LUBRICANTS FROM RENEWABLE **FEEDSTOCKS**

Edited by Subhalaxmi Pradhan Lalit Prasad Chandu Madankar S. N. Naik





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Scrivener Publishing

100 Cummings Center, Suite 541J Beverly, MA 01915-6106

Publishers at Scrivener Martin Scrivener (martin@scrivenerpublishing.com) Phillip Carmical (pcarmical@scrivenerpublishing.com)

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This edition first published 2024 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA © 2024 Scrivener Publishing LLC

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Library of Congress Cataloging-in-Publication Data

ISBN 978-139417-253-5

Cover image: Sugar Cane Field: Kennerth Kullman | Dreamstime.com Cover images: Biofuel: 350jb | Dreamstime.com Cover design by Kris Hackerott

Set in size of 11pt and Minion Pro by Manila Typesetting Company, Makati, Philippines

Printed in the USA

10 9 8 7 6 5 4 3 2 1

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Preface

Biolubricants generally derived from bio-natural resources are less toxic, biodegradable, and environmentally sustainable. Different plant oils, both edible and non-edible oil, waste cooking oil and oils produced by microorganisms are utilized to synthesize biolubricants. The application of base oils from bioresources such as castor oil, rapeseed oil, palm oil, soya oil, cod liver oil, pig oil, and other animal oil shows the adequate formulation of biolubricants and provides the required properties for lubrication, such as excellent lubricity, a high viscosity index, good degradability, a high flash point, and a low pour point. Lubricants can be categorized based on their physical state preferably oils or liquid, greases or semi-solid as well as solid lubricants. Different synthesis techniques such as epoxidation, hydrogenation, esterification, transesterification, estolide formation are used for the production of biolubricants from renewable feedstocks.

The present book covers new advancements in the field of bio-based lubricants, epoxide lubricants, hydrogenated lubricants, microbial based biolubricants, nano-biolubricants, polyester based biolubricants, lubricants from waste oils/materials, its economic and environmental acceptability and biorefinery approaches. A total of 14 chapters are included in this book. Chapter 1 is an introductory part which covers prospectus of renewable resources for biolubricant production and comparison of physicochemical properties of biolubricant with petroleum-based lubricants. Chapter 2 and 3 covers synthesis of ester based and epoxide based lubricants from renewable feedstocks and their applications. Chapter 4 and 5 includes synthesis, characterisation of bio-based hydrogenated lubricants and microbial based biolubricants respectively. Chapter 6 and 7 comprises of nanolubricants and green nanofluids, their physico-chemical properties and applications. Chapter 8 and 9 covers synthesis, characterisation and applications of polyester based biolubricants and estolide based biolubricants respectively. Chapter 10 and 11 covers biolubricant synthesis from waste cooking oil and waste management approaches towards biolubricant synthesis. Different catalysts used for synthesis of biolubricant are discussed in Chapter 12. Chapter 13 and 14 covers biorefinery approaches, economic and environmental acceptability.

This book will provide a forum for academicians, scientists, industrialists, and researchers to exchange novel concepts and viewpoints about lubricants derived from renewable feedstocks, as well as the potential for future developments and broad applications.

Prospectus of Renewable Resources for Lubricant Production

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Abstract

Lubricants aid in decreasing friction between surfaces in proximity, which in turn lowers the heat produced as the surfaces move. They are composed of 80% to 90% of base oils and 10% to 20% of additives that impart properties like antiwear, corrosion inhibition, pour point depression, etc. Petroleum-based lubricants are attributed to low biodegradability and toxicity. Demand for lubricants based on edible and nonedible plant oils or other renewable resources that are good for the environment is rising because of their enhanced lubricity, nontoxicity, and biodegradability. Biolubricants are synthesized by modifying plant oils chemically, by transesterification, estolide formation, epoxidation, etc. This chapter is intended to inform readers about renewable feedstocks for biolubricant production, comparison of physicochemical properties with petroleum-based lubricants, current scope, advantages, and challenges of biolubricant production in the future.

Keywords: Biolubricants, renewable, biodegradable, plant oils, chemical modification

Abbreviations

- RRM Renewable Raw Materials
- EU European Union

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Subhalaxmi Pradhan, Lalit Prasad, Chandu Madankar, and S.N. Naik (eds.) Lubricants from Renewable Feedstocks, (1–38) © 2024 Scrivener Publishing LLC

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CO ₂	Carbon dioxide
PAO	Poly alpha olefin
HOSO	High oleic sunflower oil
VI	Viscosity Index
PTSA	Para-toluene sulphonic acid
СОР	Coefficient of performance
FDBO	Farnesene-derived base oil
PFPE	Perfluoro polalkylether
CFC	Chlorofluoro carbon
SAPO	Silicoaluminophosphate
ZDPP	Zinc dialkyldithiophosphate
DDA	Detergent and dispersion additives
PPD	Pour point depressants
GM	Genetically modified
GHG	Greenhouse gases

1.1 Introduction

Lubricants help solid bodies move closer to each other by lowering wear and friction surfaces that interacting [1]. These are majorly used in chain saws, engines, gear boxes, metal rolling mills, etc. Lubricating oils are necessary for a variety of other tasks in addition to their fundamental roles in reducing friction and wear, such as removing heat, preventing corrosion, transferring power, creating a seal for the liquid moving contacts, and suspending, as well as removing worn-out particles [2].

Among the most promising future markets, according to the Lead Market Initiative of the European Commission, is goods made from renewable raw materials. The utilization of renewable raw materials (RRM) by way of a feedstock can help conserve fossil fuels and lessen adverse environmental effects while producing utilities, chemicals, and different bioderived products. Additionally, it could benefit the agriculture, as well as forestry industries and spur developments for manufacturing products, like biolubricants and bioplastics [3].

Vegetable oils have great lubricating performance, are biodegradable, and can be recycled, making them a promising source of ecologically beneficial (green) lubricants [4]. Triglycerides, or tri-esters, have three long-chain fatty acids connected at the –OH groups through ester bond to the glycerol backbone and make up the majority of vegetable oils. These oils contain a tiny percentage of esters with one ester group from long-chain fatty acids and fatty alcohols with various chemistries [5]. Triglycerol esters from vegetable oil contain fatty acids with variable amounts of unsaturation, all of which have a comparable length (14–22 carbons) [6]. A large proportion of vegetable oils consist of various polar and nonpolar groups in the same molecule. These oils have polar groups and are hence amphiphilic, which enables vegetable oil to be incorporated as a boundary and hydrokinetic lubricant [7]. Almost 8% (12.4 million tonnes) of world's manufacturing of renewable raw materials comes from Europe (EU-27), primarily from rape, sunflower, and soya.

The utilization of plant-based oils in lubricants depends on their fatty acid composition. Mainly, long-chain fatty acid-based plant oils are preferred for use in biolubricant manufacture. Palm, soya bean, rapeseed, and sunflower oils are hence majorly used [8]. The second largest category of products made from plant oils is lubricants. Lubricants are intricately manufactured goods of about 90% base oils along with useful additives to change inherent qualities. Vegetable oils are typically utilized for the purpose of base oils in biolubricants; however, only 50% of the oil needs to come from renewable sources to qualify as a biolubricant [9].

Biobased lubricants are used as hydraulic fluids, metal working fluids, grease, concrete mold release agents and chainsaw oils. These are majorly applied in mechanical parts, which is being utilized in ecologically sensitive regions like agriculture and machinery for forestry, jet-skis, snow mobiles, etc. Although it is currently a small portion of the overall lubricant market, the biolubricant sector is continually expanding. Similar to mineral oil alternatives, which are more accessible but still account for a relatively small fraction of the industry. Both bioderived as well as some synthetic lubricants contain biologic components. By 2023, 1.06 million tonnes of bioderived lubricants are anticipated to be consumed [10]. The worldwide lubricant market can be broken down into lubricant-based mineral oil (87.72%, 32.63 million tonnes), synthetic lubricants (9.95%, 3.70 million tonnes), and lubricants based on renewable resources (2.33%, 870000 tonnes), as represented in Figure 1.1.

The industrial reach of green lubricants is anticipated to rise to 15% and perhaps 30% in some regions over the next 15 to 20 years. This market is anticipated to increase significantly because of growing utilization of biobased lubricants in the manufacturing and transportation sectors [11].

The potential future shortage of oil and gas resources (whether in terms of availability or quantity) is a serious issue for everyone in the world.

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Figure 1.1 Distribution of global lubricant market.

Ruling bodies all across the world are attempting to lessen their reliance on foreign sources of energy as a result. In addition, bioderived lubricants have become more popular as alternatives for traditional lubricants based on petroleum sources in a variety of applications, particularly the automobile sector. Despite their advantages, biobased lubricants are still a long way from being a reliable replacement. Biobased lubricants have low cold flow characteristics, poor thermooxidation, and low hydrolytic stability because they are often made from unrefined vegetable oils. However, these flaws could be fixed by chemically altering the oils derived from natural resources or adding additives to the oils [12].

Vegetable oils have been utilized for lubrication needs for a long time. The unearthing of petroleum as well as the availability of inexpensive oils, however, led to the abandonment of this notion. Crude oils derived from fossil fuels are still utilized as primary raw material in the processing of fuels and lubricants. However, because of increased apprehension about ecological effects of lubricants based on nonrenewable resources, there has been a renewed attention to the usage of lubricants made from vegetable oils. Numerous businesses have created and sold biobased lubricants [13].

Because they preserve the mechanical characteristics of traditional lubricants, lubricants based on renewable resources are attractive substitutes for mineral oils. Bioderived lubricants have excellent lubricity, flash point viscosity index, and are biodegradable. They are made from edible and inedible vegetable oils [14].

The current chapter lays emphasis on how modern technological advancement can lead to improved manufacturing of bio lubricants. These technologies are primarily prospective for utilization of renewables as raw source, such as vegetable oils. However, there are certain constraints and impediments for full-scale implementation or commercialization like for example, the economics for development of biolubricants are not fully set or accustomed to manufacture and use of biolubricants as substitute to traditional lubricants based on petroleum sources; development of required technology and its standardization; testing and analysis in real time systems has not yet been performed on a commercial scale, etc. Nonetheless, the current research and findings in these domains can prove to be effective solution.

1.2 History

For hundreds of years, biobased materials have been utilized as efficient lubricants. Even though there has been evidence to show the usage of lubricating agents in the Copper Age, animal as well as vegetable oils had been employed in Roman era for lubricating chariot axles [10]. In the last 50 years, their adoption and use have expanded more widely, primarily due to environmental concerns, albeit in some situations, biobased components may perform better than traditional lubricant chemistry. The requirement of biobased lubricants and the production of lubricants made from biobased crude oil are both rising as there are more and more initiatives promoting sustainable sourcing and use [15]. The Industrial Revolution started in the 18th century, and has led to an increased request for oils from natural sources like olive oil, sperm oil, lard oil, rapeseed oil, and ground-nut oil [16]. With the growth of the Industrial Revolution, more oil was needed to lubricate machinery. Due to its lower price and capabilities, petroleum was exploited at least 100 years after, in the mid-19th century. As a result, oils from renewable resources were not able to contend with nonrenewable resources. The development of the petro-based market at this time was crucial to 19th and 20th century's industrial growth. However, some businesses have been working on the creation of bioderived lubricants for many years because the outcome of an increasing consciousness of the impact of petro-based oil on the natural surroundings. For instance, British Petroleum and Shell worked with French National Railways to develop biodegradable railroad track lubricant [13].

1.3 Background of Biolubricants

Lubricants are utilized in open as well as closed systems. In open systems such as construction, automotives, forestry lubricant such as power

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saw chain oils, switch lubricants, slab oils, etc. are used, are continuously exposed to the environment, and leads to loss of lubrication. In closed systems, leakages, metalworking fluids, etc. lead to environment pollution due to spillages, loss of lubrication and evaporation [17]. Hence, there is a need for lubricants which are environmentally friendly, i.e., non-toxic and biodegradable that are manufactured from raw materials from renewable sources.

When biobased products (oleochemicals) reach the end of their useful lives, they are released via a variety of processes, where the organic molecules break down into CO_2 and water. Since the quantity of CO_2 emitted is equal to the amount that was initially absorbed by the natural plants from the surroundings, the carbon cycle of oleo-based chemicals is closed. As a result, it has no impact on the atmosphere's carbon dioxide balance. On the other side, items made from mineral oils raise atmospheric carbon dioxide levels, which causes global warming and is called indirect environmental contamination. Figure 1.2 represents the series of stages encountered during biolubricant life cycle, right from its production to utilization in for commercial purpose to its waste form and conversion to CO_2 and water.



Figure 1.2 Life cycle assessment of bioderived lubricants.