



A REVIEW ON TRIBOLOGICAL AND THERMO-PHYSICAL MECHANISMS OF BIO-LUBRICANTS BASED NANO MATERIALS IN AUTOMOTIVE APPLICATIONS

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ABSTRACT

The automotive industry has put in significant effort to increase energy efficiency and decrease harmful emissions. However, friction and wear remain a persistent issue, leading to increased environmental risks due to higher fuel consumption and wear debris. Lubricants act as an anti-friction medium, reducing friction, wear, and frequent failure. Thus,

researchers have focused on modifying lubricating oils with additives to improve their characteristics, given the constant need for lubricants in transportation, agriculture, and other industrial sectors. This review article aims to highlight the research done in the area of using bio-lubricants with Nano additions for tribological applications, specifically in the automotive industry. To achieve this goal, thorough research is required to determine the appropriate Nanoparticles and bio-lubricants based on important characteristics such as viscosity, flash point, biodegradability, thermo-oxidative and storage stability of the oils, techno-economics, and sustainability. The study examined the tribological properties of a bio-lubricant made from sandbox seed oil that was enhanced with copper (II) oxide nanoparticles. The findings indicate that the addition of copper (II) oxide nanoparticles to sandbox oil improved its tribological properties. The review's contribution will help specialists and academics working in the bio-lubricant sector to address the significant challenges associated with eco-friendly oil manufacturing that relies on sustainable resources. Additionally, this review study sheds light on the tribological and thermo-physical properties of bio-lubricants, which could lead to the development of more environmentally friendly car engines.

KEYWORDS: Bio-Lubricants, Thermal Stability, Operation Noise, Vibrations, Friction, Wear, Tribology.

1. INTRODUCTION

Lubrication is the process of applying a material, known as a lubricant, between two moving surfaces to reduce wear on one or both of them. The lubricant bears the load or pressure generated between the surfaces and acts as an anti-friction medium, promoting fluid operation, ensuring reliable machine functions, and reducing the likelihood of frequent failures. Lubricants come in various forms, including semi-solid grease, coatings, and particles. The primary objectives of lubrication are to reduce wear, limit heat loss, prevent corrosion and friction, and act as a sealer against water, dirt, and other contaminants, or an insulator in transformer applications.

Although lubricants cannot eliminate wear and heat entirely, they can manage and reduce them to acceptable levels. Researchers have identified three primary purposes of lubricants, which are to reduce friction, clean the contact, and cool the surface. Mineral oils were once preferred due to their economic advantages. However, due to their toxic and non-renewable nature, the reuse of mineral oils is no longer a viable option for non-commercial vehicles. The inappropriate disposal of mineral oils has led to an increase in sewage treatment costs, reduced availability of groundwater, harm to marine and freshwater life, and a decline in air quality. To address this, researchers have turned to bio-lubricants, which are non-toxic and based on renewable resources (Zaman et al., 2022).

Lubricants can be categorized as solid, semi-solid, or liquid, depending on their physical state, and their effectiveness depends on characteristics such as viscosity, density, flash point, pour point, thermal stability, and oxidation stability. Vegetable oils have become a popular alternative to mineral oils (Syahir et al., 2017) because they are less harmful and renewable. Studies have shown that vegetable oils, particularly tricycle glycerides, offer good lubrication properties, including high viscosity index, high lubricity, high flash point, low evaporative loss, high biodegradability, low toxicity, and a good solvent for additives. The polar ester structure of vegetable oils interacts with metal surfaces, improving the lubrication. Additionally, the rapid expansion of public transit has raised concerns about the proper disposal of used mineral lubricants. Infusion of nanoparticles into the bio-lubricants is another area where the bio-lubricants can surpass the performance of synthetic or mineral-based lubricants (Owuna, 2020, Mohd et al., 2021, Caleb et al., 2021, and Heoy et al., 2022).

In this review article, the reviewers are focusing on the nano-particle based bio-lubricants and their performances in lubrication.

2. Functions of Lubricants

The protection of internal combustion engines in motor vehicles and powered equipment is one of the major applications for lubricants, particularly in the form of motor oil.

2.1 Anti-Tack Coating Versus Lubricant

Anti-stick or anti-tack coatings are designed to reduce the stickiness of a particular material. These coatings are widely used across various industries but are particularly important in the rubber, hose, and wire and cable sectors. Unlike lubricants, which aim to reduce friction between two surfaces, anti-stick compounds are intended to reduce the intrinsic adhesive properties of a given material. Lubricants, on the other hand, help keep moving parts apart in a system, which in turn reduces heat generation, noise, vibrations, friction, wear, and surface fatigue. They achieve this in several ways, such as creating a physical barrier between the moving components with a thin layer of lubricant, similar to hydroplaning. This process is known as hydrodynamic lubrication, where a thin fluid layer is formed, and some forces are transferred between the surfaces through the lubricant when there are high surface pressures or temperatures.

2.2 Reduce Friction

When a system lacks lubrication, the friction between the lubricant and the surface is typically much lower than the friction between surfaces. Therefore, the use of a lubricant reduces overall system friction. Lower friction not only improves efficiency but also results in less heat and wear particle generation. In cases where there is not enough lubricant for hydrodynamic lubrication, friction modifiers can be added to lubricants. These polar additives chemically bond to metal surfaces and protect the valve train of an automobile engine from surface friction during startup. Some base oils, such as polyester oils, may have a polar nature and can naturally bond to metal surfaces.

2.3 Transfer Heat

Lubricants, whether in liquid or gas form, can transfer heat. However, liquid lubricants are more effective at transferring heat due to their higher specific heat capacity. While lubricants can be used to control temperatures, they are often circulated to and from a cooler area of the system to remove heat. The flow rate of the lubricant affects the amount of heat that can be

removed, and high-flow systems can also lower thermal stress. This allows for the use of less expensive liquid lubricants. However, high-flow systems may require large sumps and cooling systems, and sudden system shutdowns can lead to catastrophic failure. An example is the oil-cooled turbocharger in automobiles, which relies on high flow rates to prevent the oil from oxidizing and clogging the oil channels. Grease and pastes are non-flowing lubricants that do not transfer heat efficiently, but they do help to reduce initial heat generation. The characteristic of bio-based lubricants for different applications are shown in Table 1.

Table 1: Outstanding characteristics of bio-based lubricants for different applications (Krishna et al., 2021).

Applications	Bio-lubricant type	Outstanding characteristics	Findings
Engine oils	Palm oil, rapeseed oil. Karanja oil, and castor oil.	Low volatile organic compound emission and good lubricity.	Superior tribological performance and reduce engine emission.
Metalworking fluids	Soybean, Karanja, neem, Coconut oil, palm oil, and rice bran,	Good antirust capability, low volatility, good emulsifiability, and good lubricity.	Longer tool life, stable emulsions at high temperatures, less harmful mist generation, reduce surface roughness, reduce cutting temperature, and reduce tool flank wear.
Hydraulic fluids	Sunflower, rubber seed oil, rapeseed oil, and soybean oil.	Fast air release rate and low compressibility.	Minimal vibration/noise and best pressure transmission.
Compressor oil	Soybean oil	High thermal stability.	Can tolerate the standard compressor up to -250 °C discharge temperature.
Gear oils	Complex esters	Higher weld load and good lubricity	Suitable with nano-additives

3. Challenges of Bio-Based Lubricants

Although efforts have been made to reduce oxidation stability and spillages of bio-based lubricants, they still face significant obstacles when it comes to their use in automobile engines at high temperatures. The poor low-temperature properties and oxidative stability of raw bio-oils are the main reasons for their subpar performance. Research has shown that bio-oils can experience precipitation, cloudiness, and solidification at 100C, hindering their ability to flow freely due to the creation of microcrystalline structures that allow the triglyceride backbone to stack uniformly. While bio-based lubricants have outstanding qualities for various applications, including low emissions of volatile organic compounds,

excellent lubricity, and strong antirust properties, using bio-oils directly in car engines for an extended period of time is not recommended. They need to undergo chemical alteration to overcome their limits without losing their tribological and environmental qualities. One significant challenge to the widespread use of bio-oils is the fact that many of the widely produced feedstocks, such as rapeseed oil, palm oil, and soybean oil, are edible oils. This has raised concerns about global inequality in the demand for and supply of food, as converting these edible bio-oils to lube oils for use in various mechanical applications could lead to a shortage of food. Another obstacle to securing a consistent supply of homogenous feedstocks on a large scale is the potential increase in the product's final price. To promote the usage of bio-based lubricants, governments should distribute arable land and bio-oils and offer assistance to the agriculture, research, and industry sectors. Although this development has been slow in the past century, research and government support have recently regulated the market for bio-oils, and initiatives to safeguard the environment by using more biodegradable, less toxic, and better energy-saving products will continue to be supported.

4. Carry Away Contaminants and Debris

One of the advantages of lubricant circulation systems is that they can transport external pollutants and internally generated waste to a filter for removal. Lubricants that are used in machinery that frequently generates debris or pollutants, such as car engines, often contain detergent and dispersion additives. These additives help move the debris and contaminants to the filter for removal. It is recommended to replace the oil filter in a car at the same time as the oil, as it can become clogged over time and require cleaning or replacement. In closed systems like gear boxes, a magnet may be added to the filter to attract any iron fines that are produced. Unfortunately, there are no industry standards for evaluating the filtering ability of various vehicle filters, making it difficult for consumers to choose an effective filter. The effectiveness of the filter is critical, as the oil will only be as clean as the filter can make it. Poor vehicle filters can lead to an inefficient system and significantly shorten the lifespan of the machine, including the engine.

4.1 Power Transmission

In hydrostatic power transmission, a hydraulic fluid lubricant is used. Hydraulic fluids make up a significant fraction of all lubricants manufactured worldwide. Lubricants are also used for power transmission in torque converters in automatic transmissions.

4.2 Wear Protection

Lubricants reduce wear by keeping moving parts apart. They may also contain anti-wear or extreme pressure compounds to enhance their resistance to wear and fatigue.

4.3 Corrosion Prevention

Many lubricants are formulated with chemicals that connect with surfaces or repel moisture to prevent corrosion and rust. They prevent submerged corrosion and minimize corrosion between metallic surfaces.

4.4 Gas Sealing

Capillary force causes lubricants to fill the gap between moving parts, sealing the space. This effect can be used to seal pistons and shafts.

5. Adding Nanoparticle Additives to Lubricants for Lowering Friction and Wear

Adding nano-additives to lubricants is an effective way to reduce friction, wear, energy loss, emissions, and protect the environment. Compared to non-nano additives, nano-particle additives can significantly reduce friction between lubricated surfaces. In industrial applications, nano lubricant additives have achieved technological advancements with improved tribological properties and decreased power consumption, resulting in a smoother cutting surface. Nanoparticles in lubricants can create a physical film that deposits on friction surfaces, improving the tribological qualities of friction and wear. Experimental settings have shown that nano carbide materials reduce failure strain due to their high elastic modulus and brittle behavior. Hybrid nanoparticles added to oils have also demonstrated a reduction in wear and friction. Using nano lubricants in engines has been found to decrease the temperature on the outside of the cylinder, suggesting less friction in the cylinder and piston rings.

6. Overview of Lubrication and Bio-Lubricants

The primary technique for reducing friction and wear is to lubricate the sliding contact bodies by creating a film between the mating surfaces, which minimizes their contact. Lubricant performance depends on various elements, including viscosity index, flash point, pour point, thermal stability, and oxidation resistance. The method of lubrication affects how the lubricant operates, with boundary lubrication, hydrodynamic lubrication, and elastohydrodynamic lubrication all playing a role. Bio-lubricants, made from vegetable and animal fats, are the best replacement for mineral-based lubricants due to hydrocarbon

depletion. Vegetable oils, mostly composed of triglycerides, have higher lubricating characteristics and are renewable, biodegradable, and less toxic. Vegetable oils are created using the solvent method or pressing method and are categorized based on the effect of fatty acids. Lauric oil, erucic oil, ricin oleic oil, and oleic-linoleic oil are the four categories. Adding nanoparticles to synthetic and mineral-based lubricants has been explored, but there is relatively little research on nanoparticle-based bio-lubricants. A comprehensive review is necessary to choose the appropriate nanoparticles and bio-lubricants, focusing on various characteristics. This review provides an overview of the tribological performance of bio-lubricants based on nanoparticles. The comparison between the bio-lubricants and the synthetic/Mineral Lubricants is shown in Table 2. The key finding of Various Bio-Lubricants from Different Studies are listed in Table 3.

Table 2: Comparison of Bio lubricants with Synthetic/Mineral Lubricants ((Srivyas et al., 2018).).

Oils	Method/Apparatus	Summary
Jatropha Oil with SAE 20w40	Pin on disc tribometer	Lower wear loss and lower COF were achieved
Modified Rapeseed Oil with SAE 20W40	High-frequency reciprocating tribometer	Improved cold property, better oxidation, lower COF.
Neem Oil, Olive Oil, Sunflower Oil, Mahua Oil with Petroleum-based Mineral oil	Four-ball tester rig	Lower COF, enhanced wear properties, higher viscosity, high flash point, high lubricity, low evaporation loss, economical, eco-friendly, and renewable.
Waste Palm Oil with SAE 40	Four-ball tester rig	High viscosity and lower COF were achieved
Soyabean Oil with Petroleum based Mineral oil	Four-ball tester rig	Bio-degradable, eco-friendly, non-toxic, good lubrication film formed reduction in COF and wear rate.
Soyabean Oil with Commercial Synthetic Lubricating oil	High-frequency reciprocating tribometer	High viscosity
Castrol Oil with SAE 20W40	Pin on disc tribometer	Lower volatility, higher viscosity index, and higher lubrication properties.

Table 3: Key Findings of Various Bio-Lubricants from Different Studies (Krishna et al., 2021).

Lubricants Oil	Major findings
Karanja oil	General lubrication oil is having good oxidation stability than bio-oil because bio oil is having pour point of 1 C and general lubrication of oil is -6 C Karanja oil lubricity didn't gen mush effect due to oxidation stability. It can be used for gentle lubrication.
Orange peel oil	The oxygen stability is the bio lubricant that withstands for 21 minutes under the pressure of 90 psi with oxygen. The pour point has been decreased from 10 to 2 C in the case of chemical modification of orange peel oil to bio orange peel oil chemical modification if required for better oxidation stability.
Rapeseed oil	The oxidation stability test was conducted with RPVOT (rotary pressure vessel oxidation test) by using the copper spiral as a catalyst. The oxidation stability of raw rapeseed oil is 16 minutes whereas chemically modified oil is 35 minutes. This chemically modified rapeseed oil has better performance than raw rapeseed oil.
Soyabean oil	The oxidation stability of soyabean oil is lesser when compared to mineral oil. Micro oxidation test at a temperature of 150°C for a duration of 30 to 60 mins. Vegetable oils oxypolymerize faster than unsaturation-free oils.
Rice Bran oil	Rani et al. added 0.8% Tertiary-butyl hydroquinone 1% Butyrate hydroxyl toluene 0.05% Aminophenylamine as anti-oxidant additives to rice bran oil. Oxidative stability tests performed were the hot oil oxidation test and isothermal thermo gravimetric analysis. The formulated oil resulted in a higher oxidative degradation (0.45%) compared to 0.21% of commercial analysis)

7. Addition of Nano Additives

In recent years, the field of tribology has seen a significant expansion due to the development of Nano lubrication. The potential for dispersing nanoparticles in base oils has drawn the attention of researchers to the application of Nano lubricants. Nanoparticles have diverse applications, including in tribology, medicine, space exploration, and composites. Adding nanoparticles to base oils has shown promise in improving specific tribological properties such as wear resistance and friction, while also being environmentally safe. Several studies have been conducted on the use of different types of nanoparticles as lubricant additives in combination with vegetable oils. The thermo physical properties of the bio-lubricants are shown in Table 4. The characteristics of different lubricants extracted from different bio sources are listed in Table 5.

Table 4: Thermo-Physical Properties of Bio-Lubricants (Krishna et al., 2021)

Nonedible vegetable oil	Evaporation loss	Cloud point	Pour point	Flash point	Density	Viscosity temp	Viscosity index
Karanja oil	-	4°C	1°C	251°C	0.924 kg/l	43.42cst 40°C	118
Orange peel oil	0.12%	-	10°C	-	-	-	135.17
Rapeseed oil 20%	-	-	10°C	60°C	905 kg/m ³	21.7cst 40.°C	-
Rapeseed	-	-	-11°C	320°C	-	8cst 100°C	220
Pongamia oil	-	-	-	252°C	-	35.98mm ² /s 40°C	338
Palm oil	0.09%	-	-	304.3°C	-	42.66 cst 40°C	187
Calophyllum	-	-	-	221°C	-	71.98 cst 40. °C	-
Paraffin mineral oil	-	-	-	-	0.8238 g/cm ³	14.85cst 40.°C	110
Mongongo oil 12%	-	-	-	176.°C	-	31.cst 40.°C	185.13
Jatropha	-	-	-	97°C	0.9819 g/cm ³	18 cst 40°C	104
Moringa oil 12%	-	-	-	176°C	-	31 cst 40°C	185.13
Coconut oil	-	0°C	-	112°C	805 kg/ m ³	2.75 mm ^{2/5}	-
Soyabean oil	-	1°C	-	176°C	885 kg/ m ³	4.05 mm ^{2/5}	-
Sunflower oil	-	3.42°C	-	185°C	878 kg/ m ³	4.45 mm ^{2/5}	-
Olive oil	-	-	-	179°C	892 kg/ m ³	4.52 mm ^{2/5}	-
Peanut oil	-	5°C	-	177°C	882 kg/ m ³	4.92 mm ^{2/5}	-
Rice barn oil	0.45%	0.3°C	- 18.12°C	294°C	886 kg/ m ³	495 mm ^{2/5}	-

Table 5: Characteristics of Bio-lubricants (Srivyas et al., 2018).

Oil	Characteristics
Cotton-Seed oil	More susceptible to oxidation (Anti-oxidant are used to make them more stable) Exhibit good anti-wear properties
Soyabean oil	A large percentage of polyunsaturated acid
Sunflower oil	Better oxidation stability better additive solubility Exhibit good anti-wear properties
Palm oil	Exhibit good anti-wear properties Reduce poisonous gases in the environment
Olive oil	Resistant to oxidation

8. Characterization of Bio Lubricants

Based on the test results, the characteristics of the bio lubricant can be seen. A bio lubricant has several properties, including Kinematic viscosity, Viscosity index, and Total base number shown in Table 6.

Table 6: Displays the typical values of a few bio-lubricants (Zaman et al., 2022).

Properties	Soyabean Oil	Sunflower Oil	Rapeseed Oil	Castor Oil	Palm Oil
Kinematic viscosity 40°C(cSt)	32.93	40.05	45.6	220.6	40.24
Kinematic viscosity @100°C(cSt)	8.08	8.65	10.07	19.72	7.89
Viscosity index	219	206.	2016	220	110
Total base number (mgKOHg-1)	0.61	-	1.4	1.4	-
Pour point (°C) & Flash point (°C)	-9 240	-12 252	-12 240	-27 250	-21 220

CONCLUSION

This paper provides an overview of current knowledge on the lubrication mechanism of nanoparticle additives, performance parameters, and tribological behavior of lubricants with Nano additives. The majority of studies have reported improved lubricant performance with the addition of nanoparticles as additives. The dispersion stability of nanoparticles is a crucial factor for optimal lubricant performance, and experimental testing can help identify the ideal concentration ratio. The addition of nanoparticles can lead to the formation of films, tribofilms, thin layers, Nanosheets, and nameplates, resulting in reduced wear and friction coefficient values.

Nanoparticle-based friction treatments can also smooth out the surface of the friction pair, resulting in less shear stress and a reduction in wear and surface roughness. This study focuses on the use of bio-lubrication oils in vehicle engines and their impact on engine performance. The addition of nanoparticles to sandbox oil as a bio lubricant has the potential to enhance its tribological properties, with copper (II) oxide nanoparticles showing promise in improving tribological qualities. Overall, the study suggests that bio-lubricants have the potential to be a substitute for conventional lubricants, with enhanced tribological performance and less negative environmental impact.

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