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Review

# Development of biolubricants from vegetable oils via chemical modification

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ABSTRACT

In response to the increasing environmental pollution concern and depleting petroleum reserves, bio-based lubricants have received a great deal of interest as a substitute for mineral oil-based lubricants. Biolubricants have a number of advantages over mineral lubricants, including the high biodegradability, low toxicity, excellent lubrication performance, and minimal impact on human health/environment. This paper reviewed the most recent advancements in the synthesis of biolubricants from vegetable oils through chemical modification methods such as esterification/transesterification, estolide formation, and epoxidation of vegetable oils.



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## Introduction

With concern over global climate change and depleting petroleum reserves growing, the search for environmentally sustainable alternatives to current practices continues to intensify [1]. One area of interest which could serve to reduce both reliance on petroleum and anthropogenic impact on the environment, is the use of vegetable oil-based lubricants in place of the commonly used petroleum-based lubricants. These products, known as "biolubricants", carry several environmental, health, and performance benefits over current petroleum-based lubricants.

It is estimated that 20% of the 5.2 million tons of lubricant consumed every year in Europe is released into the environment, and a kilogram of said mineral oil is capable of polluting a million liters of water [2]. Therefore, pollution caused by lubricants is far from insignificant. The petroleum-based lubricants can also contaminate soil directly, and pollute the air due to its volatility [3]. This pollution is hazardous to not only plants and animals

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inhabiting the contaminated areas, but potentially human residents as well [4]. Several studies have documented the harmful effects of petroleum based lubricants on human health. Chronic inhalation or dermal exposure to petroleum-based lubricants can have inflammatory effects on the respiratory system and location of contact, while also being carcinogenic [5–7]. These negative effects are even more severe in the used petroleum-based oils, as degradation leads to increased toxicity [8]. Many biolubricants however, are rapidly biodegradable and nontoxic, and therefore pose little or no risk to the environment or operators [4,9,10]. Biolubricants also boast several performance benefits, including better lubricity, higher flash point, lower volatility, higher viscosity indices, higher shear stability, lower compressibility, higher detergency, higher resistance to humidity, and higher dispersancy [4,9,11–16].

Despite these advantages, biolubricants are still not widely used due to several major challenges and difficulties regarding its performance and production. Aside from issues regarding feedstock reliability and consistency as well as industry acceptance, biolubricants also have two main negative physical properties: poor low temperature performance, and low thermal oxidative stability [3,9,10,12,17,18]. However, through appropriate chemical modification processes, these two properties can be improved to make biolubricants a feasible alternative to mineral lubricants for various applications. Much research has been done in previous years on the exploration of new feedstocks and modification methods, development of more efficient catalysts for modification of vegetable oils, and optimization of modification. However, there is need for a review paper on this topic. This paper aims to summarize the most current research focused on chemical modification methods and their respective advantages and disadvantages. The paper will also provide information on common feedstocks and the required properties of biolubricants, as well as the relevant testing methods. It is noteworthy that the focus is on the development of base oil for biolubricants from vegetable oils, therefore bio-based additive development is beyond the scope of this paper.

## Feedstock considerations

The most commonly used feedstock for developing biolubricants is vegetable oils. Molecularly, vegetable oils are triglycerides, esters of glycerol and three straight chained fatty acids. The chain length of the fatty acids is usually in the range of C12–C24. The three fatty acids vary between feedstocks, and play an important role in determining the properties of the oil. The two main variables among fatty acids are the number of double bonds and the chain length. In general, a longer chain length results in a higher melting point and viscosity, and more double bonds correspond to lower melting points, decreased viscosity, and decreased thermo-oxidative stability [2]. Monounsaturated fatty acids, such as oleic and palmitoleic acid, have been found to have a good balance of low melting point, with good thermo-oxidative stability and viscosity [2,3,17]. It is for this reason feedstocks with high oleic or palmitoleic acid contents are generally preferred and sought after.

Vegetable oil can be extracted from the over 350 different crops with oil-bearing seeds throughout the world [1,19]. Popular feedstocks include palm, canola, soybean, sunflower, coconut, safflower, rapeseed, cottonseed, jatropha, karanja, castor, lesquerella, pennycress, and peanut oils, with many others being tested for potential use. While both edible and non-edible crops are currently being researched, non-edible crops are more desirable for several reasons. Non-edible vegetable oils are often derived from plants that are not in direct competition with cultivation of edible oil crops. For example, rubber seed oil, which is collected from rubber trees, cannot be used for edible purposes due to the presence of glycoside. However, the tree can grow in a wide range of pH values, meaning it could be produced on land that is largely unproductive [20]. Non-edible crop oils such as jatropha, linseed, karanja, neem, castor, coriander, cuphea, rice bran, milkweed, and many others have little to no impact on world food prices or production, as they can be grown on nutrient-deficient land and do not compete with existing agricultural resources [2,19,21]. However, harvesting, cultivation, and processing of these crops are often a challenge, as many of these crops had little incentive to be purposely produced until recently [21].

Genetic modification of oil-bearing crops is also a topic to consider when examining feedstocks. A majority of the genetic research in the field of lubricants involves the creation of high-oleic varieties of oil seed crops. As mentioned above, oleic acid is one of the most favorable fatty acids in biolubricant production due to its good balance of low temperature properties and high temperature thermo-oxidative stability. Sunflower, palm, camelina, rapeseed, and soybean all have genetically modified varieties which alter the composition of the seed oils [22–26].

Another feedstock which is being investigated is waste cooking oil. One of the biggest barriers for biolubricant production is the high cost of feedstock, which can account for 70–80% of the total production cost [27]. Waste cooking oil is significantly cheaper than unused edible vegetable oils, and has therefore been examined as a possible alternative feedstock [27–30]. Waste cooking oil is generally 30–60% cheaper than regular vegetable oil, which makes it a potentially promising candidate for profitable biolubricant production [27].

## Performance requirements of biolubricants

The main function of a lubricant is to reduce the friction between contacting surfaces. Lubricants are used in a variety of industries such as agriculture, forestry, mining, automobile, and fishing, serving as engine oils, chainsaw oils, transmission oils, and hydraulic oils. With different applications, lubricants may have specifically required characteristics in terms of viscosity, chemical stability, fluidity, flammability, range of working temperature and water solubility. Currently, there are not a wide array of specifications for biolubricants, but generally the properties of biolubricants must be comparable to those of mineral oil based lubricants as regulated in USA or European standards. Table 1 shows some lubricant specifications, as well as some unmodified vegetable oil properties. One of the most popular sources for evaluation methods of lubricants is ASTM International, formerly known as the American Society for Testing and Materials. Their website contains over 1200 different testing methods relevant to lubricants, demonstrating how broad the use of lubricants is. Some of the most common ASTM tests include D97, D445, D2270, D2500, and D4172 which measure the most important properties such as pour point, viscosity, viscosity index, cloud point, and anti-wear characteristics, respectively [38–44].

## Modification methods

Most currently available vegetable oils cannot be used as lubricants directly due to poor low temperature performance and low oxidative and thermal stability. There are a number of methods to improve these undesired properties, such as genetic modification of fatty acid profile of vegetable oils, direct addition of antioxidants, viscosity modifiers, and pour point depressant to vegetable oils, emulsification of vegetable oils, and chemical modification of vegetable oils [3,9,12]. Among these methods, chemical modification is the most promising one with great potential to improve chemical and broad temperature range stability. Chemical modification