane (COTMP) ester.

4.3.4.2 Variation of viscosity with temperature

Figure 4.19 presents changes in temperature-ramp profile for three distinct lubricants: compound oil, oil soluble phosphate ester (OSPE), and the COTMP ester. As temperature rises, the dynamic viscosity consistently diminishes. This trend in viscosity variation with temperature holds true for all three lubricants and aligns with Reynolds' equation [19]. As one can be seen, among the tested lubricants, the compound oil exhibits the highest dynamic viscosity, measuring 12 Pa·s at 20°C. It also displays the steepest negative gradient concerning temperature, signifying a high susceptibility to temperature variations. On the contrary, OSPE and COTMP ester exhibit relatively lower dynamic viscosity values, approximately 0.6 Pa·s and 0.09 Pa·s at 20°C, respectively. These lower values of negative temperature gradient in dynamic viscosity for OSPE and COTMP ester can be attributed to their synthetic origins, indicating greater stability in the face of temperature variations when compared to the compound oil. Consequently, of the three lubricants assessed, the COTMP ester appears to possess the most promising properties.

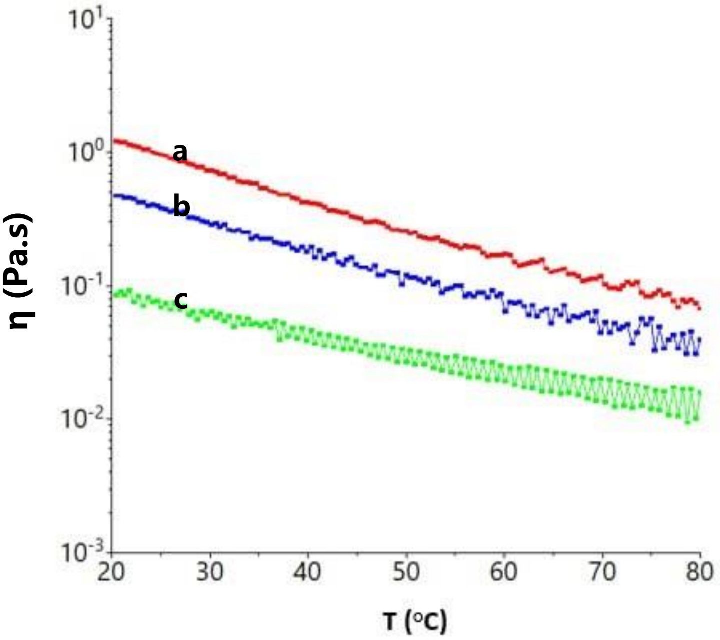

Figure 4.19: Variation of dynamic viscosity with temperature for a) compound oil, b) oil soluble phosphate ester (OSPE), c) canola oil trimethylolpropane (COTMP) ester.

4.4 Conclusions

In summary, catalyst-facilitated hydrolysis provides a viable alternative to supercritical hydrolysis, allowing for efficient substrate conversion with reduced operating severity. In this study, the canola oil was first hydrolyzed employing conc. sulfuric acid and PTSA catalyst, respectively. The obtained product has an acid number of 194.35 mg KOH/g and triglyceride conversion was 97.62% by using PTSA catalyst, compared with an acid value of 196.28 mg KOH/g and triglyceride conversion of 98.08% using conc. sulfuric acid as the catalyst. Thus, PTSA catalyst proved to be a more environmentally friendly (less corrosive) substitute for conc. sulfuric acid as an effective catalyst for the canola oil hydrolysis reaction. The best conditions for the hydrolysis reaction of canola oil were: 190°C and 200°C with PTSA and conc. H_2SO_4, respectively, 6h reaction time, 30:1 water to oil molar ratio, and 5 wt.% catalyst loading.

For the esterification reaction of FFAs with TMP the maximum obtained yield of 87% and conversion of 85 wt.% were obtained at the best conditions of 150°C, 10 h, 1 wt.% catalyst loading, and FFAs to TMP molar ratio of 4:1. Furthermore, the mixture of SN240 with ester samples obtained by esterification reaction of hydrolyzed canola oil and various polyhydric and fatty alcohols demonstrated excellent anti-wear properties (0.33 mm), suggesting promise in application as metalworking fluids.

4.5 References

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Chapter 5

5 Production of high-end bio-lubricant products via epoxidation of canola oil trimethylolpropane (COTMP) esters

Abstract

Trimethylolpropane esters of free fatty acids obtained from canola oil were epoxidized using a heterogeneous catalyst. The heterogeneous catalyst was obtained by the direct functionalization of ethanolamine with montmorillonite K10 clay and then immobilization with molybdenum compound. The catalyst was characterized by X-ray diffractometry (XRD), scanning electron microscopy coupled in an energy-dispersive X-ray spectrometer (SEM-EDS), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR). The epoxidation reactions were carried out using tert-butyl hydroperoxide (TBHP) as the oxidizing agent. The best results for epoxidation reactions were observed under conditions of 85°C for 50 h and molar ratio of canola oil trimethylolpropane ester to TBHP of 1:1.5, leading to 95.2% conversion and 98.62% selectivity. The obtained epoxidized canola oil trimethylolpropane (ECOTMP) ester was characterized using FTIR and nuclear magnetic resonance (NMR) spectroscopies. A titration method was used to determine the epoxy value, iodine value, oxygen oxirane content, conversion, and selectivity. At the optimum conditions, the process achieved 95.7% conversion oxirane (RCO) and the final product with 4.12% oxygen oxirane content (OOC) and 3.4g I_2/g iodine value (IV), respectively. ECOTMP ester proved to be a good candidate as an intermediate compound for further chemical modification and conversion to high-end bio-lubricant products. In addition, the ECOTMP ester demonstrated good physicochemical characteristics that can be useful in many industrial applications.

5.1 Introduction

Trimethylolpropane (TMP) triester, obtained from esterification/transesterification of different vegetable oils, has good physicochemical characteristics (e.g., good viscosity and viscosity index (VI), perfect anti-wear properties, biodegradability, and thermal stability). These qualities make them well-suited for bio-lubrication in many industrial applications, especially in metalworking fluids systems [1-4]. However, esterified/transesterified TMP esters from vegetable oils do not have suitable oxidation stability due to the presence of carbon-carbon double bonds (C=C) in their structure [5,6]. Therefore, for many lubricating applications, oxidation of industrial lubricants is a major concern that limits their use. In fact, oxidation causes the polymerization of lubricants over time, leading to a decrease in the performance of the ester lubricant along with decomposition and corrosion within lubrication systems [7,8].

One of the favorite methods for removing the carbon-carbon double bond in the molecular structure of vegetable oils in order to convert them into fully saturated esters and enhance oxidation stability is the epoxidation reaction [9-11]. Epoxidation is a chemical reaction where an epoxide, also known as an oxirane or an epoxy, is generated from a reactant containing a double bond. Epoxides are three-membered cyclic ethers characterized by a ring structure composed of one oxygen atom and two carbon atoms [12-14]. The versatility and significance of the epoxidation reaction in various applications make it widely employed in both laboratory and industrial settings [15]. Epoxides serve as essential materials in the synthesis of numerous organic compounds, including pharmaceuticals, polymers, and fine chemicals [16,17].

The epoxidation reaction of vegetable oils has garnered significant attention from numerous researchers owing to the high reactivity of the epoxide group [18-20]. Epoxidized vegetable oils can be used in many parts of industry as plasticizers in the production of polyvinyl chloride (PVC) products, coalescing agent and film-forming additive in waterborne coatings and paints, plasticizer and tackifier in adhesives and sealants, processing aid and stabilizer in the rubber industry, and food-grade plasticizer and stabilizer in food packaging materials [21-23]. In addition, the exploration of epoxidized vegetable oils extends to various additional applications, including lubricants, metalworking fluids, agricultural chemicals, and as a precursor for the synthesis of bio-based epoxy resins [24,25].

The most common method for epoxidation is the reaction of an olefin (a molecule with a carbon-carbon double bond) with an oxidizing agent (e.g., oxygen, hydrogen peroxide, tert-Butyl hydroperoxide (TBHP), and sodium hypochlorite) [26,27]. The oxidizing agent introduces an oxygen atom into the double bond, resulting in the formation of the epoxide [28].

Nowadays, TBHP is preferred in many epoxidation reactions due to its high reactivity that facilitates efficient conversion of double bonds in vegetable oils to epoxy groups, good selectivity that allows for the production of higher-quality epoxidized vegetable oils with minimal side reactions, ease of handling that makes it convenient to handle and use in industrial-scale epoxidation processes, and compatibility with catalysts that provides flexibility in choosing the catalyst system with specific requirements of the epoxidation process [29,30]. Furthermore, TBHP has been widely accepted and utilized in the industry for epoxidation reactions. Its effectiveness and established track record have contributed to its popularity and adoption in many epoxidation processes [31]. However, the cost and availability of TBHP can vary depending on location and market conditions and should be taken into consideration.

Usually, the industrial epoxidation process of vegetable oils involves the utilization of peracids (oxidizing agents) along with strong mineral acids (as catalysts). However, this method is associated with equipment corrosion and significant waste [10,32]. On the other hand, to address these issues and achieve a good selectivity, the use of transition metal complexes as homogeneous or heterogeneous catalysts has attracted the attention of many researchers [33-35]. Heterogeneous catalysts are known for their ease of separation from the products after the reaction for recycling and for reducing operating costs [36]. However, their catalytic activity is lower compared to homogeneous catalyst systems [37].

Recent studies indicate that many researchers have paid special attention to the heterogenization of homogeneous catalysts, including widely used materials such as clay, silica, and polymer reagents in organic synthesis. For instance, Sohrabi et al. [38] indicated that the role of immobilized Ni (II) complexes with macrocyclic ligands within montmorillonite and MCM-41 as catalysts in epoxidation of cyclohexane, cyclopentene, norbornene, styrene and α-methylstyrene with TBHP. Pereira et al. [39], employed vanadyl acetylacetonate anchored onto amine-functionalized clays as a heterogenous catalyst for epoxidation of geraniol. Kureshy et al. [40], developed the immobilization of dicationic chiral Mn (III) salen complexes via an exchange process in the interlayer of montmorillonite in epoxidation of styrene, achieving a remarkable epoxide selectivity of more than 99% for all alkenes except styrene. In another study, Jiang et al. [41], investigated the epoxidation reaction of cyclohexane by air using cobalt salophen complex immobilized into montmorillonite as a catalyst demonstrating high activity and selectivity for epoxidation of cyclohexene. The epoxidation of oleic acid methyl ester and fatty acid methyl esters of vegetable oil was also studied with different kinds of Ti-MCM-41 materials and Ti (IV)-grafted silica catalysts using TBHP as oxidant by Guidotti et al. [42] and Rios et al. [43], respectively. Recently, Martínez et al. [44] evaluated the epoxidation of soybean oil using TBHP as an oxidizing agent and a functionalized gallium metal-organic framework with active dioxo-molybdenum (VI) centers as a catalyst. They claimed that the highest epoxide selectivity (91%) was obtained at 110°C after 4 h of reaction.

As a matter of fact, among the transition metal complexes molybdenum complexes have gained considerable interest as catalysts for promoting epoxidation reactions. One of the key factors contributing to their effectiveness is their ability to activate molecular oxygen (O_2) and transfer an oxygen atom to the substrate [45]. On the other hand, montmorillonite is a type of layered clay mineral with a high surface area and cation-exchange capacity, making it a suitable support material for anchoring metal complexes [46]. Functionalizing montmorillonite with ethanolamine involves modifying the clay surface with amino groups, which can enhance the interaction between the clay and metal complex and potentially improve the catalytic performance [47]. Immobilizing molybdenum acetylacetonate onto functionalized montmorillonite with ethanolamine offers several advantages. The clay support can provide a stable environment for the catalyst, prevent leaching of the active species, and facilitate the separation and recycling of the catalyst. Additionally, the interaction between the metal complex and the clay surface can influence the catalytic activity and selectivity of the system.

Overall, anchoring molybdenum acetylacetonate with functionalized montmorillonite with ethanolamine as a catalyst for epoxidation reactions of TMP esters is a promising approach that combines the advantages of both the metal complex and the clay support. It offers the potential for improved catalytic performance and recyclability, which are desirable features in industrial processes.

In this study, the epoxidation reaction of canola oil trimethylolpropane (COTMP) ester using TBHP as the oxidant agent and a heterogeneous catalyst obtained by the immobilization of bis(acetylacetonate)dioxo-molybdenum (VI) [$MoO_2(acac)_2$] with montmorillonite (K10)-ethanolamine was evaluated. Various reaction parameters, including the molar ratio of TBHP to COTMP ester, reaction time and temperature were investigated. The resulting epoxidized complex esters were analyzed using FTIR, and ^{1}H NMR. The epoxy value (EV), selectivity, iodine value (IV), and oxygen oxirane content (OOC) of the epoxidized canola oil trimethylolpropane (ECOTMP) ester were determined using a titration method. In addition, the heterogenous catalyst was analyzed by XRD, SEM-EDS, and FTIR. Furthermore, the physicochemical, tribological, and rheological properties of the final product were characterized for biolubricant application.

5.2 Materials and Methods

5.2.1 Materials

COTMP ester was obtained from our previous work [14]. All chemicals including K10-montmorillonite, tertbutyl hydroperoxide solution 5.0–6.0 M in decane, bis(acetylacetonato)dioxo-molybdenum (VI) [$MoO_2(acac)_2$], glacial acetic acid (reagent grade, 100%), potassium iodide, carbon tetrachloride (reagent grade, 99.9%), pure iodine (≥99%), sodium thiosulphate (0.1 N), starch solution (0.1 N), crystal violet, potassium hydrogen phthalate, chlorobenzene (reagent grade, 99%), chloroform (reagent grade, 99%), dry toluene (reagent grade, 99.5%), hydrogen bromide (33 wt.% in acetic acid), anhydrous tetraethylammonium bromide, perchloric acid were purchased from Aldrich and used without further purification .

5.2.2 Functionalization of the montmorillonite K10 with ethanolamine

Before starting the experiment, the montmorillonite K10 was heated in an oven at 120°C for 3 hours under vacuum. Afterwards, ethanolamine was grafted onto montmorillonite by refluxing a mixture containing montmorillonite K10 (30 g) and ethanolamine (200 ml) for 24 h at 90°C. The obtained solid (K10-ETA) was centrifuged at 3000 rpm. The K10-ETA was then washed with ethanol (99%) and centrifuged. The resulting solid was dried at 60°C overnight and used in the next step. [39,40]

5.2.3 Immobilization of [$MoO_2(acac)_2$] complex on K10-ethanolamine (ETA) clay

Functionalized clay (K10-ETA) (25 g) was refluxed with a solution of [$MoO_2(acac)_2$] (1.7 g, 95 mmol) in 150 cm^3 chloroform for 24 h at room temperature. After completion of the experiment, the obtained powder was filtered and refluxed with chloroform (100 cm3) for 2 h to remove unreacted [$MoO_2(acac)_2$] from the final catalyst. Afterwards, the resulting solids were recovered by vacuum filtration and then dried in an oven at 120°C for 3 h under vacuum [39]. These materials were identified as [$MoO_2(acac)_2$]@K10-ETA. **Figure** 5.1 indicates the proposed mechanism for the direct immobilization of metal complex ([$MoO_2(acac)_2$]) on K10-ETA clay.

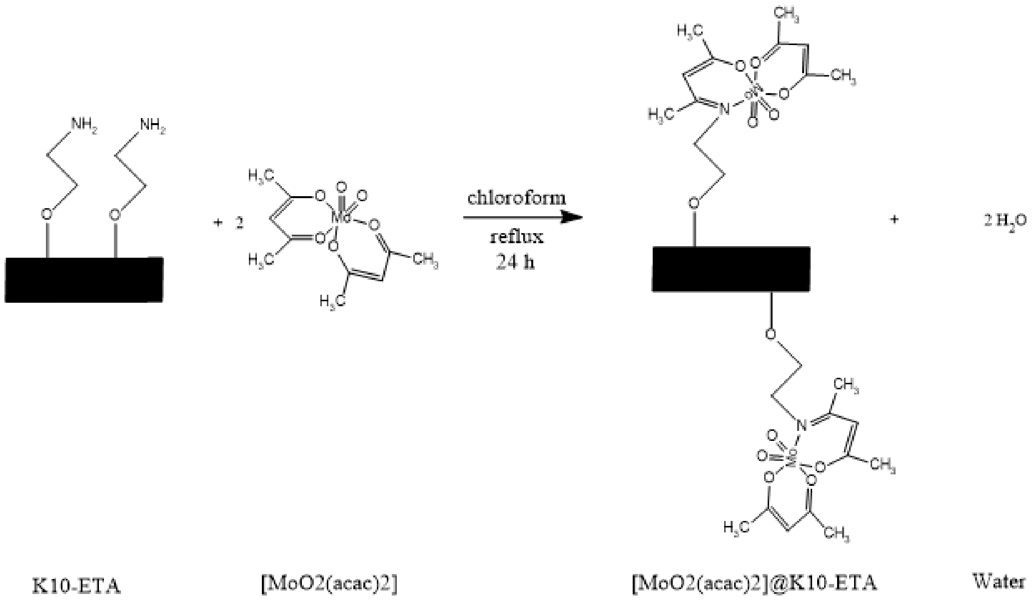


Figure 5.1: Schematic presentation of the synthesis of molybdenum oxide acetylacetonate immobilized to montmorillonite K10-ethanolamine clay.

5.2.4 Epoxidation reaction

In a 50 mL round-bottomed flask equipped with a reflux condenser, a mixture of COTMP ester (5 g; 5.4 mmol) and toluene (20 mL) was prepared. To the flask, [MoO$_2$(acac)$_2$]@K10-ETA catalyst (0.5 g; containing 2.6 wt.% of Mo) and anhydrous TBHP (equivalent to the double bonds) were added. The mixture was vigorously stirred at 85°C for desired reaction time ranging from 5 to 70 h. The catalyst was then separated from the reaction mixture through filtration. The filtrate was cooled in an ice bath, followed by a slow addition of sodium bisulfite solution (15% w/v) to remove the unreacted peroxide. The organic phase was separated, dried using anhydrous sodium sulfate, filtered, and the solvent was removed using a rotary evaporator. Catalyst recycling tests were conducted by washing the collected catalyst with toluene, drying it at 110°C under reduced pressure for 6 hours, and using it for subsequent catalytic runs under the optimal reaction conditions. Additional reactions using only montmorillonite K10 clay as the catalyst and without any catalyst were also performed. All reactions were conducted independently at least three times, demonstrating good reproducibility with an error below 5%. **Figure** 5.2 illustrates the mechanism for producing ECOTMP ester.

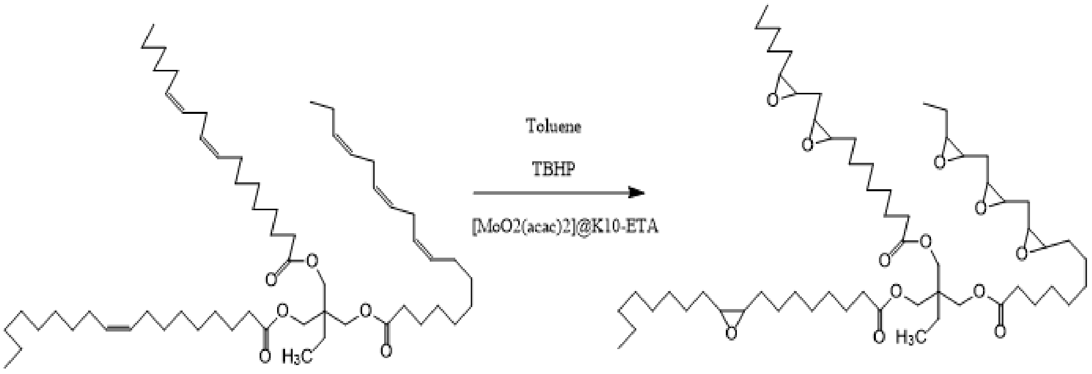


Figure 5.2: Schematic presentation of the epoxidation reaction of COTMP ester with TBHP in presence of [MoO$_2$(acac)$_2$]@K10-ETA as catalyst.

5.2.5 Characterization methods

X-ray diffractograms of the resulting solid [MoO2(acac)$_2$]@K10-ETA were obtained with a Rigaku SmartLab X-ray diffraction system in Bragg-Brentano geometry. Diffraction data were acquired over a 2θ range from 3° to 20° with a step width of 0.02° and a scan speed of 3° min^{-1}.

The morphology determination involved capturing micrographs through scanning electron microscopy (SEM) using a JEOL JSM-6300F microscope coupled with a Noran System Instruments EDX energy dispersive X-ray spectrometer (EDS) at an acceleration potential of 15 kV. Back-scattering detection was utilized for acquiring SEM images. To prepare the samples, they were mounted on an aluminum support, secured to a carbon ribbon, and subjected to carbon electrodeposition under vacuum for metallization.

Fourier-transform infrared (FTIR) spectra of the compounds were acquired using a Jasco FTIR-460 Plus spectrophotometer, covering the range of 400-4000 cm^{-1}. For the solid samples, the spectra were obtained using KBr pellets of spectroscopic grade from Merck.

Thermogravimetric (TG) analyses were conducted on an SDTQ600 instrument, employing a heating rate of 10°C/min. The temperature range for the TG analyses was from 25 to 800°C under a flowing N_2 atmosphere at a rate of 100 mL/min.

^{1}H NMR spectra of the samples were recorded using a Bruker® Ultrashield spectrometer with a frequency of 300 Hz. Chemical shifts observed in each spectrum were referenced in parts per million (ppm) relative to the signal of tetra-methyl silane (TMS). To prepare the samples, approximately 200 µl of each sample was directly transferred into 5-mm NMR tubes containing deuterated chloroform ($CDCl_3$). The volume was then adjusted to 600 µl by adding $CDCl_3$ containing 0.05% TMS.

The final ECOTMP ester underwent various measurements to determine its viscosity, viscosity index (VI), Pour point, Flash point (using the open cup method), and Four-ball properties. The measurements were performed using the following ASTM methods: D445 for viscosity, D2270 for viscosity index (VI), D97 (using a Pour Point Tester manufactured by HK Petroleum Co., China) for Pour point, D92-18 (using a Flash Point Tester manufactured by HK Petroleum Co., China) for Flash point, and D4172 for Four-ball testing.

The oxirane oxygen content (OOC), iodine value (IV), and epoxy value (Eν) of the samples were obtained according to AOCS Official Method Cd 9-57, AOCS Official Method Cd 1-25, and ASTM D1652-11, respectively.

The conversion and selectivity of the ECOTMP esters were calculated based on following equations:

$$Conversion\,(\%) = \frac{I_{v_0} - I_v}{I_{v_0}} \times 100\% \tag{1}$$

$$S\,(\%) = \frac{E_v}{(I_{v_0} - I_v)/253g/mol} \times 100\% \tag{2}$$

Where I_{v_0} is the iodine number of the methyl ester/vegetable oil before epoxidation, $gI_2/100g$ of the oil, I_v is the iodine number of the methyl ester/vegetable oil after epoxidation, $gI_2/100g$ of the oil, E_v is the epoxy number of the ester of a vegetable oil after the epoxidation reaction, mol/100g of the epoxidized oil, and 253.8 g/mol is molecular weight of I_2.

Rheology analysis of the COTMP ester was done using a Thermo Scientific MARS iQ Air rheometer equipped with a P25 parallel plate for investigation the behavior of dynamic viscosity against shear rate and temperature ramp in CR mode.

5.3 Results and Discussion

5.3.1 Characterization of the $[MoO_2(acac)_2]$@K10-ETA

5.3.1.1 SEM-EDS

SEM analysis revealed a noticeable alteration in the morphology of $[MoO_2(acac)_2]$@K10-ETA, as depicted in **Figure** 5.3a and b. The SEM micrographs exhibited the deposition or clustering of metal complex particles on the modified clay's surface (**Figure** 3b). This observation suggests that the Mo species have interacted with the clay matrix, resulting in the formation of clusters or localized deposits. Furthermore, the EDS spectrum (as shown in **Figure** 5.4) was obtained to qualitatively assess the composition of the entire section, confirming the presence of molybdenum immobilized within the K10-ETA clay (**Figure** 5.4b). The EDS analysis disclosed a Mo content of 2.6 wt.% in the immobilized catalyst. The presence of metal deposits on the clay surface implies that Mo is on the surface of catalyst particles [48,49]. While the EDS analysis confirms the presence of Mo in the sample, it does not provide detailed information about whether the molybdenum is primarily located on the surface or distributed within the interior of the catalyst particles. Therefore, the XRD test was conducted to further elucidate the distribution and structural characteristics of the molybdenum-containing species.

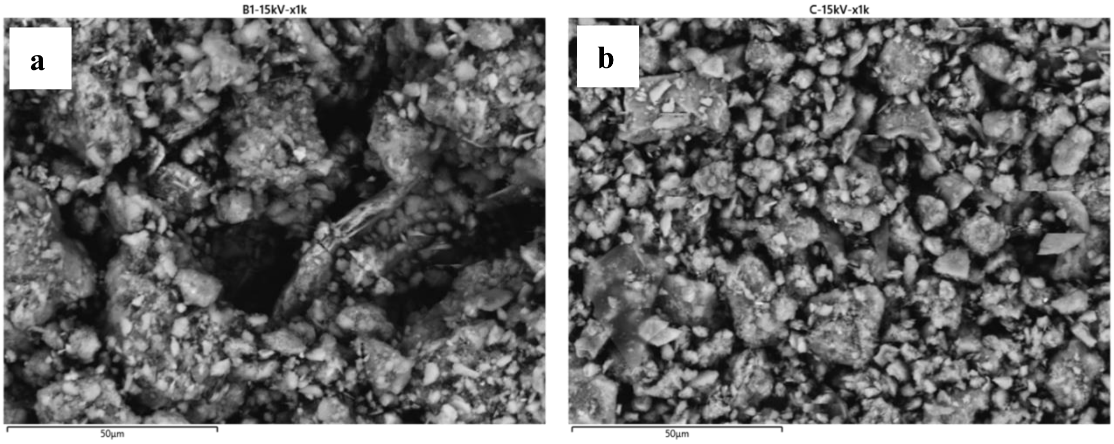
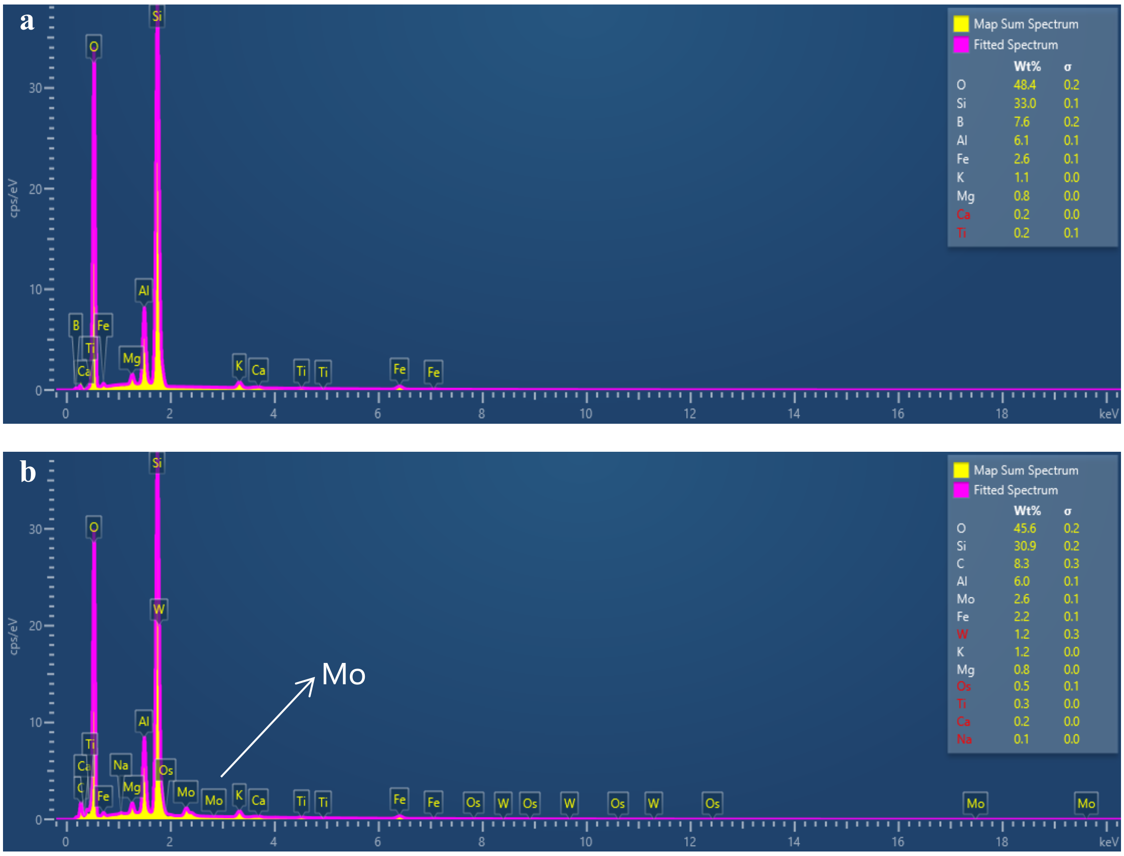


Figure 5.3: Scanning electronic microscopy analysis (SEM) of (a) K10 and (b) $[MoO_2(acac)_2]$@K10-ETA.



a

	Wt%	σ
O	48.4	0.2
Si	33.0	0.1
B	7.6	0.2
Al	6.1	0.1
Fe	2.6	0.1
K	1.1	0.0
Mg	0.8	0.0
Ca	0.2	0.0
Ti	0.2	0.1

b

	Wt%	σ
O	45.6	0.2
Si	30.9	0.2
C	8.3	0.3
Al	6.0	0.1
Mo	2.6	0.1
Fe	2.2	0.1
W	1.2	0.3
K	1.2	0.0
Mg	0.8	0.0
Os	0.5	0.1
Ti	0.3	0.0
Ca	0.2	0.0
Na	0.1	0.0

Figure 5.4: Eergy dispersive X-ray spectrometer (EDS) spectra of (a) K10 and (b) $[MoO_2(acac)_2]$@K10-ETA.

5.3.1.2 XRD

The diffractograms for both the K10 and $[MoO_2(acac)_2]$@K10-ETA are illustrated in **Figure** 5.5. In accordance with expectations for this type of material, the diffraction pattern for K10 reveals a d001 basal spacing of 9Å. However, in the case of $[MoO_2(acac)_2]$@K10-ETA, we observe not only the diffraction peak at $2\theta \approx 8.9°$ but also a broad peak centered at 2θ around 6.4°. This outcome suggests that the clay experiences swelling as a result of the intercalation of $[MoO_2(acac)_2]$ between the layers. The resemblance between the diffractograms of these materials implies that the clay's structural integrity is preserved throughout the complex immobilization process. This phenomenon is in good agreement with previous literature concerning the immobilization of complexes between the clay layers of K10 montmorillonite [48,49].

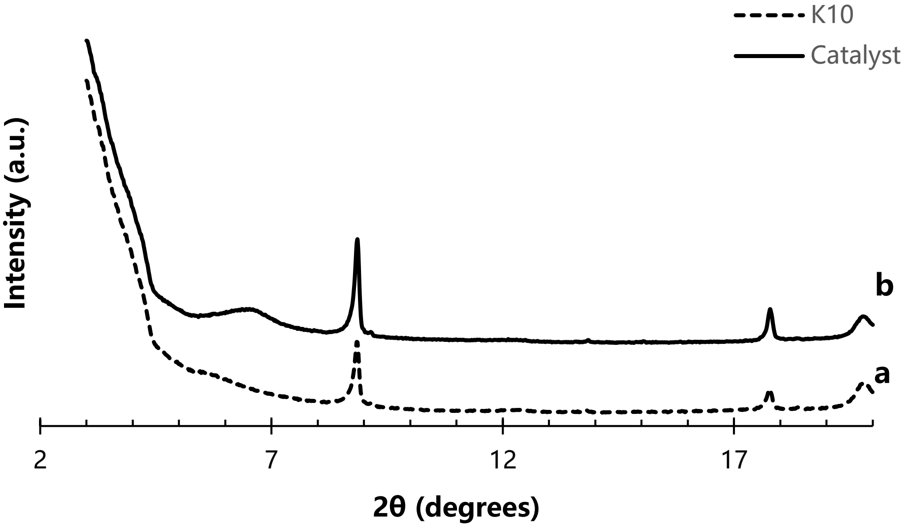


Figure 5.5: X-ray diffractograms for (a) K10 and (b) $[MoO_2(acac)_2]$@K10-ETA.

5.3.1.3 FTIR of K10 and $[MoO_2(acac)_2]$@K10-ETA

The FTIR spectra of the K10 and $[MoO_2(acac)_2]$@K10-ETA is illustrated in **Figure** 5.6. Before the anchoring reaction (K10 montmorillonite to ethanolamine), the IR spectrum of the clay (referred to as K10) shows bands related to OH stretching vibrations (3624 and 3692 cm^{-1}) coordinated to octahedral cations (mainly Al, but also Mg and Fe), a broad band centered at 3412 cm^{-1} associated with OH stretching vibration (physisorbed interlayer water), OH deformation (1632 cm^{-1}), Si-O stretching vibrations (1200-1000 cm^{-1}), Si-O-Al (octahedral Al, 528 cm^{-1}), and Si-O-Si bending vibrations (463 cm^{-1}) [50-54].

For the catalyst ([$MoO_2(acac)_2$]@K10-ETA), a decrease in the intensity of the broad band centered at 3410 cm^{-1} suggests the presence of hydrogen bonds between the pseudo-π system of the acac ligand and the protons of the clay's silanol groups. The presence of peaks at 2904 cm^{-1} and 2958 cm^{-1}, which correspond to the symmetric CH_2 and asymmetric CH_2 vibrations of the alkyl chains associated with the K10-ETA, confirms the successful grafting of $MoO_2(acac)_2$ onto the K10-ETA support [39,50].

The new bands at approximately 1660, 1510, and 1454 cm^{-1} in the spectrum of [$MoO_2(acac)_2$]@K10-ETA passibly result from a combination of vibration modes. These modes include stretching vibrations of the new C=N bond introduced in the chelate ring of the acac ligand through the anchoring reaction and the reaction between amine groups of the grafted ethanolamine and the C=O group from the coordinated acetylacetonate ligand. This observation suggests the consumption of OH groups and supports an immobilization mechanism for [$MoO_2(acac)_2$] [12,39].

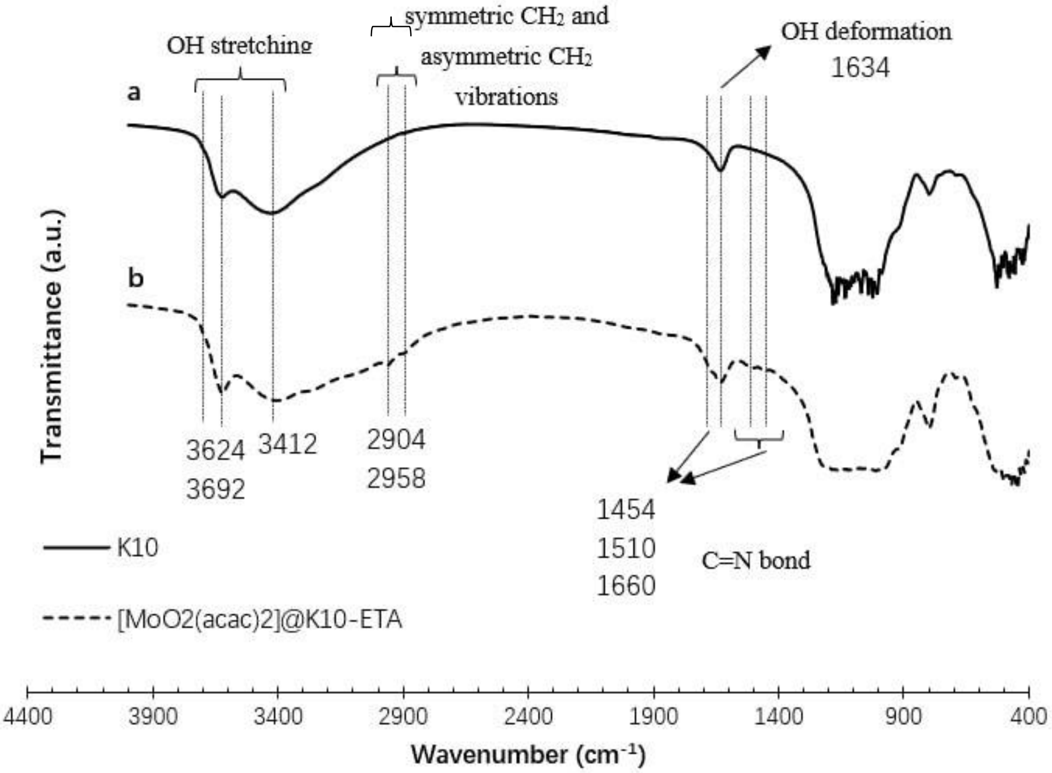


Figure 5.6: FTIR spectrum of (a) K10 and (b) [$MoO_2(acac)_2$]@K10-ETA.

5.3.2 Epoxidation reaction

To identify the optimum reaction condition, various parameters (e.g., reaction time, molar ratio of COTMP ester to TBHP, and reaction temperature) were investigated, utilizing the known data for theoretical oxirane oxygen content (OOC_{th}) and initial iodine value (IV_0) of COTMP ester, which were 4.31% and 71.38 mg I_2/g, respectively. For this purpose, the conversion percentage of carbon-carbon double bonds to oxygen rings and the property of oxirane oxygen content (OOC_{exp}) were determined for each experiment and the outcomes of these optimization experiments are summarized in **Table** 5.1.

Table 5.1: Epoxidation of COTMP ester under various reaction conditions in the presence of [MoO2(acac)2]@K10-ETA as a catalyst. (OOC_{exp}: experimental oxirane oxygen content, RCO: relative percentage of oxygen).

Entry	Reaction time (h)	Molar ratio of COTMP ester:	Temp. (°C)	OOC_{exp} (%)	RCO (%)	Conversion (%)	Selectivity (%)

		TBHP					
1	30	1:1	75	2.81±0.25	65.22±3.8	71.4	80.89
2	50	1:1	75	3.28±0.12	76.10±3.04	83.2	85.21
3	70	1:1	75	3.12±0.2	72.41±4.2	82.8	87.79
4	50	1:1	85	3.67±0.18	85.15±4.4	90.1	94.46
5	50	1:1	95	3.45±0.11	80.09±2.8	85.7	58.31
6	50	1:1	105	3.03±0.23	70.26±5.4	83.1	57.57
7	50	1:1.5	85	4.12±0.1	95.70±2.9	95.2	98.62
8	50	1:2	85	3.50±0.14	81.27±3.4	94.9	97.12
9	50	1:2.5	85	3.35±0.25	77.73±5.9	94.8	97.57

5.3.2.1 Effects of reaction time

The effect of reaction time on OOC_{exp} of the ECOTMP ester is shown in **Figure** 5.7. The reaction time indicates a significant impact on the conversion of the double bonds C=C in COTMP ester (up to 83.2%) to the corresponding epoxide. It is observed that the OOC_{exp} gradually increases from 0.9% (5 h) to 3.28 % (50 h). Furthermore, under these reaction conditions, the iodine value measured 12 mg I_2/g, indicating enhancements in the conversion of C=C double bonds to oxirane rings. The reaction time exhibits minimal effect on the epoxide selectivity (**Table** 5.1, entries 1–3). Thus, a reaction time of 50 h was chosen as the optimum condition yielding a 76% of relative percentage of oxygen (RCO) for subsequent steps.

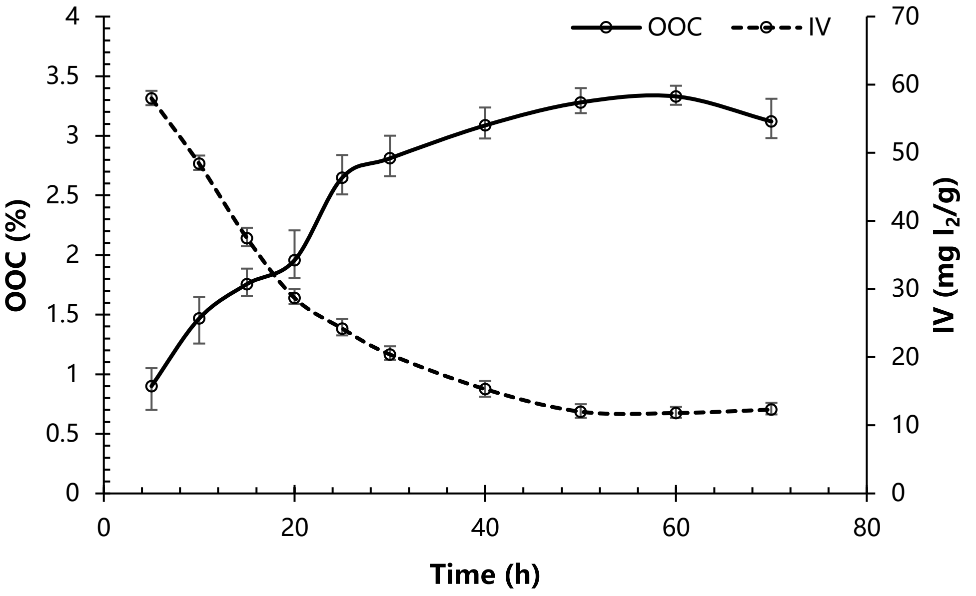


Figure 5.7: Effect of reaction time on oxirane oxygen content (OOC_{exp}) and iodine value (IV) of canola oil trimethylolpropane (COTMP) ester via epoxidation reaction. (Other reaction parameters: molar ratio of substrate TBHP: 1:1; temperature: 75°C; catalyst loading: 1 wt.%).

5.3.2.2 Effects of reaction temperature

To determine the most effective reaction temperature for the epoxidation process, a sequence of experiments was conducted following the outlined procedure, with variations in reaction temperature (from 65 to 105°C as detailed in **Table** 5.1, entries 4–6). The peak conversion of COTMP ester and the highest degree of selectivity towards epoxide were achieved at 85°C, reaching 90.1% and 94.46%, respectively. However, further increasing the reaction temperature (up to 105°C) resulted in a substantial decline in both OOC_{exp} and epoxide selectivity. In addition, as indicated in **Figure** 5.8, the maximum OOC_{exp} and minimum iodine value for ECOTMP ester was obtained at 85°C which was 3.67% and 7.1 mg I_2/g, respectively. Consequently, a temperature of 85°C was adopted as the optimal reaction temperature for all subsequent experiments.

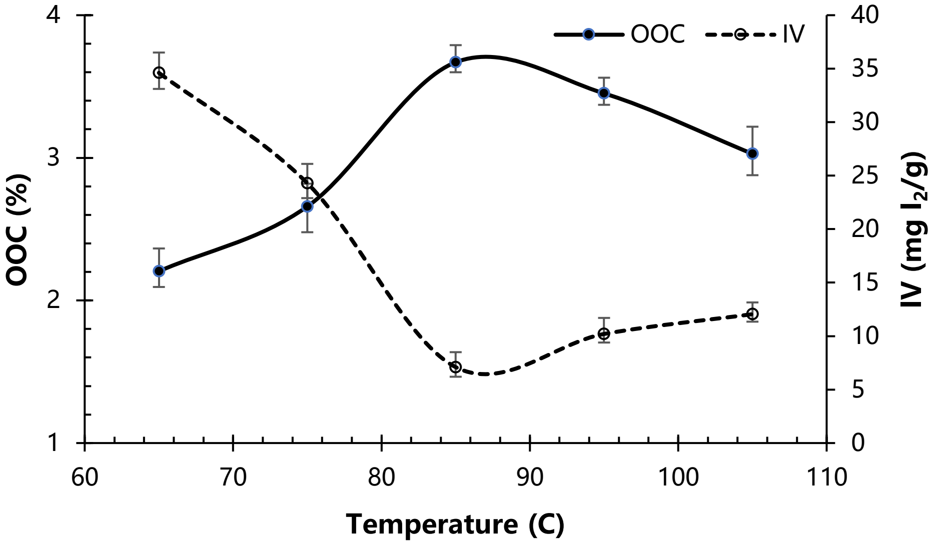


Figure 5.8: Effect of reaction temperature on oxirane oxygen content (OOC_{exp}) and iodine value (IV) of canola oil trimethylolpropane (COTMP) ester via epoxidation

reaction. (Other reaction parameters: molar ratio of substrate to TBHP: 1:1; time: 50 h; catalyst loading 1 wt.%).

5.3.2.3 Effects of molar ratio of (tert-Butyl hydroperoxide) TBHP to carbon-carbon double bond in COTMP ester

The impact of the molar ratio on conversion of C=C double bonds to epoxide was investigated by varying the molar ratio across a range from 1:1 to 1:2.5 (as documented in **Table** 5.1, entries 7–9). Notably, at a molar ratio of 1:1.5, the OOC_{exp} increased significantly to 4.12% (RCO=96%), implying that nearly all of the unsaturated C=C double bonds were converted into epoxides (**Figure** 5.9). According to **Table** 5.1, the conversion and epoxide selectivity were maximum for all tested three molar ratios (e.g., 1:1.5, 1:2, and 1:2.5). It should be noted that the amount of catalyst was fixed in all epoxidation reactions (50 mg, 1 wt.%). Based on the results obtained above, the optimized reaction conditions for epoxidation of COTMP ester should include a catalyst loading of 1 wt.%, a molar ratio of COTMP ester to TBHP at 1:1.5, a reaction time of 50 h, and a temperature of 85°C.

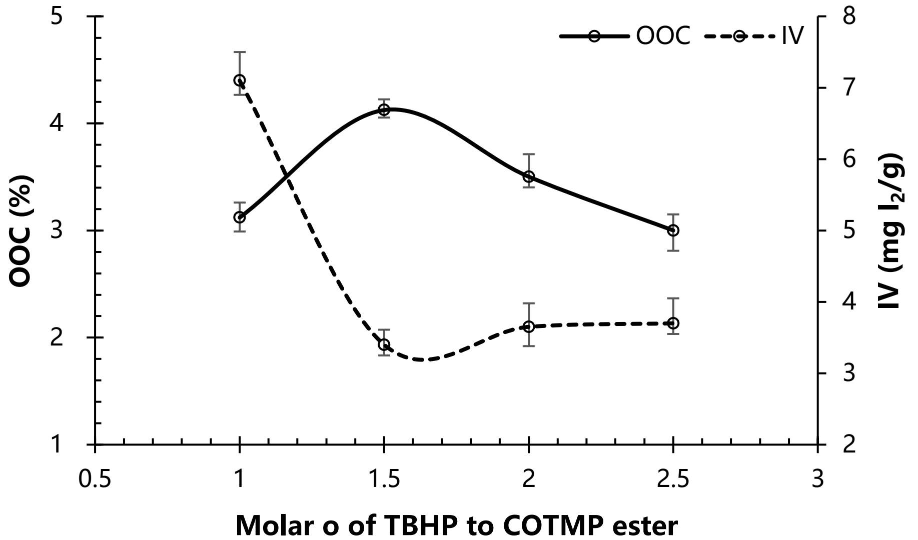


Figure 5.9: Effect of molar ratio of TBHP to double bonds C=C on oxirane oxygen content (OOC_{exp}) and iodine value (IV) of canola oil trimethylolpropane (COTMP) ester via epoxidation reaction. (Other reaction parameters: temperature: 85°C; time:

50 h; catalyst loading 1 wt.%).

5.3.3 Properties of the products

5.3.3.1 FTIR

In the FTIR spectrum of ECOTMP ester with $[MoO_2(acac)_2]$@K10-ETA as catalyst (**Figure** 5.10b), several characteristic peaks can be identified. The C-H sp^3 stretch, associated with the carbon-hydrogen bonds in the molecule, appears in the range of 2856-2926 cm^{-1}. This range corresponds to the stretching vibrations of the aliphatic C-H bonds present in the molecule [55]. The C-O-C vibration resulting from the oxirane ring, which is characteristic of the epoxy group, appears as a peak at 825 cm^{-1} [56,57]. This peak indicates the presence of the epoxy functional group in the ECOTMP ester. Comparing the FTIR spectra of ECOTMP ester with COTMP ester (**Figure** 5.10a), a notable difference can be observed. Specifically, the disappearance of the C=C olefin peak in the epoxidized spectrum indicates the conversion of the double bonds into epoxy groups. The corresponding peak for the C=C bond typically appears at around 3003 cm^{-1} in the FTIR spectra of COTMP ester [55]. The absence of this peak in the FTIR spectrum of ECOTMP ester suggests that the double bonds have reacted and transformed into epoxy groups. Furthermore, the comparison between **Figure** 5.10c (epoxidation reaction with K10 as catalyst) and **Figure** 5.10d (epoxidation reaction without catalyst) reveals that the presence of a peak corresponding to the epoxy group is minimal or insignificant. Furthermore, as indicated in **Table** 5.2, the OOC_{exp} value was measured for epoxidation reaction of COTMP ester with TBHP in three situations (e.g., with K10, $[MoO_2(acac)_2]$@K10-ETA, and no catalyst) at 85°C and 50 h. The RCO for ECOTMP ester using $[MoO_2(acac)_2]$@K10-ETA was 95.7% which clearly depicts the completion of epoxidation reaction compared to other ones.

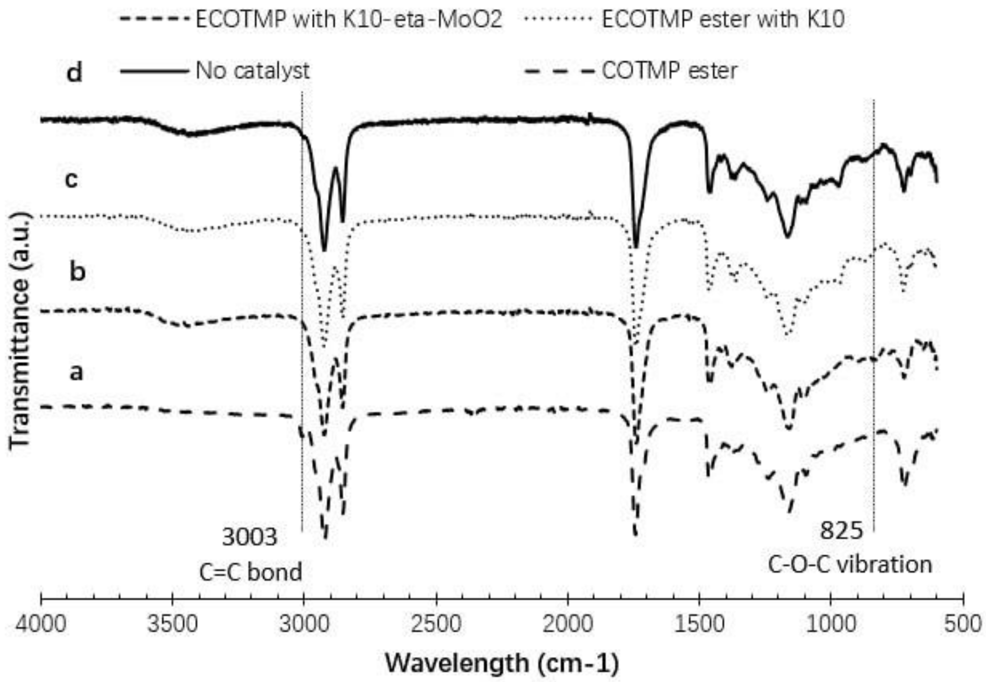


Figure 5.10: FTIR spectrum of COTMP ester and ECOTMP ester produced with/without catalyst. a) COTMP ester, b) epoxidation reaction with catalyst ([$MoO_2(acac)_2$]@K10-ETA), c) epoxidation reaction with K10, d) epoxidation reaction without catalyst.

Table 5.2: The OOC_{exp} and RCO of ECOTMP ester without catalyst and in presence of K10 and [$MoO_2(acac)_2$]@K10-ETA.

Type of catalyst in epoxidation reaction	OOC_{exp} (%)	RCO (%)
No catalyst	0.83	19.24
K10	0.94	21.77
[$MoO_2(acac)_2$]@K10-ETA	4.12	95.7

5.3.3.2 ^{1}H NMR

^{1}H NMR spectroscopy was employed to confirm the structure of COTMP and ECOTMP ester. Deuterated chloroform served as the solvent for sample dissolution, and the ^{1}H NMR spectra were recorded at δ 7.24 ppm. **Figure** 5.11a indicates the ^{1}H NMR spectrum of COTMP ester. The signal at δ 0.84-0.88 ppm (a) corresponds to the terminal methyl protons ($-CH_2C\mathbf{H}_3$). The two protons in the bridging methylene group adjacent to the terminal methyl group at δ 1.43-1.48 ppm (c) are assigned to $-C\mathbf{H}_2CH_3$

and exhibit quadruple splitting. Most bridging methylene protons overlap with δ 1.23-1.33 ppm at peak b [$-CH_2C\mathbf{H}_2CH_2$ and $-(CH_2)_3CC\mathbf{H}_2CH_3$] due to the shielding effect caused by their proximity to high electron density.

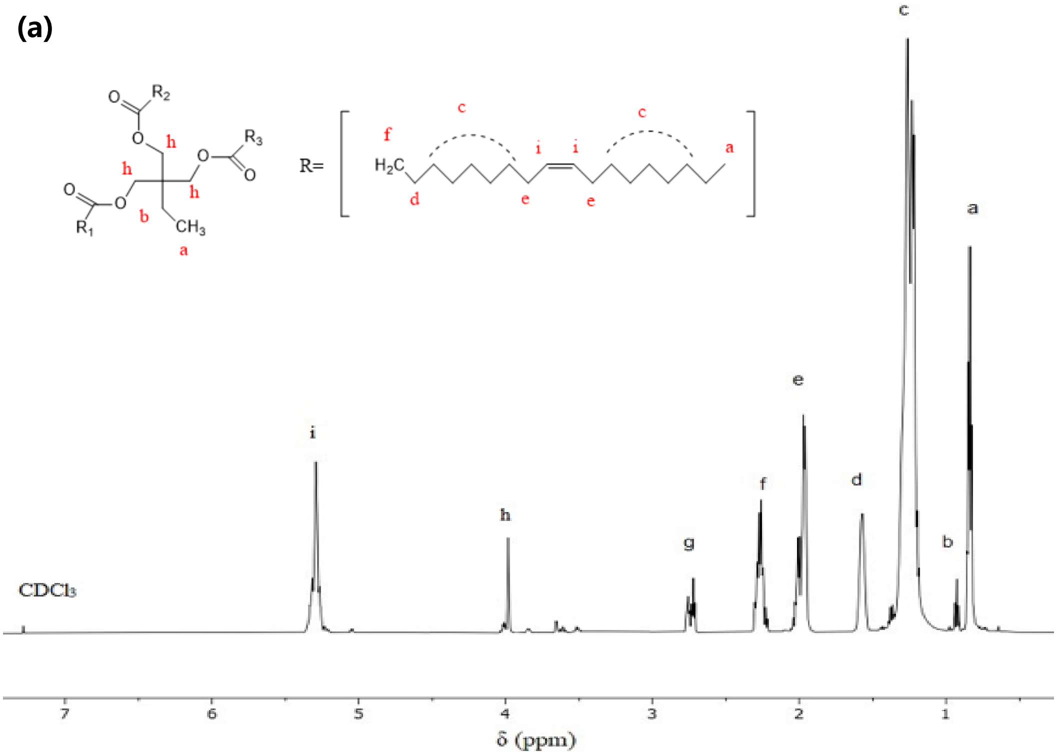
Six protons are found in the bridging methylene group at the β position at δ 1.56-1.60 ppm (d) ($-C\mathbf{H}_2-CH_2-C=O-$) and at the α position at δ 2.25-2.32 ppm (f) ($-CH_2-C\mathbf{H}_2-C=O-$), respectively. The proton adjacent to the ester linkage is assigned to δ 3.97-4.02 ppm (h) ($-\alpha-C\mathbf{H}_2-O-C$) in the COTMP ester structure. The bridging methylene group adjacent to the vinyl group at δ 1.95-2.05 ppm (e) corresponds to ($-CH_2C\mathbf{H}_2-CH=CH$). The presence of unsaturated double bonds in the COTMP ester is confirmed by δ 5.27-5.38 ppm (i) for the methine protons ($-C\mathbf{H}=C\mathbf{H}-$). The bridging methylene group between the two methine groups is assigned to δ 2.73-2.77 ppm (g) ($-CH=CH-C\mathbf{H}_2-CH=CH-$), representing the linoleic fatty acid moiety in the COTMP ester structure.

In **Figure** 5.11b, the ^1H NMR spectrum of ECOTMP ester is shown. The signal at δ 0.84-0.89 ppm (a) is attributed to the terminal methylene protons of ($-CH_2C\mathbf{H}_3$). The bridging methylene signals at δ 1.21-1.35 ppm (b) correspond to ($-CH_2.C\mathbf{H}_2-CH_2-$) and $-(CH_2)_3CC\mathbf{H}_2CH_3$, while the protons in the bridging methylene group adjacent to the terminal methylene at δ 1.36-1.42 ppm (d) are assigned to ($-CH_2-CH=CH-CH_2-CH=CH-CH_2\mathbf{-}$).

The bridging methylene group at the β position is represented by δ 1.56-1.60 ppm (e) ($-C\mathbf{H}_2-CH_2C=O-$), and at the α position, it corresponds to δ 2.26-2.32 ppm (g) ($-CH_2C\mathbf{H}_2-C=O-$). Peaks around δ 3.96-4.02 ppm (k) are attributed to the ester link ($\alpha-C\mathbf{H}_2-O-C$). Additionally, a peak at δ 1.45-1.48 ppm (c) ($-CH_2C\mathbf{H}_2-CHOCH-CH_2CH_2-$) is observed, which is deshielded due to the strong anisotropy effect of the adjacent oxygen in the epoxy group [58].

In ^1H NMR spectrum of ECOTMP ester, as it is evident, the unsaturated C=C signals observed in COTMP ester at δ 2.73-2.77 ppm (g) and δ 5.27-5.38 ppm (i) are largely replaced by the epoxy group. Epoxide signals appear at δ 2.83-3.11 ppm (h, i, and j), likely originating from the methine protons in ECOTMP ester. The presence of monoepoxide rings in ECOTMP ester is confirmed by methine protons at δ 2.83-2.89 ppm (h) [(-C**H**OC**H**-) and (-C**H**OC**H**-CH$_2$CH=CH-)]. Diepoxide chemical shifts in ECOTMP ester are found at δ 2.92-2.98 ppm (i) (-C**H**OCH-CH$_2$-CHOC**H**-) and δ 3.02-3.11 ppm (j) (-CHOC**H**-CH2-C**H**OCH-).

In conclusion, the NMR results are consistent with the findings obtained from FTIR and OOC methods.



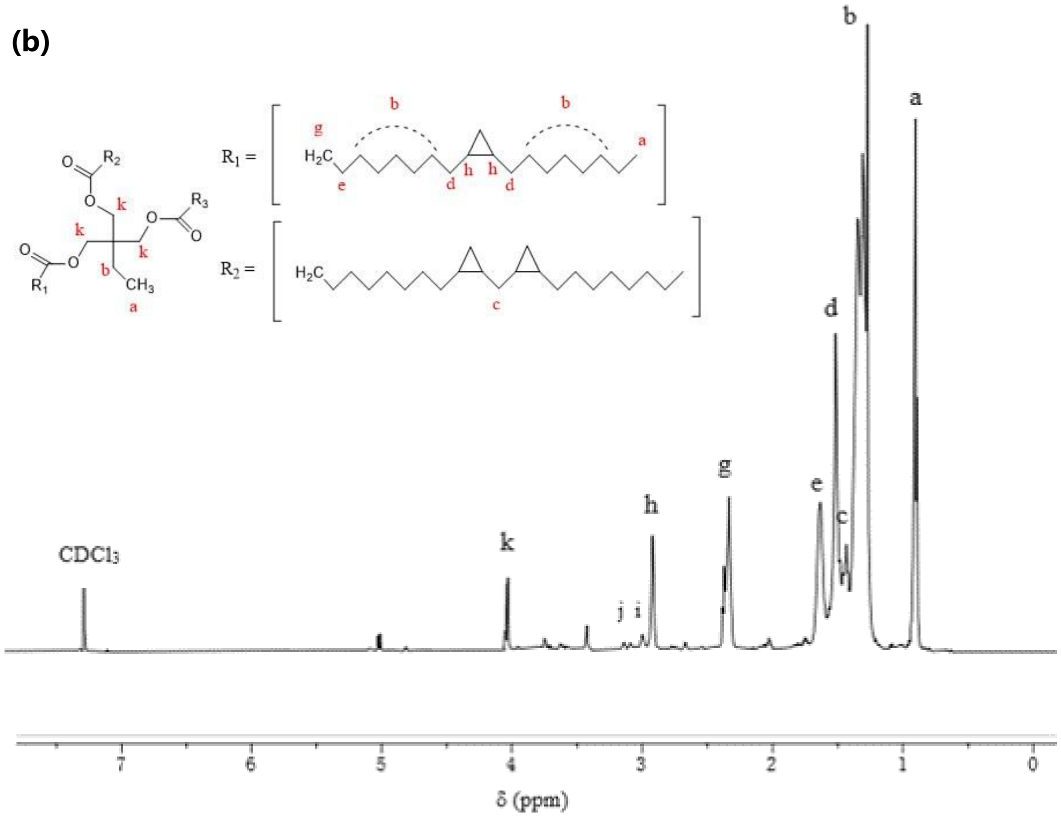


Figure 5.11: ^{1}H NMR spectrum of (a) canola oil trimethylolpropane (COTMP) ester and b) epoxidized canola oil trimethylolpropane (ECOTMP) ester obtained at the best reaction conditions.

5.3.4 Physical characteristics

Table 5.3 presents a comparison of the physical properties of crude canola oil, COTMP ester obtained by esterification of hydrolyzed canola oil with TMP, the resulting esters (ECOTMP ester) obtained by epoxidation of COTMP ester with TBHP in presence of [$MoO_2(acac)_2$]@K10-ETA as catalyst, and EP 220 (Castrol) as commercial lubricant. These properties were assessed using ASTM standards, specifically ASTM D445, D2270, D97, D 92-18, and D4172, to measure viscosity, viscosity index (VI), pour point, flash point (open cup method), and Fourball properties, respectively.

As shown in **Table** 5.3, ECOTMP ester has a higher flash point (298°C) compared to crude canola oil and COTMP ester which was expected due to its higher molecular weight. The kinematic viscosity of ECOTMP ester at 40°C was 236.17 cSt, which is completely consistent with the results obtained in the rheology section. In addition, considering the iodine value and the pour point of ECOTMP ester, which stand at 3.4 mg I_2/g and -3°C, respectively, it can be confidently concluded that the epoxidation reaction has been effectively executed. Indeed, the pour point value tends to decrease as the number of carbon-carbon double bonds in the molecule's structure increases. The current pour point value for ECOTMP ester (-3°C) needs to be improved, especially to make it suitable for industrial applications. Enhancing this value can be achieved through the incorporation of various pour point depressant (PPD) additives such as alkylaromatics and aliphatic polymers. Furthermore, the ECOTMP ester has acceptable VI (157) suggests that these esters can operate effectively across a wide range of temperatures. The wear scar diameter (WSD) for crude canola oil, COTMP ester, ECOTMP ester, and EP 220 (Castrol; commercial oil) was measured to be 0.94 mm, 0.78 mm, 0.75 mm, and 0.45 mm, respectively. Hence, ECOTMP ester as an intermediate product without adding extreme pressure (EP) additives has an acceptable WSD (0.75 mm) compared to Castrol Alphasyn (0.45 mm).

Table 5.3: Properties of crude canola oil, COTMP ester, and ECOTMP ester.

Samples	Kinematic viscosity @ 40°C	Kinematic viscosity @ 100°C	Viscosity index (VI)	Pour point (°C)	Flash point (°C)	IV (mg I_2/g)	WSD (mm)
Crude canola oil	35.8±0.11	8.2±0.08	216±4.1	-18	205±1	-	0.84±0.041
COTMP ester	30.58±0.1	6.43±0.09	170±3.5	-12	277±1	71.38±0.3	0.78±0.023
ECOTMP ester	236.17±0.1	27.02±0.1	157±3.8	-3	298±1	3.4±0.13	0.75±0.034
EP 220 (Castrol Alphasyn)	220±0.1	26.4±0.1	223±3.1	-42	220±1	-	0.45±0.022

5.3.5 Rheological characteristics

5.3.5.1 Variation of viscosity with shear rate

Figure 5.12 displays how viscosity changes with shear rate at both 20°C and 90°C. The dashed outline on the graph indicates the range within which the MARS iQ Air rheometer, equipped with the P25 parallel plate, can accurately measure. The collected data indicates Newtonian behaviour of samples (e.g., ECOTMP ester, EP 220 (Castrol), and oil soluble phosphate ester (OSPE)) which is common for most pure lubricants. As it is illustrated with increasing shear rates, there is minimal change in dynamic viscosity, which remains relatively constant throughout the entire range. One can be seen in **Figure** 5.12 that ECOTMP ester has highest variation of dynamic viscosity with shear rate (around 4 Pa.s at 20°C and 0.07 Pa.s at 90°C) which is related to its higher kinematic viscosity at 40°C (**Table** 5.3). These results confirm the data obtained in the physical characteristics section in which ECOTMP ester has higher kinematic viscosity at 40°C (236.17 cSt) compared to EP 220 (220 cSt).

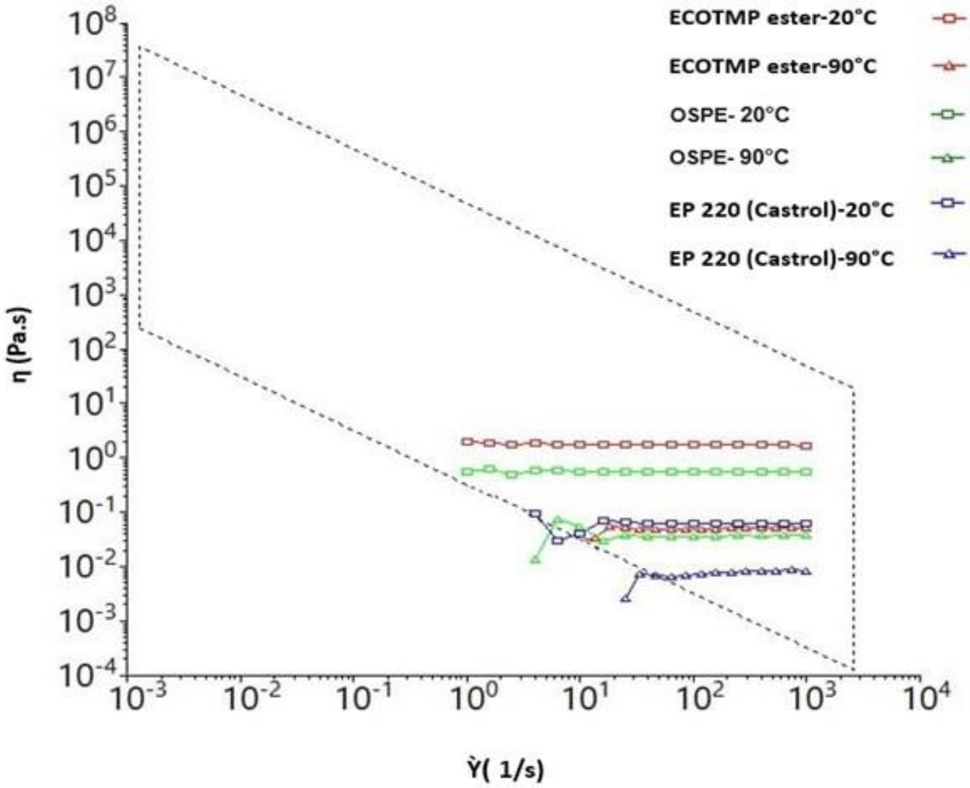


Figure 5.12: Variation of viscosity with the shear rate for ECOTMP ester, oil soluble phosphate ester (OSPE), and EP 220 (Castrol) at 20°C and 90°C.

5.3.5.2 Variation of viscosity with temperature

Figure 5.13 illustrates the temperature-ramp profiles for three distinct lubricants: ECOTMP ester, oil soluble phosphate ester (OSPE), and EP220 (Castrol). As the temperature increases, dynamic viscosity consistently decreases. This viscosity trend is observed for all three lubricants and is consistent with Reynolds' equation [59,60]. Among the tested lubricants, the ECOTMP ester stands out with the highest dynamic viscosity, measuring 8.5 Pa·s at 5°C. It also exhibits the most significant negative gradient with respect to temperature, indicating a high sensitivity to temperature fluctuations. However, the behavior of dynamic viscosity of ECOTMP ester with temperature ramp is very close to EP 220 (Castrol) and therefore this can be acceptable in terms of thermal stability. Generally, the thermal stability of such compounds can be influenced by factors like the degree of epoxidation, the nature of the starting materials, and any additional stabilizers or additives that may have been used during its production. In contrast, OSPE ester showed relatively lower dynamic viscosity values, approximately 0.2 Pa.s at 5°C. This lower negative temperature gradients in dynamic viscosity for OSPE can be attributed to its synthetic origin and lower kinematic viscosity at 40°C, suggesting greater stability in the face of temperature variations compared to the ECOTMP ester and EP 220 (Castrol).

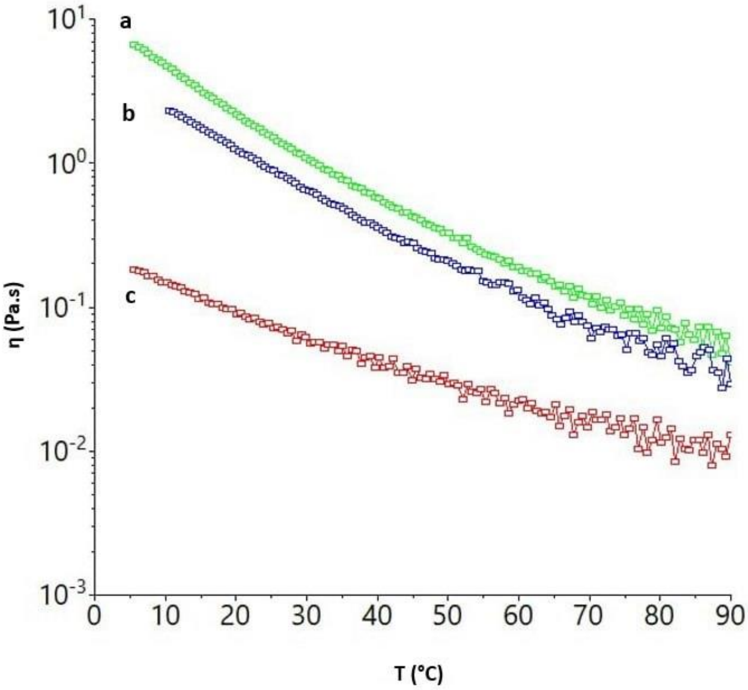


Figure 5.13: Variation of dynamic viscosity with temperature for a) ECOTMP ester, b) EP 220 (Castrol), and c) oil soluble phosphate ester (OSPE).

5.3.6 Catalyst reusability

The catalyst [$MoO_2(acac)_2$]@K10-ETA's reusability was determined by conducting four successive epoxidation reactions of COTMP ester with TBHP, using the same catalyst each time (1 wt.%). The reaction was carried out under the following conditions: 50 h of reaction time, a temperature of 85°C, and a molar ratio of oxidant to substrate at 1.5:1. The reuse of the catalyst has shown an increase in its catalytic activity, indicating that the catalyst's surface may have become activated during the prior reaction, with no detectable molybdenum leaching. The observed initial enhancement in catalytic activity could be attributed to the release of water molecules trapped within the clay through hydrogen bonds, which subsequently improves the accessibility of substrates to the active sites [48]. This explanation aligns with the findings derived from FT-IR (**Figure** 5.14) and thermogravimetric analysis (**Figure** 5.15).

The FTIR spectra, as depicted in **Figure** 5.14, were obtained for K10, [$MoO_2(acac)_2$]@K10-ETA, [$MoO_2(acac)_2$]@K10-ETA (2nd run), and [$MoO_2(acac)_2$]@K10-ETA (4th run). In the spectral range spanning from 3100 to 3750 cm^{-1}, a broad band is typically associated with absorbed water molecules. This band diminishes with the catalyst's increased reuse, indicating the removal of physisorbed water located within the catalyst's structure voids. A similar trend is observed through thermogravimetric analysis (as shown in **Figure** 5.15), where the initial weight loss below 150°C is attributed to the detachment of physisorbed water molecules weakly adhering to the material. In this context, [$MoO_2(acac)_2$]@K10-ETA (**Figure** 5.14) exhibited a weight percentage loss of 4.3% below 150°C. However, both [$MoO_2(acac)_2$]@K10-ETA (2nd run, **Figure** 5.14a) and [$MoO_2(acac)_2$]@K10-ETA (4th run, **Figure** 5.14b) displayed values of less than 1%, within the same temperature range.

Therefore, it can be inferred that the fresh [$MoO_2(acac)_2$]@K10-ETA is less selective than the reused ones, possibly due to the presence of -OH groups that might accelerate the epoxide ring opening [60]. The thermogravimetric (TG) curves of reused [$MoO_2(acac)_2$]@K10-ETA from 2nd run (**Figure** 5.14a) and 4th run (**Figure** 5.14b) also exhibited a distinct mass loss, commencing at around 250°C which is passibly attributed to the thermal decomposition of undigested oxygen-carrying functionalities. Furthermore, the final mass loss observed within the temperature range of 460–700°C can be ascribed to the gradual decomposition of the MO-based complex [48,61].

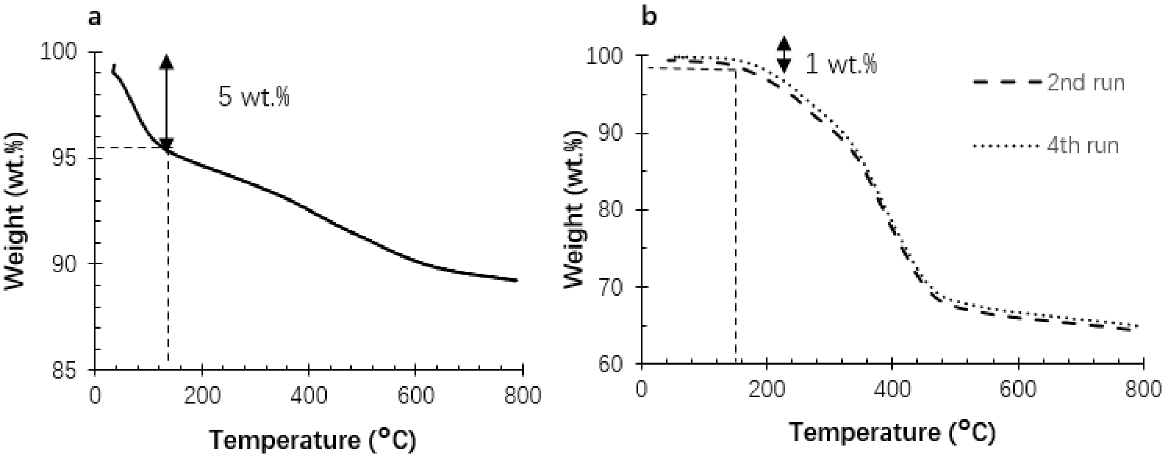


Figure 5.14: TG curves of (a) [$MoO_2(acac)_2$]@K10-ETA; (b) reused [$MoO_2(acac)_2$]@K10-ETA (2nd and 4th run).

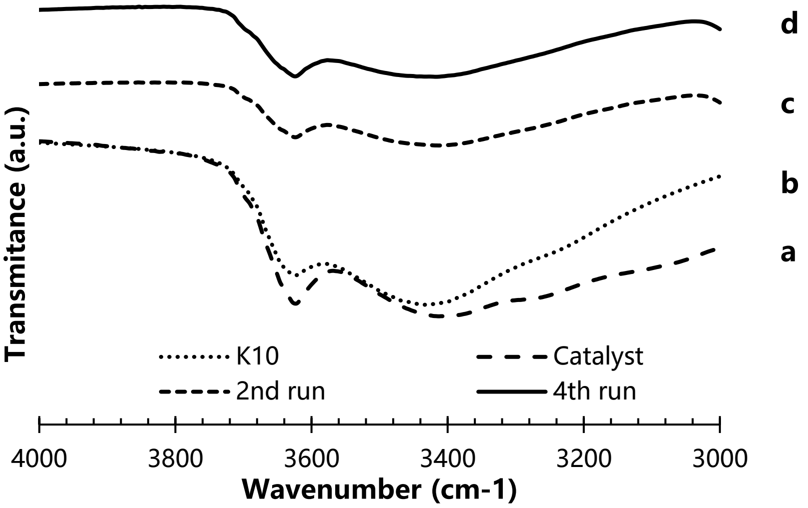


Figure 5.15: FTIR spectra of (a) K10; (b) [$MoO_2(acac)_2$]@K10-ETA; (c) [$MoO_2(acac)_2$]@K10-ETA (2nd run); and (d) [$MoO_2(acac)_2$]@K10-ETA (4th run).

5.4 Conclusions

In this study, the epoxidation of COTMP ester and TBHP (containing C=C double bonds) in the presence of [MoO2(acac)2]@K10-ETA as a heterogeneous catalyst was successfully demonstrated. The optimal reaction conditions were determined to be 85°C, 50 h, and a TBHP-to-COTMP ester molar ratio of 1.5:1. The heterogeneous catalyst exhibited exceptional performance in the epoxidation of COTMP ester, achieving 95.2% conversion, 98.62% selectivity and the final product has an OOC content and iodine value of 4.12% and 3.4 mg I_2/g, respectively. Furthermore, the physical and rheological properties of the epoxidized COTMP ester demonstrated good lubricant performance comparable to a commercial counterpart (Castrol Alphasyn, EP 220), with flash point, pour point, viscosity index, and WSD values of 298°C, -3°C, 157, and 0.75 mm, respectively. However, the pour point of epoxidized products must be improved by using PPD additives. Interestingly, the recycled catalyst showed an increase in selectivity, which was likely attributed to the removal of water molecules that prevent the opening of the epoxy ring.

5.5 References

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Chapter 6

6 Conclusions and Recommendations for the Future Work

6.1 Conclusions

This work has accomplished the primary objective of this PhD project, i.e., to determine the most important distinguishing parameters for producing high-performance biolubricants and production of complex esters with high efficiency from vegetable oils through a chemical modification process. A two-step transesterification-transesterification process and a two-step hydrolysis-esterification process were developed, where the first step involves the conversion of vegetable oil to ethyl ester or FFAs and the second step involves the conversion of ethyl esters/FFAs to TMP esters. On the other hand, in order to further increase the thermal and oxidative stability of COTMP ester, another chemical modification aimed at removing carbon-carbon double bonds in the complex ester structure using TBHP as an oxidizing agent and [$MoO_2(acac)_2$]@K10-ETA as a heterogeneous catalyst was used. In addition, this research investigated the physicochemical characteristics and rheological/tribological properties of the final product in order to validate its effectiveness in the lubricating industry.

The following detailed conclusions were drawn from this research:

(1) The final COTMP ester product (through the 2-step transesterification-transesterification process) obtained at the best conditions contains 67% TMP triester and 82% total concentration of TE/DE/ME and has a Pour point at –9°C, a Flash point at 309°C, and kinematic viscosities of 30.13 cSt @ 40°C and 6.27 cSt @ 100°C.

(2) The obtained COTMP ester product (through the 2-step transesterification-transesterification process) with 2% prophos900 as additive exhibits perfect wear preventive performance than other samples with WSD of 0.42 mm. Moreover, the

additive-free COTMP ester exhibits good quenching performance, superior rheological and tribological properties over a commercial lubricating oil, as well as excellent biodegradability (90%) after 144 h.

(3) The obtained product (through hydrolysis process) has an acid number of 194.35 mg KOH/g and triglyceride conversion was 99.03% by using PTSA catalyst, compared with an acid value of 196.28 mg KOH/g and triglyceride conversion of 98.98% using concentrated sulfuric acid as the catalyst.

(4) The best conditions for the hydrolysis reaction of canola oil were determined at: 190°C and 200°C with PTSA and concentrated H_2SO_4, respectively, 6h reaction time, 30:1 water to oil molar ratio, and 5 wt.% catalyst concentration. For the esterification reaction of FFAs with TMP, the maximum obtained yield of 87 wt.% and conversion of 85 wt.% were obtained at 150°C, 10 h, 1 wt.% catalyst loading, and FFAs to TMP molar ratio of 4:1.

(5) Five ester samples obtained by esterification reaction of hydrolyzed canola oil and polyhydric/fatty alcohols demonstrated excellent anti-wear properties, suggesting promise in application as metalworking fluids.

(6) For the epoxidation reaction, the optimal reaction conditions were determined to be 85°C, 50 h, and a TBHP-to-COTMP ester molar ratio of 1.5:1. The heterogeneous catalyst exhibited exceptional performance in the epoxidation of COTMP ester, achieving 95.2% conversion, and 98.62% selectivity and the final product has an OOC content of 4.12%.

(7) The physical and rheological properties of the epoxidized COTMP ester demonstrated good lubricant performance comparable to a commercial counterpart (Castrol Alphasyn, EP 220), with flash point, pour point, viscosity index, and WSD values of 298°C, -3°C, 157, and 0.75 mm, respectively.

(8) The recycled catalyst showed an increase in selectivity, which was likely attributed to the removal of water molecules that prevent the opening of the epoxy ring.

(9) While this thesis has provided comprehensive insights into the synthesis, characterization, and application of complex esters derived from canola oil, it is important to acknowledge certain limitations. Firstly, the research primarily

focused on three specific reaction pathways for the production of complex esters, namely two-step transesterification-transesterification, two-step hydrolysis esterification, and epoxidation reactions. While these pathways were explored extensively, the findings may not fully represent the entirety of potential reaction pathways or conditions for complex ester synthesis. Additionally, the characterization of the complex esters primarily relied on physical properties such as viscosity, VI, pour point, flash point, FTIR, HNMR, TGA, and rheology tests. While these analyses provided valuable insights into the properties of the complex esters, other analytical techniques or parameters may offer further insights into their behavior and performance. Furthermore, the evaluation of catalyst performance primarily involved SEM-EDS and XRD tests, which may not capture all aspects of catalyst activity and stability. Finally, while efforts were made to measure key parameters such as OOC, IV, selectivity, and conversion for the epoxidation reaction, additional studies may be necessary to explore the full range of factors influencing reaction efficiency and product characteristics.

6.2 Limitations of the thesis's findings

(1) The final COTMP ester product obtained through the 2-step transesterification-transesterification process exhibits favorable physical properties such as low pour point and high flash point, indicating its potential suitability as a lubricant. However, the achieved triglyceride conversion and TMP triester concentration may not be optimal for certain applications, suggesting potential room for improvement in reaction conditions or catalyst selection to enhance product purity and yield.

(2) While the COTMP ester product with prophos900 additive demonstrates excellent wear preventive performance and biodegradability, the study primarily focused on a specific additive and may not encompass the full range of additives or formulations available for enhancing lubricant properties. Additionally, while the biodegradability of

the ester product is promising, further investigations into its long-term environmental fate and degradation kinetics may be necessary to fully assess its environmental impact.

(3) The hydrolysis process yielded a product with high triglyceride conversion and acid number, indicating successful conversion of canola oil to esters. However, the study primarily compared catalysts based on their conversion efficiency and acid value, without considering other factors such as catalyst stability, recyclability, or potential byproduct formation, which could influence the overall process economics and environmental impact.

(4) The optimal conditions for the hydrolysis and esterification reactions were determined based on specific parameters such as temperature, reaction time, and catalyst loading. However, the study did not explore the potential interactions between these parameters or assess the robustness of the optimal conditions under varying reaction conditions or feedstock compositions, which could affect the scalability and reproducibility of the processes.

(5) The physical and rheological properties of the epoxidized COTMP ester demonstrated good lubricant performance comparable to a commercial counterpart. However, the study did not investigate the long-term stability or performance of the epoxidized ester under actual operating conditions, which could provide valuable insights into its suitability for specific lubrication applications.

(6) The increase in selectivity observed with the recycled catalyst suggests potential benefits in catalyst regeneration. However, the study did not investigate the mechanism underlying the improvement in selectivity or assess the potential impact of catalyst regeneration on other reaction parameters or byproduct formation, warranting further investigation into the recycling process's feasibility and effectiveness.

6.3 Recommendations for Future Work

(1) It is crucial to underscore the significance of future investigations centered on techno-economic analysis. Emphasizing this aspect will enable a comprehensive understanding of the economic feasibility and technological viability of proposed solutions. By conducting thorough techno-economic evaluations, researchers can pinpoint areas ripe for optimization, anticipate potential challenges, and identify pathways for successful commercialization. Moreover, a techno-economic perspective facilitates the identification of strategies to maximize resource efficiency, minimize costs, and enhance the overall process viability.

(2) In transesterification reactions or hydrolysis reactions, it is challenging to separate water as a byproduct from the final product on an industrial scale. Because the use of the distillation system is time-consuming. As a result, it is suggested to develop an alternative method for water separation, e.g., using a centrifuge system (Disc Stack Centrifuge) on an industrial scale.

(3) Future research should focus on conducting kinetics studies of key reactions involved in the production of complex esters, including hydrolysis, esterification/transesterification, and epoxidation reactions. Investigating the reaction kinetics will enable optimization of reaction conditions, understanding of reaction mechanisms, and future upscaling the processes. Insights gained from these studies will help select the reaction parameters, leading to improved product quality and yield.

(4) While the current research focused on the synthesis and characterization of the biolubricant products, evaluating their stability and durability over time is essential for their practical application and commercialization. Incorporating shelf-life assessments would provide valuable insights into the long-term performance of the products under various storage conditions and environmental factors. This includes monitoring changes in viscosity, oxidative stability, and other relevant properties over extended periods to ensure product quality and reliability. Furthermore, understanding the factors influencing shelf-life will enable the development of

strategies to enhance product stability and prolong their usability. Therefore, future studies should prioritize conducting comprehensive shelf-life evaluations to ensure the viability and efficacy of the developed biolubricants for industrial applications.

(5) Future research can also focus on converting waste cooking oils into purified oils for the production of biolubricants or bio-based complex esters. Investigating the conversion process and analyzing the oil's physicochemical properties will provide crucial insights into its suitability for lubricant applications. This research direction offers a more economical and sustainable route to developing environmentally friendly lubricants from renewable resources.

(6) Although [$MoO_2(acac)_2$]@K10-ETA as a heterogeneous catalyst in the epoxidation reaction of complex esters achieved ECOTMP ester with a high percentage of selectivity, the reaction time (50 h) is considerable on an industrial scale. Therefore, more research is needed to develop more active new heterogeneous catalysts for the epoxidation reaction of complex esters in order to reduce the reaction time.

(7) Epoxidized ester lubricants are often used in metalworking fluids, automotive lubricants, grease, plasticizers, and fuel additives. They provide excellent lubrication and thermal stability, which is crucial for metal machining processes like cutting, grinding, and milling. However, additional modifications (e.g., oxirane ring opening followed by esterification reaction) may be desirable to tailor the properties of the lubricants to meet specific performance criteria.

(8) There is lack of research on epoxidized esters as an effective additive for increasing the cooling performance of cutting fluids and decreasing wear scar diameter of metal-to-metal contact in metalworking industries on an industrial scale. Therefore, forthcoming research focused on formulating a range of industrial lubricants with epoxidized complex esters will provide significant insights, contributing to the establishment of the practical feasibility of using epoxidized esters to enhance the efficiency and durability of industrial lubricants.

(9) Epoxidized vegetable oil esters are intermediate products and can be used in the formulation of a wide range of lubricants. However, it is more desirable to perform further chemical modifications such as ring opening process followed by

transesterification reactions in order to further improve their physicochemical characteristics.

(10) Additionally, future research could explore methods to enhance the biodegradability of vegetable oil-based lubricants and develop strategies for mitigating the impact of contaminants on their performance and environmental fate.

6.4 Contributions

In Chapter 3, a process to produce biolubricant complex esters with improved thermal and oxidative stability from vegetable oils (in particular Canola oil, abundantly produced in Canada) for non-internal combustion engine applications, by converting vegetable oil triglyceride into TMP esters via a 2-step transesterification-transesterification process.

In Chapter 4, a two-step hydrolysis-esterification process has been developed for synthesizing biodegradable esters, compatible with mineral or synthetic oils, and their wear and friction properties in metalworking systems were evaluated by combining with base oils and appropriate additives.

In Chapter 5, epoxidized canola oil trimethylolpropane (ECOTMP) ester was successfully synthesized using TBHP as an oxidant agent and a novel heterogeneous catalyst obtained by immobilization of bis(acetylacetonate)dioxo-molybdenum (VI) [$MoO_2(acac)_2$] with montmorillonite (K10)-ethanolamine.

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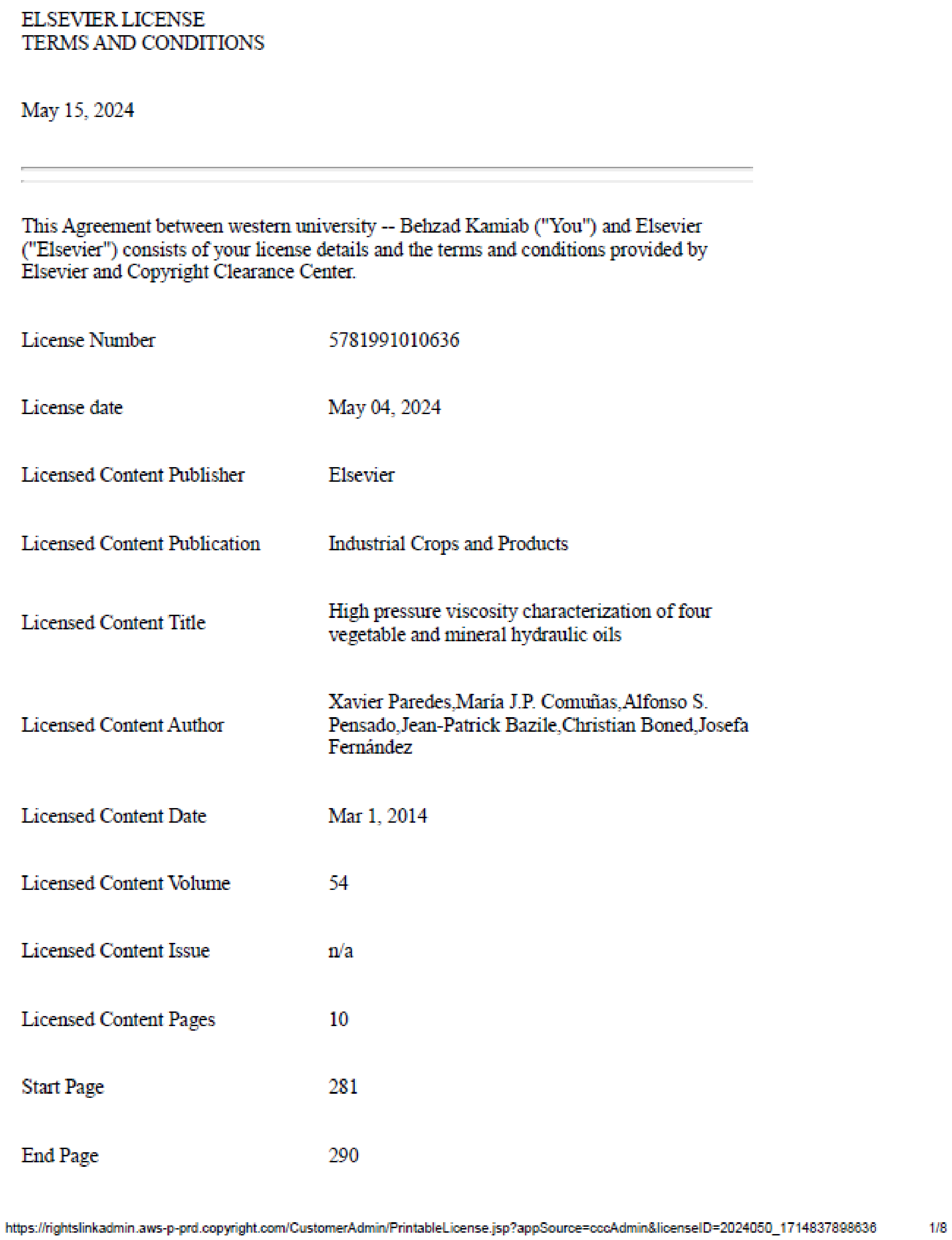

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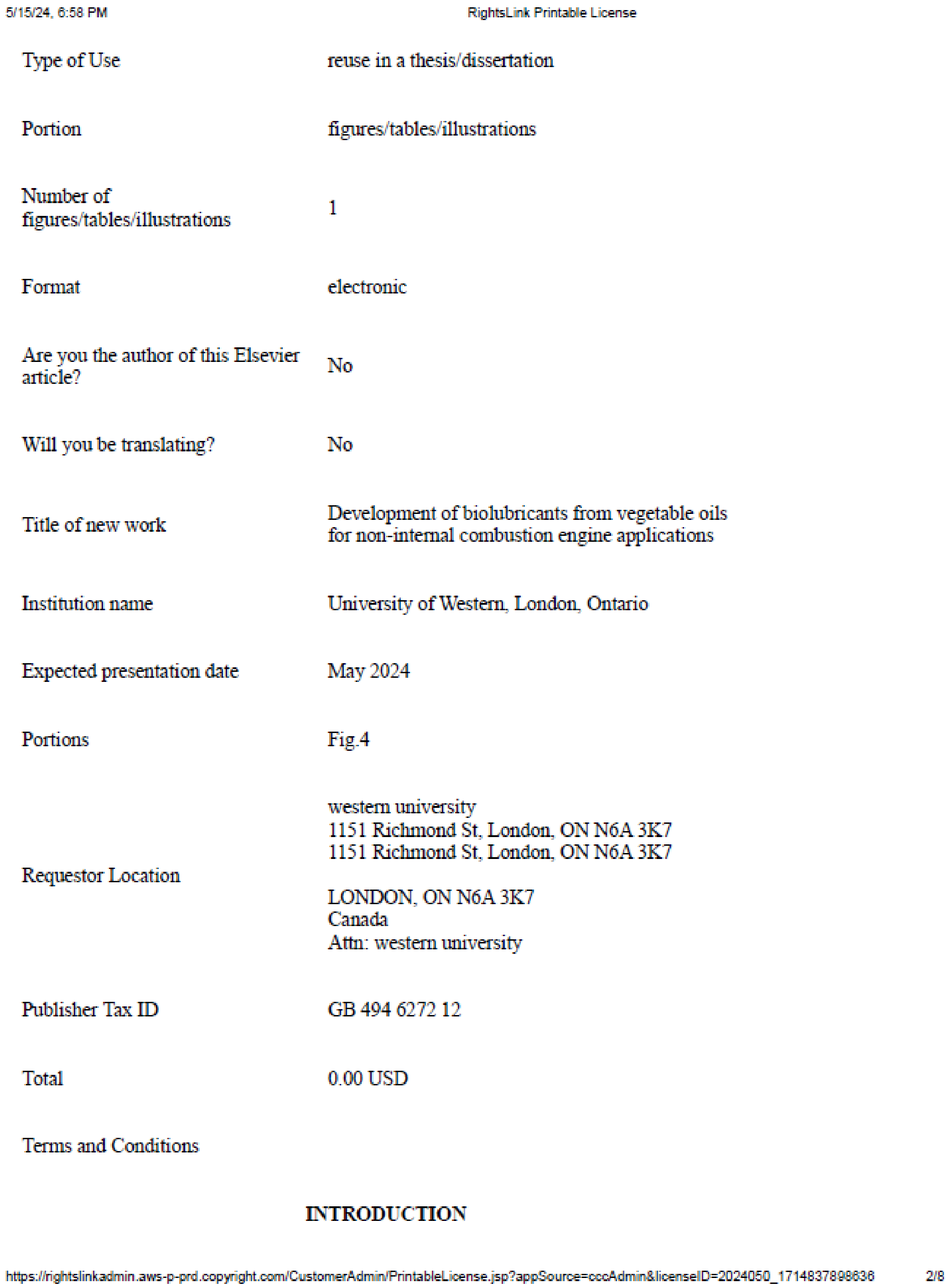

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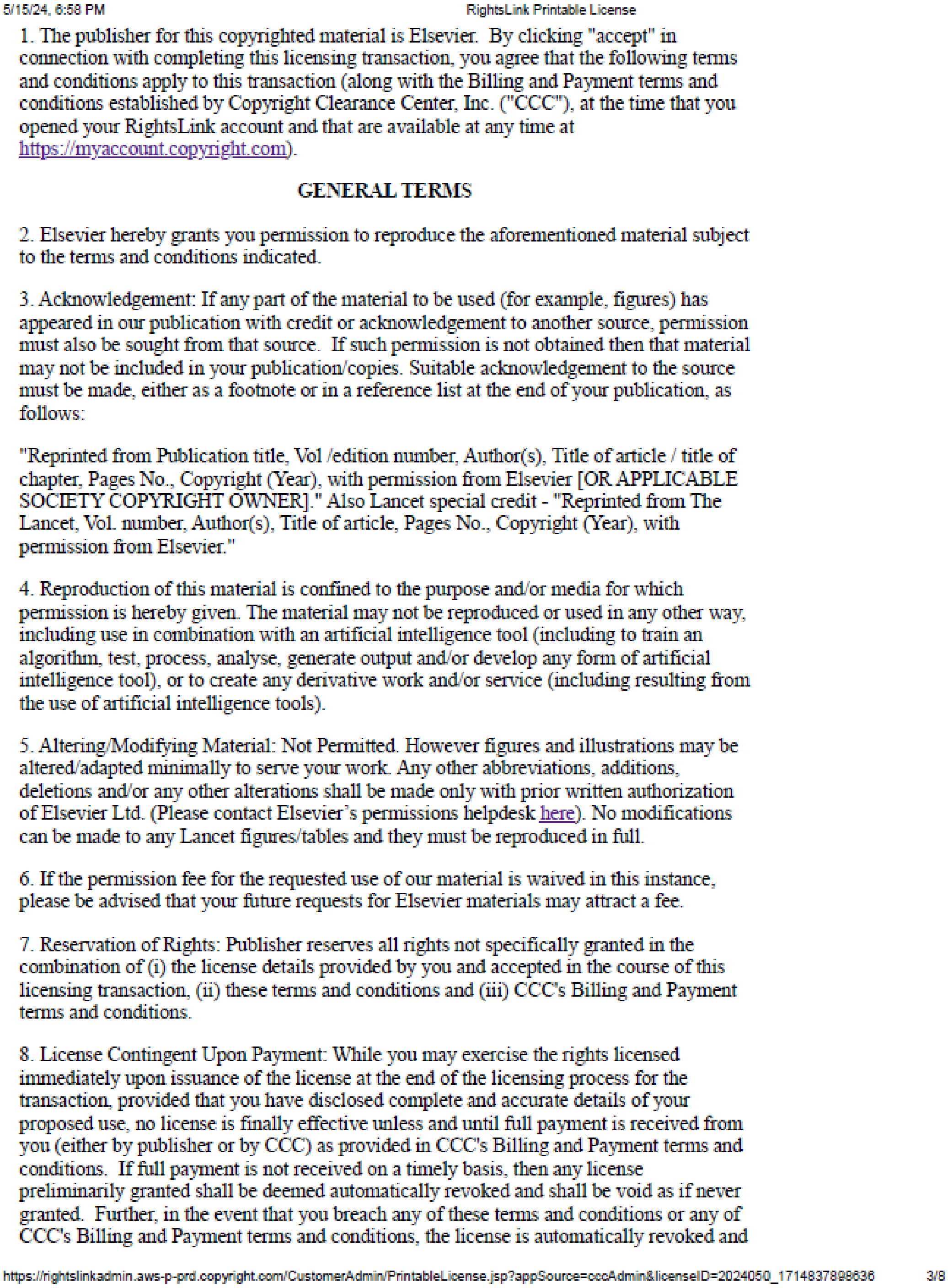

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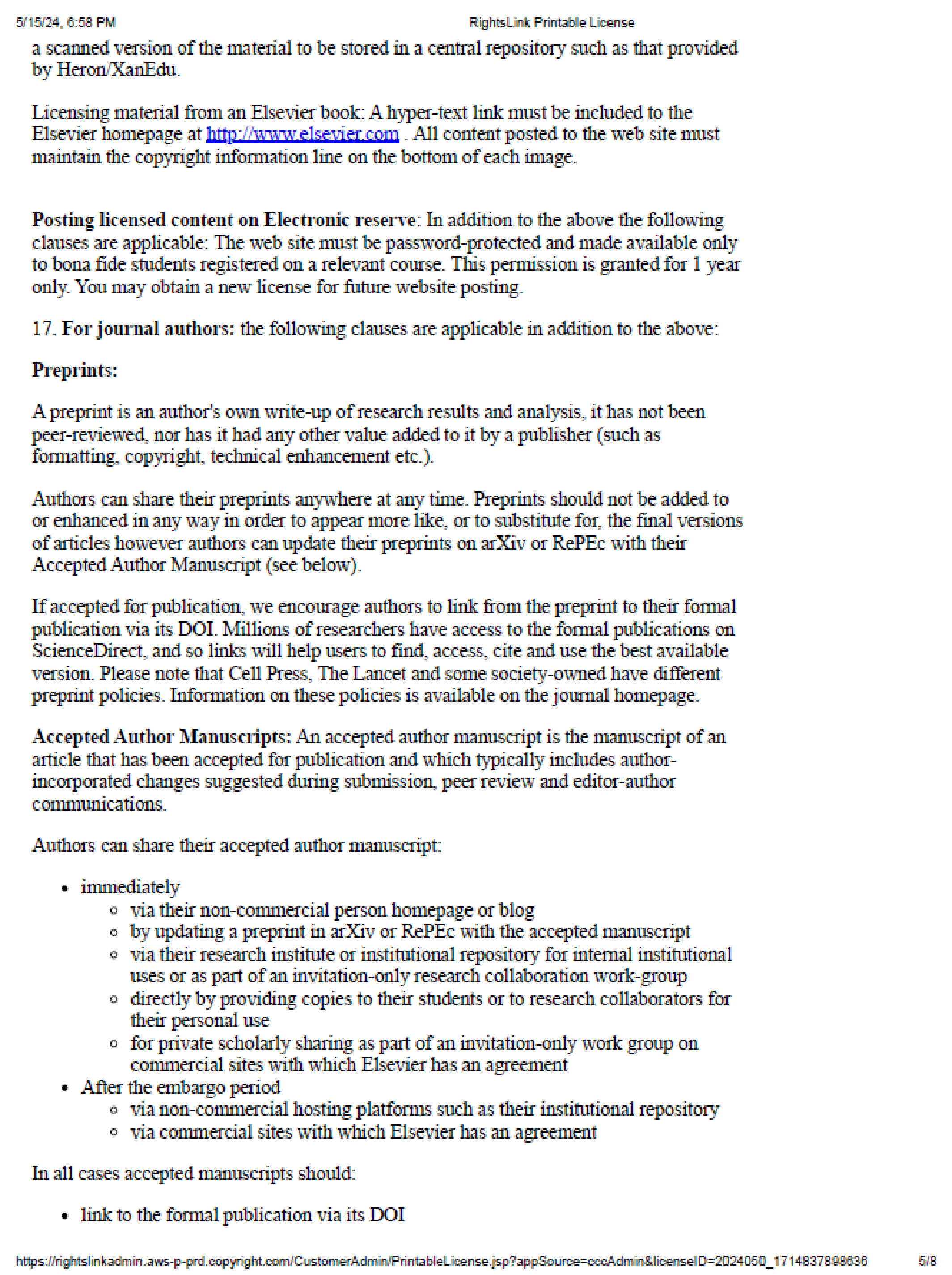

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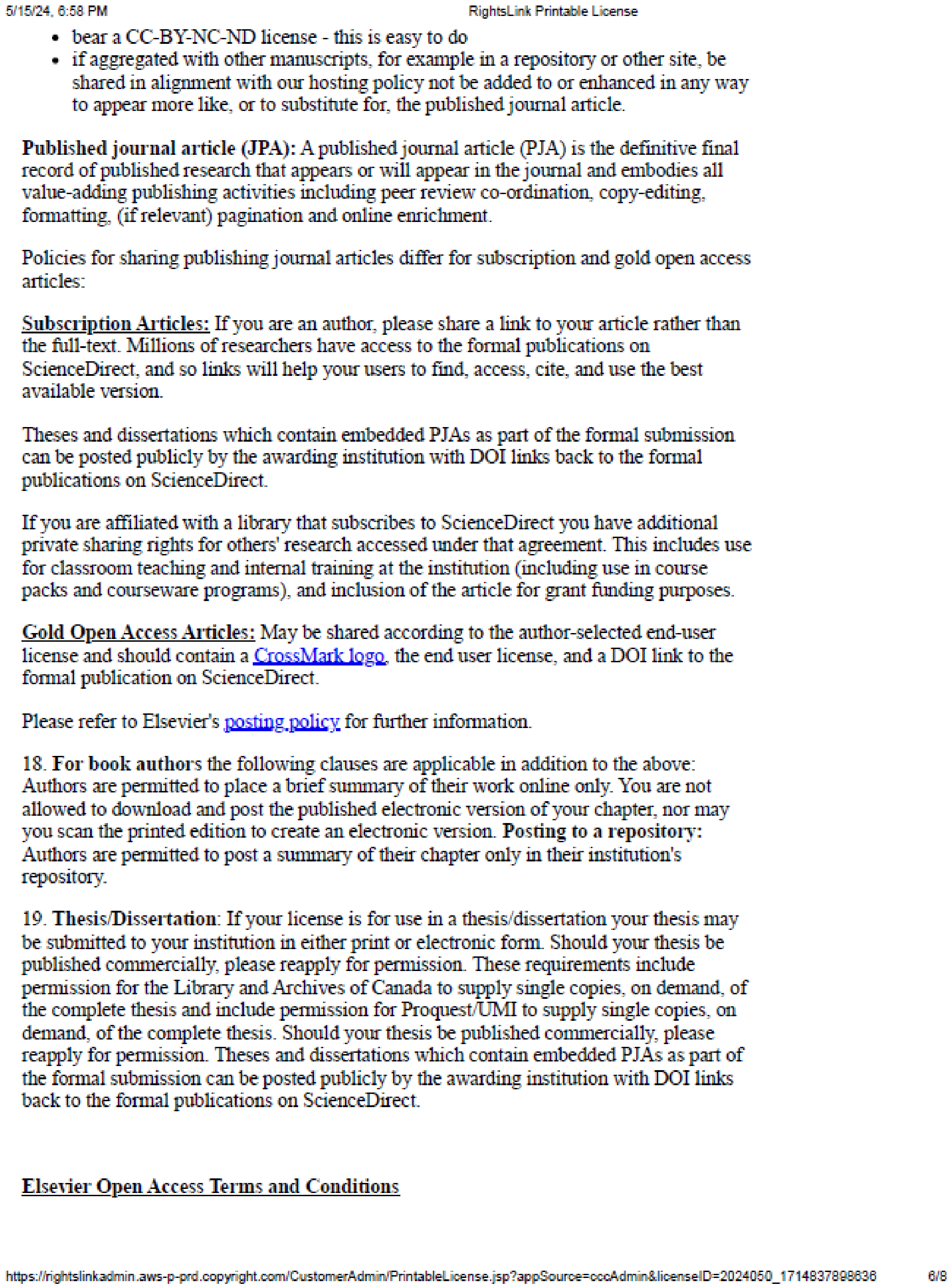

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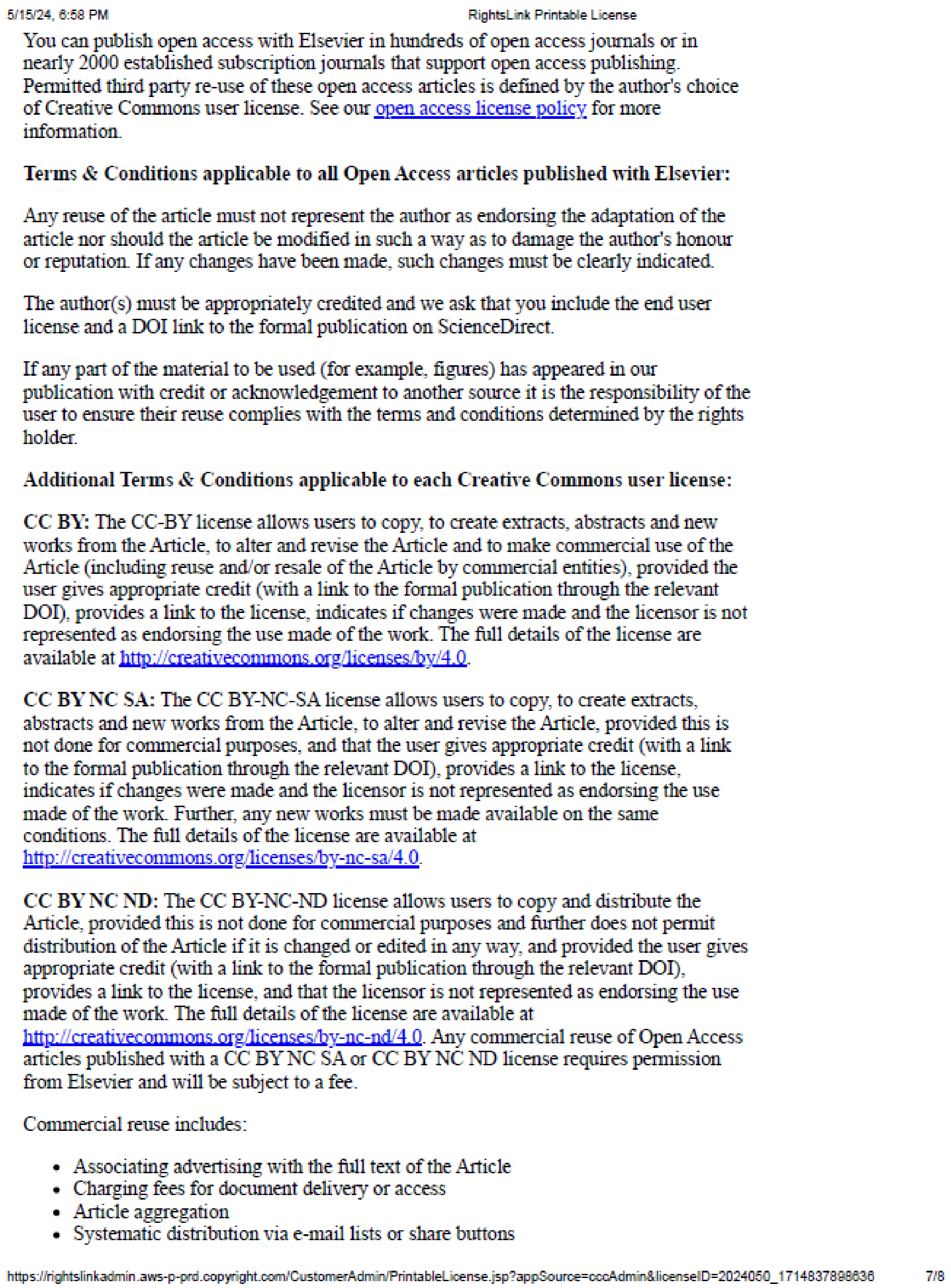

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NEW WORK DETAILS

Title	Development of biolubricants from vegetable oils for non-internal combustion engine applications	**Institution Name**	University of Western, London, Ontario
Instructor Name	Behzad Kamiab	**Expected Presentation Date**	2024-05-30

ADDITIONAL DETAILS

Order Reference Number	N/A	**The Requesting Person / Organization to Appear on the License**	Behzad Kamiab

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Crystallization behavior of vegetable oil molecules with PPD	**Title of the Article / Chapter the Portion Is From**	Study on the performance mechanism of methacrylate pour point depressant in soybean biodiesel blends
Editor of Portion(s)	Ma, Peng; Xue, Yuan; Zhao, Weina; Lan, Guoxian; Hang, Zhijun; Liu, Fan; Han, Sheng	**Author of Portion(s)**	Ma, Peng; Xue, Yuan; Zhao, Weina; Lan, Guoxian; Hang, Zhijun; Liu, Fan; Han, Sheng
Volume / Edition	5	**Issue, if Republishing an Article From a Serial**	109
Page or Page Range of Portion	90144-90149	**Publication Date of Portion**	2015-11-21

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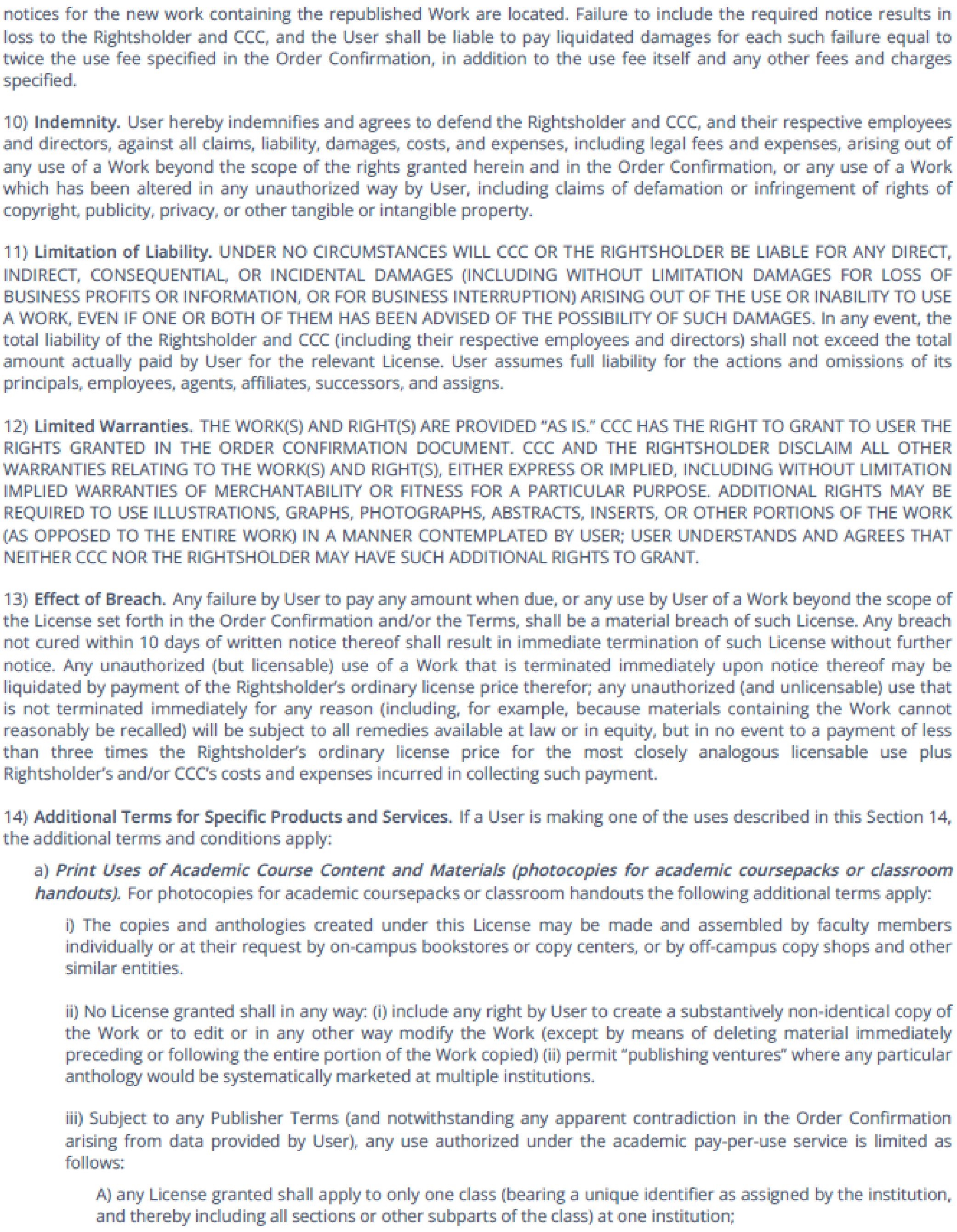

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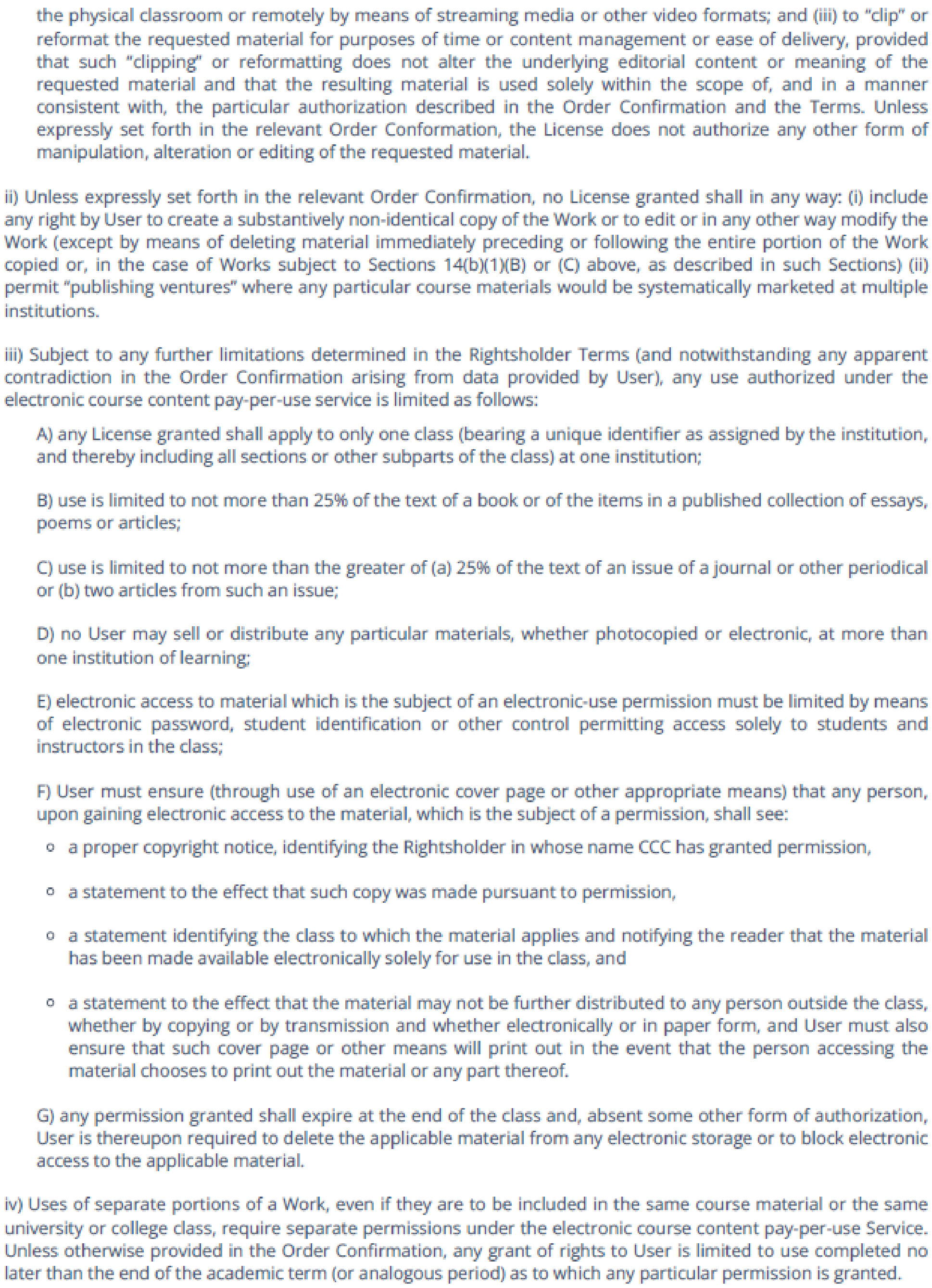

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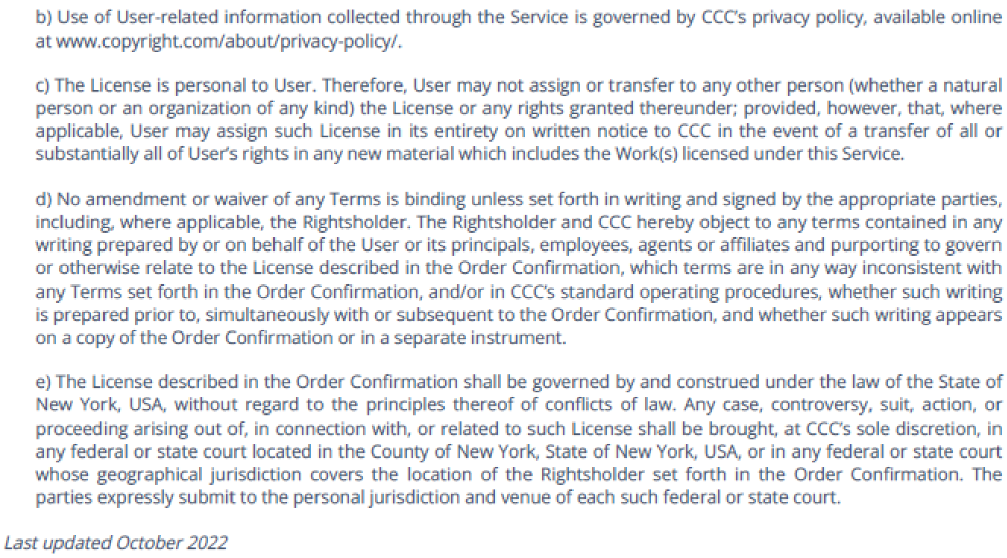

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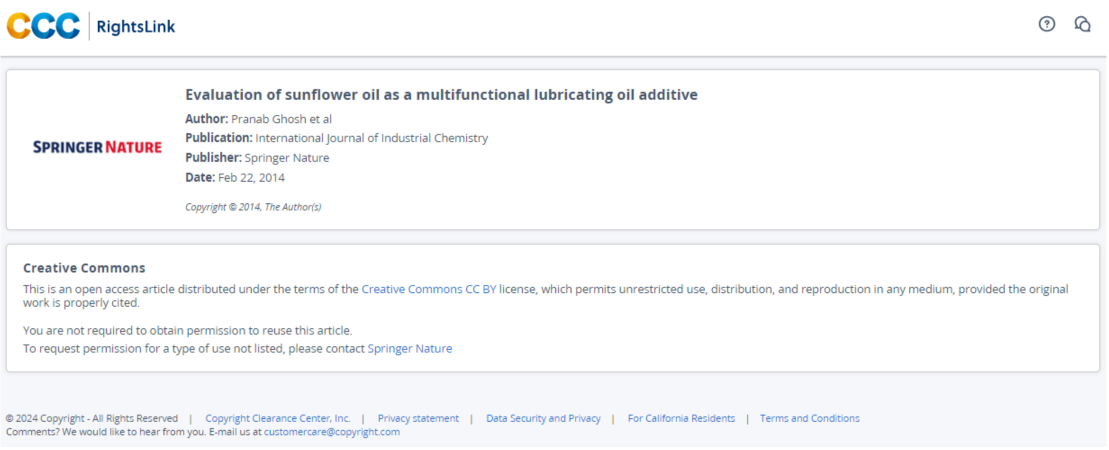
Last updated October 2022

Table 2.5, reference number [64].



Evaluation of sunflower oil as a multifunctional lubricating oil additive

Author: Pranab Ghosh et al
Publication: International Journal of Industrial Chemistry
Publisher: Springer Nature
Date: Feb 22, 2014

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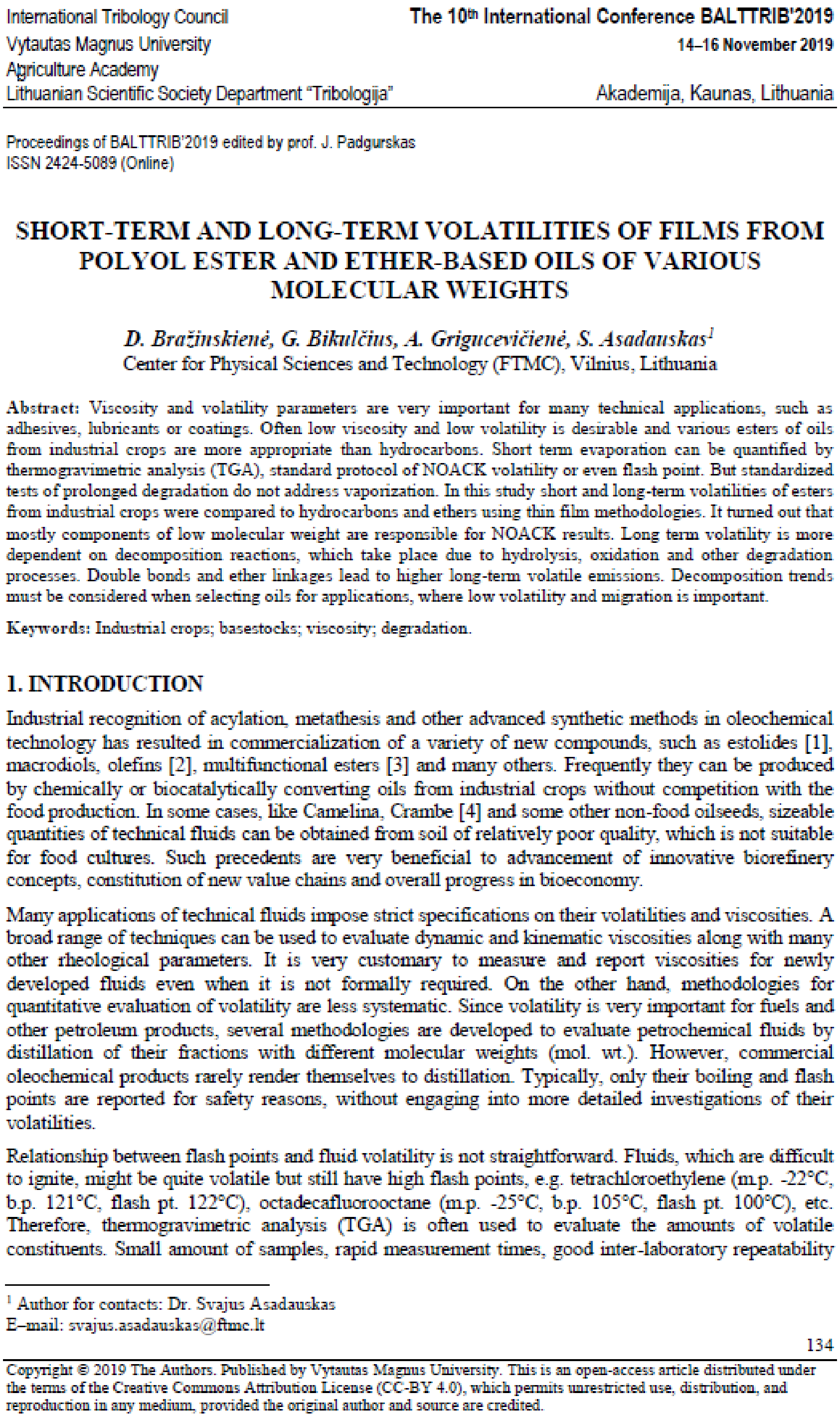
Figure 2.4 and **Figure** 2.5, reference number [72].



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SHORT-TERM AND LONG-TERM VOLATILITIES OF FILMS FROM POLYOL ESTER AND ETHER-BASED OILS OF VARIOUS MOLECULAR WEIGHTS

D. Bražinskienė, G. Bikulčius, A. Grigucevičienė, S. Asadauskas[1]
Center for Physical Sciences and Technology (FTMC), Vilnius, Lithuania

Abstract: Viscosity and volatility parameters are very important for many technical applications, such as adhesives, lubricants or coatings. Often low viscosity and low volatility is desirable and various esters of oils from industrial crops are more appropriate than hydrocarbons. Short term evaporation can be quantified by thermogravimetric analysis (TGA), standard protocol of NOACK volatility or even flash point. But standardized tests of prolonged degradation do not address vaporization. In this study short and long-term volatilities of esters from industrial crops were compared to hydrocarbons and ethers using thin film methodologies. It turned out that mostly components of low molecular weight are responsible for NOACK results. Long term volatility is more dependent on decomposition reactions, which take place due to hydrolysis, oxidation and other degradation processes. Double bonds and ether linkages lead to higher long-term volatile emissions. Decomposition trends must be considered when selecting oils for applications, where low volatility and migration is important.

Keywords: Industrial crops; basestocks; viscosity; degradation.

1. INTRODUCTION

Industrial recognition of acylation, metathesis and other advanced synthetic methods in oleochemical technology has resulted in commercialization of a variety of new compounds, such as estolides [1], macrodiols, olefins [2], multifunctional esters [3] and many others. Frequently they can be produced by chemically or biocatalytically converting oils from industrial crops without competition with the food production. In some cases, like Camelina, Crambe [4] and some other non-food oilseeds, sizeable quantities of technical fluids can be obtained from soil of relatively poor quality, which is not suitable for food cultures. Such precedents are very beneficial to advancement of innovative biorefinery concepts, constitution of new value chains and overall progress in bioeconomy.

Many applications of technical fluids impose strict specifications on their volatilities and viscosities. A broad range of techniques can be used to evaluate dynamic and kinematic viscosities along with many other rheological parameters. It is very customary to measure and report viscosities for newly developed fluids even when it is not formally required. On the other hand, methodologies for quantitative evaluation of volatility are less systematic. Since volatility is very important for fuels and other petroleum products, several methodologies are developed to evaluate petrochemical fluids by distillation of their fractions with different molecular weights (mol. wt.). However, commercial oleochemical products rarely render themselves to distillation. Typically, only their boiling and flash points are reported for safety reasons, without engaging into more detailed investigations of their volatilities.

Relationship between flash points and fluid volatility is not straightforward. Fluids, which are difficult to ignite, might be quite volatile but still have high flash points, e.g. tetrachloroethylene (m.p. -22°C, b.p. 121°C, flash pt. 122°C), octadecafluorooctane (m.p. -25°C, b.p. 105°C, flash pt. 100°C), etc. Therefore, thermogravimetric analysis (TGA) is often used to evaluate the amounts of volatile constituents. Small amount of samples, rapid measurement times, good inter-laboratory repeatability

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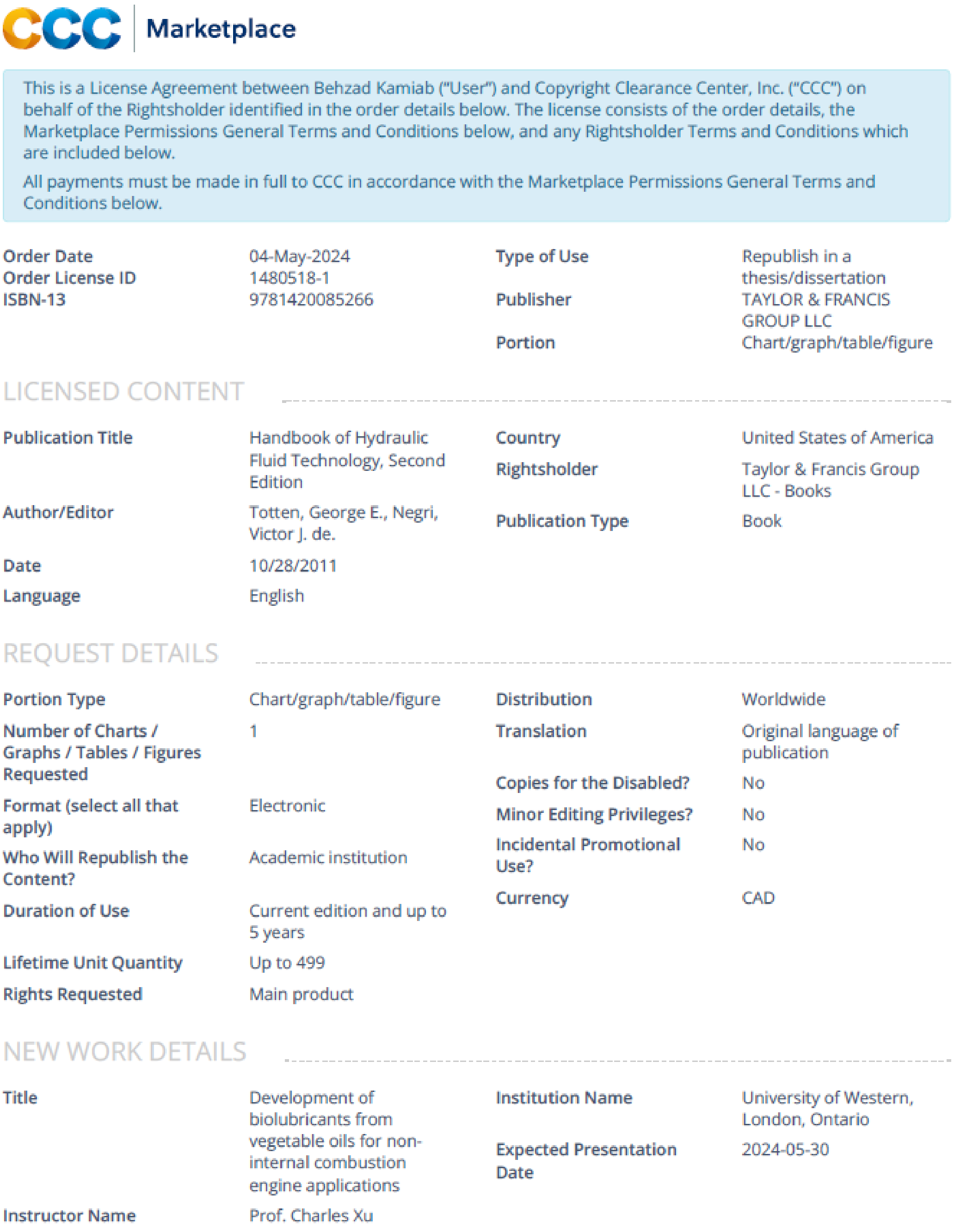
[1] Author for contacts: Dr. Svajus Asadauskas
E–mail: svajus.asadauskas@ftmc.lt

134

Table 2.7, reference number [78].



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ISBN-13	9781420085266	**Portion**	Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Handbook of Hydraulic Fluid Technology, Second Edition	**Country**	United States of America
Author/Editor	Totten, George E., Negri, Victor J. de.	**Rightsholder**	Taylor & Francis Group LLC - Books
Date	10/28/2011	**Publication Type**	Book
Language	English		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	Worldwide
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language of publication
Format (select all that apply)	Electronic	**Copies for the Disabled?**	No
Who Will Republish the Content?	Academic institution	**Minor Editing Privileges?**	No
Duration of Use	Current edition and up to 5 years	**Incidental Promotional Use?**	No
Lifetime Unit Quantity	Up to 499	**Currency**	CAD
Rights Requested	Main product		

NEW WORK DETAILS

Title	Development of biolubricants from vegetable oils for non-internal combustion engine applications	**Institution Name**	University of Western, London, Ontario
Instructor Name	Prof. Charles Xu	**Expected Presentation Date**	2024-05-30

ADDITIONAL DETAILS

Order Reference Number	N/A	**The Requesting Person / Organization to Appear on the License**	Behzad Kamiab

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Comparison of biodegradability and other physicochemical characteristics between HEES, HEPG, vegetable oils, and mineral base fluids	**Title of the Article / Chapter the Portion Is From**	Chapter 3
		Author of Portion(s)	Totten, George E.; Negri, Victor J. de.
		Issue, if Republishing an Article From a Serial	N/A
Editor of Portion(s)	G.E. Totten	**Publication Date of Portion**	2011-10-28
Volume / Edition	2		
Page or Page Range of Portion	103-108		

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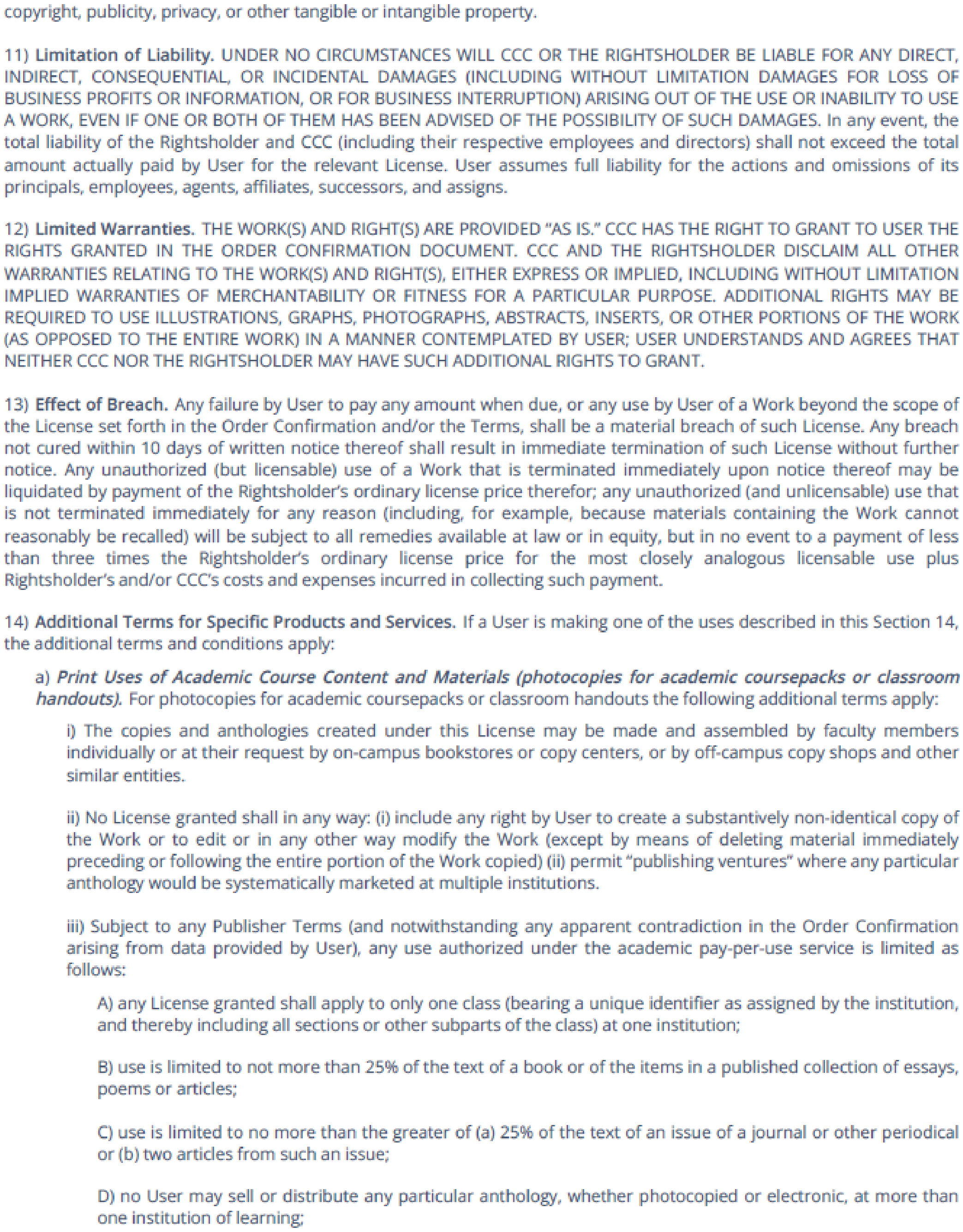

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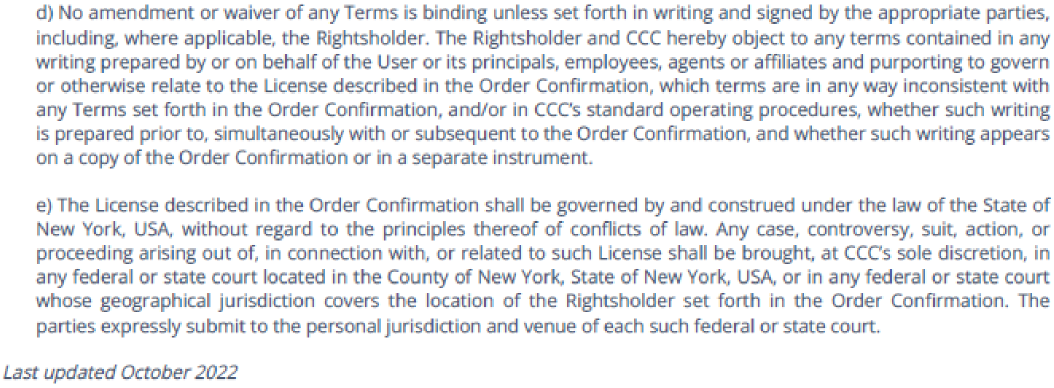

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Last updated October 2022

Figure 2.7, reference number [106].

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ISSN	1558-9331	**Portion**	Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Journal of the American Oil Chemists' Society	**Publication Type**	e-Journal
Article Title	Diesters from Oleic Acid: Synthesis, Low Temperature Properties, and Oxidation Stability	**Start Page**	675
		End Page	680
		Issue	7
		Volume	84
Author/Editor	American Oil Chemists' Society.	**URL**	http://firstsearch.oclc.org/journal=0003-021x;screen=info;ECOIP
Date	01/01/1947		
Language	English		
Country	Germany		
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Lifetime Unit Quantity	Up to 499		
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NEW WORK DETAILS

Title	Development of biolubricants from vegetable oils for non-internal combustion engine applications	**Institution Name**	University of western, London, Ontario
		Expected Presentation Date	2024-05-30
Instructor Name	Prof. Charles Xu		

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REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Synthesis of diesters from oleic acid. Note: R¢ in 10–17 contains a carbonyl group at carbon 1, resulting in an ester; Pr = propyl; iPr = isopropyl; Oc = octyl; 2-EH = 2-ethylhexyl	**Title of the Article / Chapter the Portion Is From**	Diesters from Oleic Acid: Synthesis, Low Temperature Properties, and Oxidation Stability
		Author of Portion(s)	Bryan, R., Moser; Brajendra, K., Sharma; Kenneth, M., Doll; Sevim, Z., Erhan
Editor of Portion(s)	Bryan, R., Moser; Brajendra, K., Sharma; Kenneth, M., Doll; Sevim, Z., Erhan	**Publication Date of Portion**	2007-07-01
Volume / Edition	84		
Page or Page Range of Portion	675-680		

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5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

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10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

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14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other

similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

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- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and

- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

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iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

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d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

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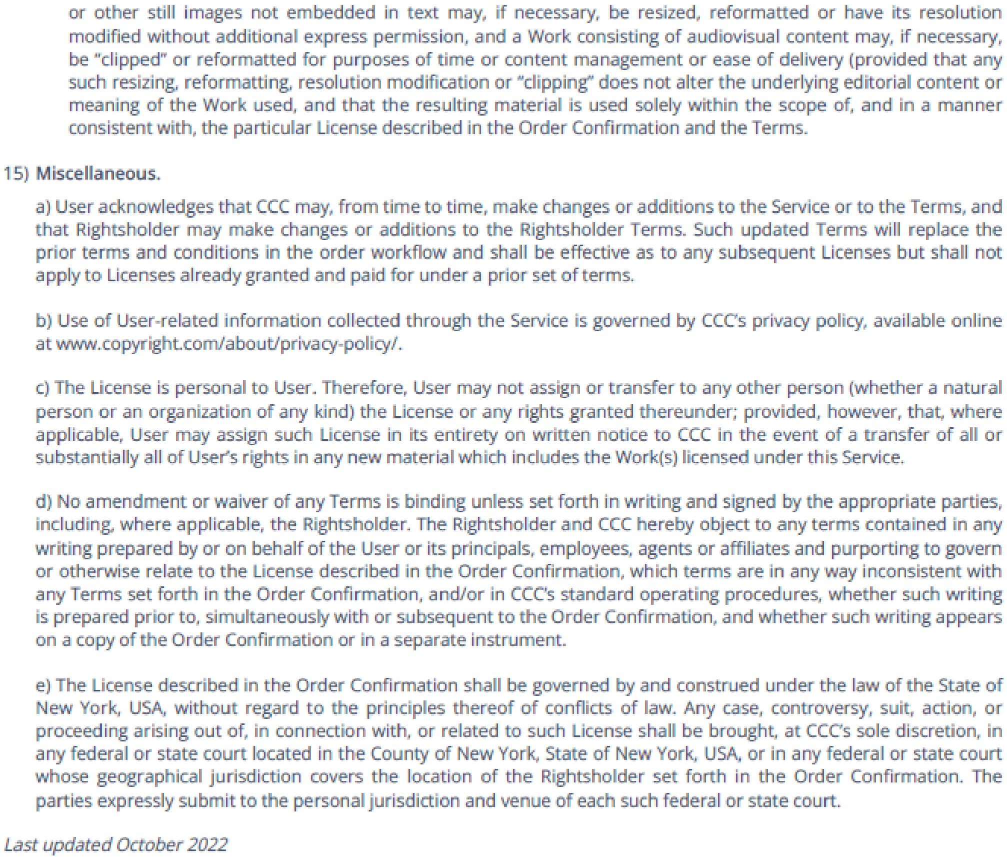

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15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

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d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

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Last updated October 2022

Figure 2.12, reference number [133].

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Article Title	Fatty Acid Estolides: A Review	**Start Page**	231
Author/Editor	American Oil Chemists' Society.	**End Page**	241
Date	01/01/1947	**Issue**	3
Language	English	**Volume**	97
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		Expected Presentation Date	2024-05-30
Instructor Name	Prof. Charles Xu		

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Editor of Portion(s)	Chen, Yunzhi; Biresaw, Girma; Cermak, Steven C.; Isbell, Terry A.; Ngo, Helen L.; Chen, Li; Durham, Amber L.	**Author of Portion(s)**	Chen, Yunzhi; Biresaw, Girma; Cermak, Steven C.; Isbell, Terry A.; Ngo, Helen L.; Chen, Li; Durham, Amber L.
Volume / Edition	97	**Publication Date of Portion**	2020-03-01
Page or Page Range of Portion	231-241		

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10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

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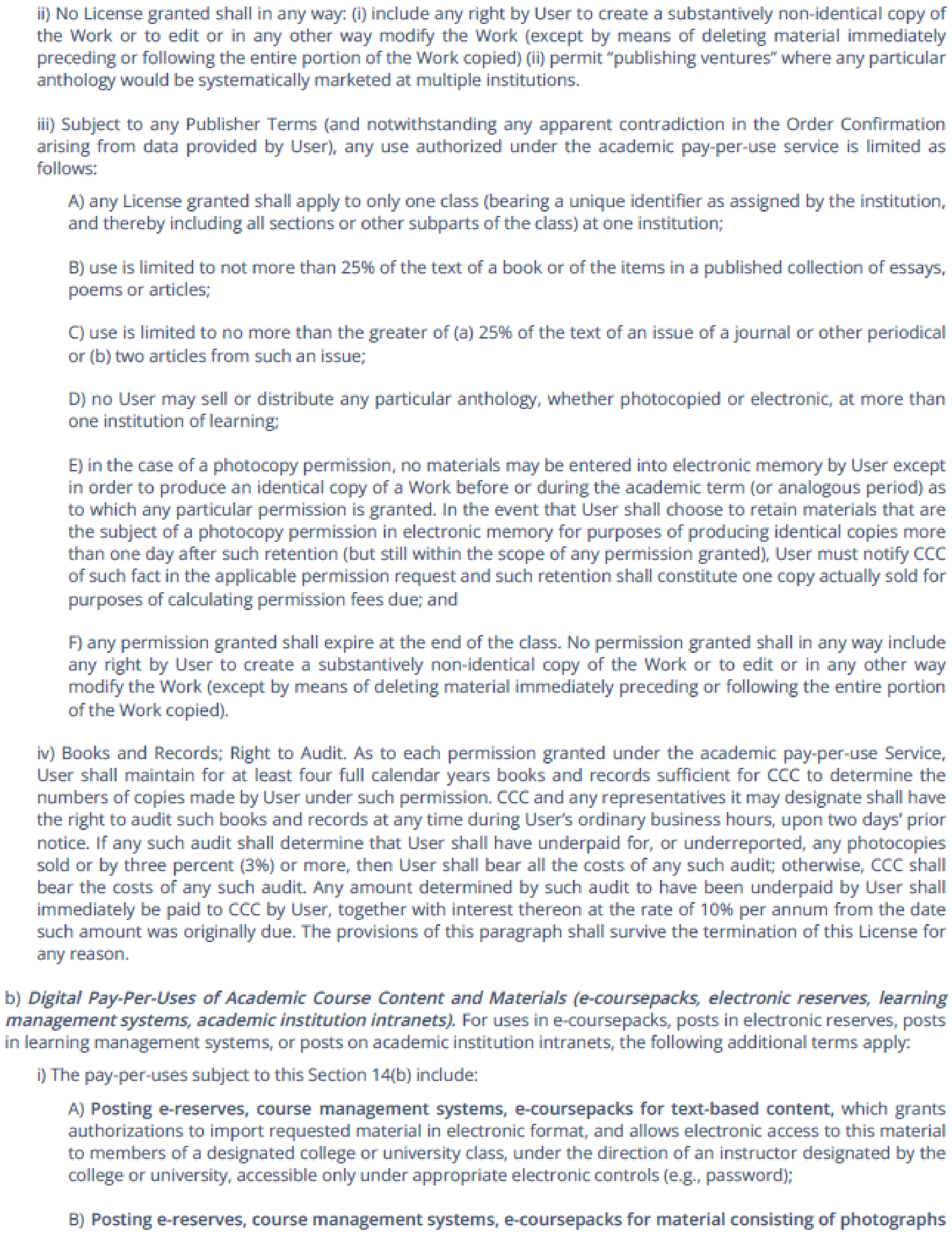
14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.



ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs**

or other still images not embedded in text, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

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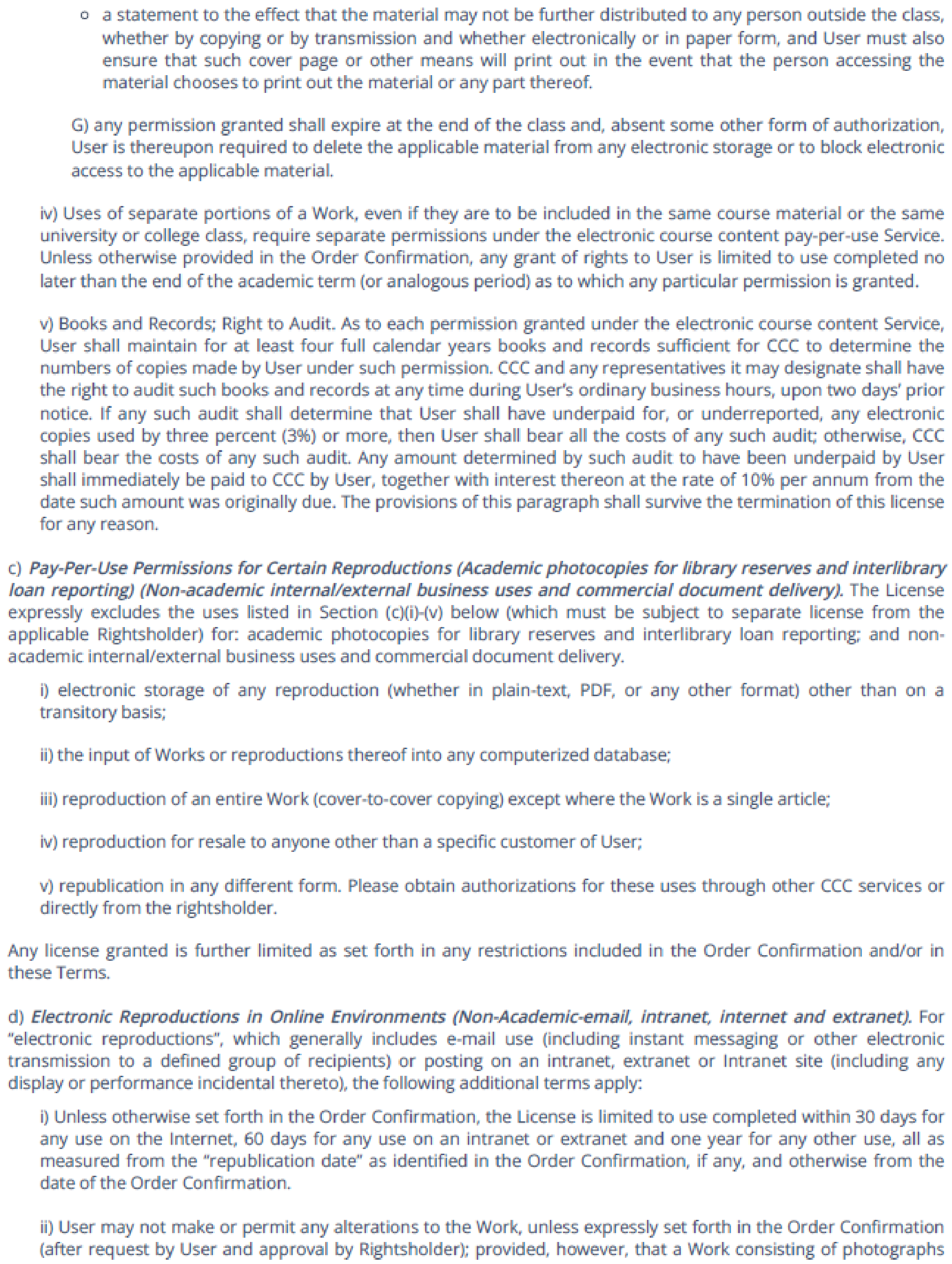
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and



- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

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iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

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d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

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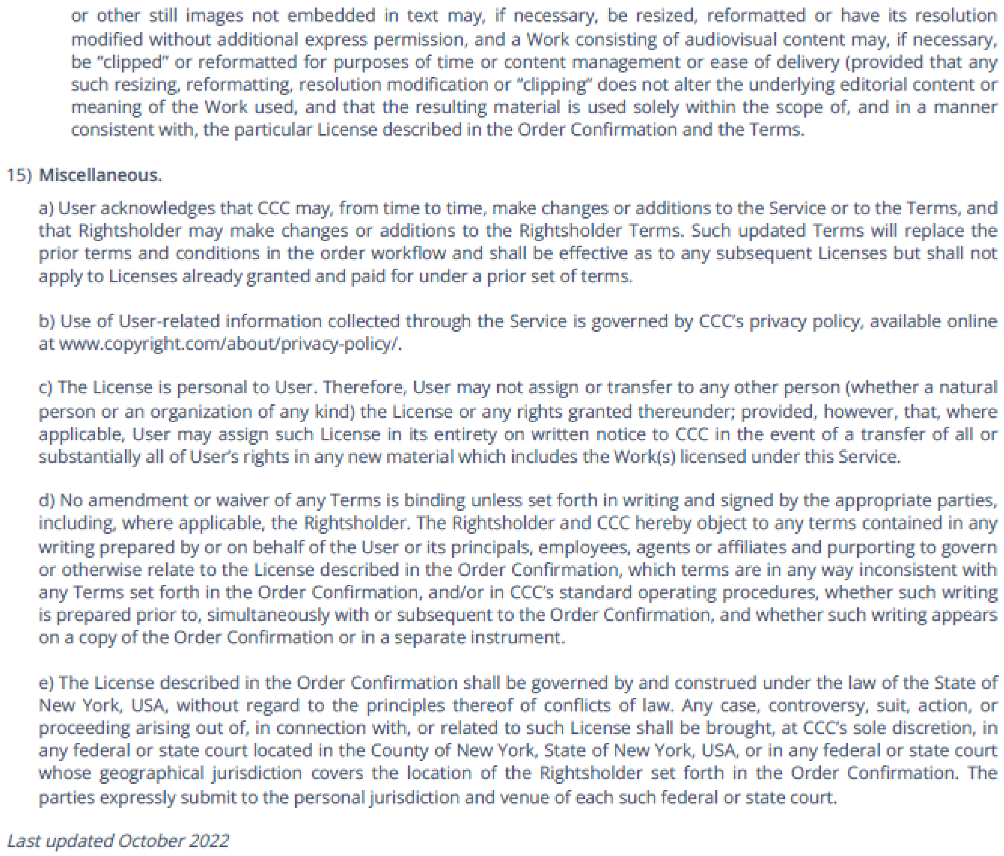

or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

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a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

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e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022

Curriculum Vitae

Behzad Kamiab, PhD Candidate

EDUCATION

Ph.D. (01/Sep/2021-01/Sep/2024)
Institution: Department of chemical and biochemical engineering, University of Western, London, Ontario, Canada.
MSc (23/Sep/2009 – 03/Mar/2012)
Institution: Department of Chemical Engineering, Isfahan University of Technology, Isfahan, Iran.
Bachelor (01/Sep/2003-01-Sep/2008)
Institution: Department of Chemical Engineering, Kashan University

PROFESSIONAL EXPERIENCES

-R&D manager at Progressive Industrial Fluids Ltd. September 2021-present.
-R&D and Project Manager at Ravankaran Ehya Sepahan Co. December 2013 –2021.

PUBLICATIONS

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[1] B. Kamyab, H. Zilouei, B. Rahmanian, Investigation of the effect of hydraulic retention time on anaerobic digestion of potato leachate in two-stage Mixed-UASB system. Biomass and Bioenergy, 130 (2019) p. 105383. https://doi.org/10.1016/j.biombioe.2019.105383

[2] B. Kamyab, H. Zilouei, Evaluation of anaerobic digestion performance of baker's yeast wastewater by comparing results between laboratory model and modeling performed on Two-Stage Mixed-UASB reactor. Fuel, 285 (2021) p. 119198. https://doi.org/10.1016/j.fuel.2020.119198

[3] B. Kamyab, R.F. Beims, C. Chio, W. Qin, D.W. Chambers, C.C. Xu, Synthesis of TMP esters as a biolubricant from canola oil via a two-step transesterification–transesterification process. *CJCE,* 102 (1) (2024) pp. 35-52. https://doi.org/10.1002/cjce.25024

[4] B. Kamyab, R.F. Beims, D.W. Chambers, A.S. Bassi, C.C. Xu, Sustainable production of high-performance bio-based hydraulic fluids from vegetable oils: Recent advances, current challenges, and future perspectives. Biomass and Bioenergy, 183 (2024) 107160. https://doi.org/10.1016/j.biombioe.2024.107160

[5] B. Kamyab, H. Wang, C.C. Xu, D.W. Chambers, A.S. Bassi, Preparing vegetable oils-based metalworking fluids by a hydrolysis-esterification two-step process. Biomass and Bioenergy, 183 (2024) 107175. https://doi.org/10.1016/j.biombioe.2024.107175

CONFERENCES

Oral presentation at Consortium for Industrial Bioproduct Innovation (CIBI), Western University. “Production of bio-lubricants from vegetable oils”. July 27, 2022.

Skills

-Analytical and Research: Experience with GC-MS/FID, FT-IR, TGA, Fourball, rheological tester (Mars IQ Air), and lubricant tests
-Software: Origin, MATLAB
-MS Office: MS Word/Excel/Powerpoint