FRICTION, WEAR AND LUBRICATION

MEMM 1343

Chemistry, production, and technological potential of biobased lubricants

Fossil fuels play a major role in fulfilling global energy demands for centuries. However, fossil fuels are depleting over the years due to the increasing energy demands resulting from industrialization and population growth. The ever-increasing consumption of these energy sources is alarming since the depletion of fossil fuels will have a serious impact on people's lives.

The demand for mineral oils will likely surpass its supply by 2015, however, this is constrained by strong recession pressures caused by the decrease in demand and thus, the demand for mineral oils is parallel with its supply.

The depletion of fossil fuels and the growing concern on the detrimental impact of fossil fuels on the environment has led to the critical need to explore alternative sources of energy.

The use of vegetable oils for lubrication purposes has been in practice for many years. However, this idea was scrapped due to the discovery of petroleum and the availability of low-cost oils.

To date, fossil fuel-based crude oils are used as the raw materials to produce fuels and lubricants. However, there is new interest in the use of lubricants from vegetable oils due to growing concern over the environmental impact of fossil fuels. Bio-based lubricants have been produced and marketed by a number of companies.

Bio-based lubricants are promising alternatives for mineral oils since they retain the technical specifications of conventional lubricants. Bio-based lubricants are biodegradable lubricants, derived from edible and non-edible vegetable oils and they have high lubricity, viscosity index and flash point.

However, bio-based lubricants also have several disadvantages. For instance, these lubricants have poor cold flow properties and oxidation stability, which will lead to polymerization and degradation.

This problem can be overcome by chemical modifications of vegetable oils in order to eliminate the beta-hydrogen atoms in glycerol.

The main factors which influence the tribological properties of vegetable oils are the carbon chain length, the type of fatty acids as well as polarity.

Historical development of bio-based lubricants

Animal fats and vegetable oils have lubricated every type of machine and moving parts for thousands of years. Ancient Egyptians used greases based on calcium soaps of olive oil as wheel axis lubricants in carriages. By the of the 18th century, the Industrial Revolution began and this pushed the demand for natural oils such as sperm oil, lard oil, olive oil, rapeseed oil and ground-nut oil.

More oil was required for lubrication of machinery as the Industrial Revolution started to bloom. Less than 100 years later, in the mid-19th century, the exploitation of petroleum-based lubricants started due its lower price and capabilities and thus, animal and vegetable oils could not compete with petroleum.

The beginning of the petroleum industry during this period is important to support the industrial expansion in the 19th and 20th centuries. However, due to a growing awareness regarding the effect of petroleum-based oil on the environment, several companies have been involved in the development of bio-based lubricants in the past few years.

For example, Shell and British Petroleum collaborated with French National Railways in the development of biodegradable railway track grease. Mobil Chemicals implemented a clean lubricant production line as part of the Agriculture for Chemicals and Energy (AGRICE) programme.

In Malaysia, Malaysian Palm Oil Board (MPOB) plays an important role to develop palm oil as industrial lubricant.

In general, bio-based lubricants can be defined as products with low toxicity and excellent biodegradability. Bio-based lubricants are not necessarily derived from vegetable based oils but they are usually derived from animal based oils.

Thus, it can be classed as renewable because plants can be regrown. Bio-based lubricants may also be synthetic esters, which are partially derived from various natural sources such as solid fats, waste materials and tallow.

The Unites States Secretary of Agriculture defined the term "bio-based product" as "a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant and animal) or forestry materials".

Bio-based lubricants can be categorized as sustainable because it is derived from renewable raw materials. The sustainability of the application of raw materials can be classified into two aspects; the origin of the resources and the pollution caused by it.

In the case of bio-based products (oleochemicals), it is discharged via several pathways at the end of their lifespan and the organic chemicals are disintegrated into carbon dioxide and water.

The carbon cycle of oleochemicals is closed because the amount of carbon dioxide released equals to the carbon dioxide that was originally taken up by the plants from the atmosphere. Therefore, it has zero effect with regard to the carbon dioxide balance of the atmosphere.

On the other hand, the mineral oil-based products increase the atmospheric carbon dioxide and therefore lead to global warming, which can be referred to as indirect environment pollution.

The main component of vegetable oils is triacylglycerols (98%) as well as a variety of fatty acid molecules attached to a single glycerol structure.

The minor components of vegetable oils are diglycerols (0.5%), free fatty acids (0.1%), sterols (0.3%), and tocopherols (0.1%).

The triglyceride structure consists of three hydroxyl groups esterified with carboxyl groups of fatty acids, as shown in Figure 1.

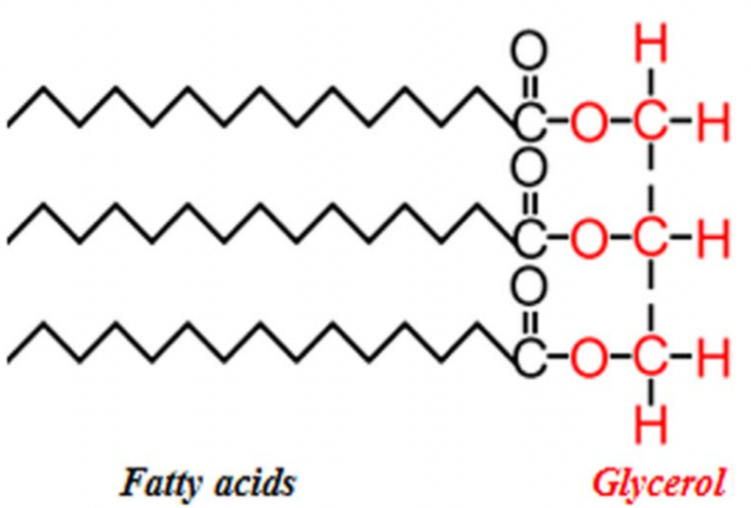

Figure 1: Triglyceride structure.

The triglyceride structure gives these esters a high viscosity (and thus, high viscosity index) because of their high molecular weight. The triglyceride structure is also responsible for the structural stability of the esters over a reasonable operating temperature range.

The carbon chain of a fully saturated fatty acid is almost straight.

The carbon atoms share a double instead of a single bond when the hydrogen atoms are missing from the adjacent carbon atoms. This type of fatty acid is known as unsaturated fatty acid.

In contrast, the fatty acid is known as polyunsaturated fatty acid if the double bonds occur at multiple sites.

In general, fatty acids can be classified as saturated, mono-, di- and tri-unsaturated fatty acids. Excessive amounts of long-chain saturated long chain fatty acids lead to poor low-temperature behaviour whereas excessive amounts of certain polyunsaturated fatty acids lead to unfavourable oxidation behaviour as well as resignation at high temperatures.

The flash point of the lubricant is also higher due to the very low vapour pressure and volatility. This reduces potential fire hazards of the lubricant during use. It should be noted that even monounsaturated fatty acids with long chains will deteriorate the low-temperature behaviour of the lubricant.

Even though bio-based lubricants have poor oxidation stability compared to mineral oils and these lubricants are unable to withstand reservoir temperatures more than 80°C, these issues can be addressed by the use of antioxidants.

Bio-based lubricants are also less hydrolytically stable such that these lubricants create more foam and they reduce filterability compared to mineral oils. Thus, vegetable oil products are ideally suited for applications such as lubrication of sawmill blades or chain drives, whereby the lubricant is used on a single use basis. These lubricants are also more suitable for applications where low toxicity is required.

Vegetable oils can be generally classified as edible and inedible oils, as shown in Table 1. The vegetable oils used to produce bio-based lubricants may differ from one country to another due to climatic and geographical factors.

For example, rapeseed and sunflower oils are often used in Europe whereas soybean oils are mainly used in the US. In contrast, the main feedstocks of bio-based lubricants in Asia are palm and coconut oils.

Nowadays, it is more desirable to use inedible oils to produce bio-based lubricants since these oils are derived from waste crops and this eliminates the use of food crops for lubricant production. However, the use of inedible oils for bio-based lubricants is only favourable if there is sufficient land area for both edible and inedible crops.

In addition, economic factors may also be a reason which will lead farmers to switch from producing food crops to biofuel crops even if the latter is inedible. This scenario will create an unbalanced market since food prices will increase if food production decreases.

Table 1: Type of vegetable oils used to produce bio-based lubricant, their requirements and their producers.

Vegetable oils	Requirements	Major producers
Sunflower oil (Edible)	Sunflowers need full sun and highly tolerant to drought. They grow best in fertile, moist well-drained soils with heavy mulch.	Russia, Europe, Ukraine, Argentina
Rapeseed oil (Edible)	Rapeseed grows best in mild maritime climates. The growth of rapeseed is most vigorous in temperatures from 10 to 30 °C. However, the optimum temperature is 20 °C.	European Union, Canada, United States, Australia, China, India
Soybean oil (Edible)	Cultivation is successful in climates with hot summers as well as optimum growing conditions. The recommended mean temperature is within a range of 20–30 °C. Temperatures less than 20 °C and more than 40 °C will retard growth significantly.	United States, Argentina, Brazil, China, India
Palm oil and palm kernel oil (Edible)	Oil palm is a tropical palm tree and therefore, it can be cultivated easily in Malaysia. Oil palm in Malaysia originates from West Africa where it typically grows in the wild but it is later cultivated as an agricultural crop.	Malaysia, Indonesia
Coconut oil (Edible)	This plant thrives well on sandy soils and it is highly tolerant of salinity. It colonizes shorelines of the tropical regions since it prefers areas with abundant sunlight and regular rainfall (1500–2500 mm annually). This plant achieves good growth when the temperature is within a range of 28–37 °C.	Indonesia, India, The Philippines, Sri Lanka
Canola oil (Edible)	This plant is well-adapted to the cool extremes of temperate zones and it grows well on medium-textured, fertile and well-drained soils. Canola requires about 406–460 mm of water during its growing season.	European Union, Canada, China, India, Australia
Olive oil (Edible)	The olive plant prefers hot weather and sunny areas without any shade. This plant tolerates drought conditions well due to its firm and extensive root system.	Spain, Italy, Greece
Jatropha oil (Non-Edible)	*Jatropha* is a drought-resistant shrub or tree with low fertility and moisture demands. This is able to grow in a number of climatic zones where the amount of rainfall ranges from 250 to 1200 mm.	Mexico, Nicaragua, Thailand, India, Indonesia, Nepal, Malaysia,
Callophyllum inophyllum oil (Non-edible	*Callophyllum inophyllum* is widely cultivated in all tropical regions of the world. This plants requires annual rainfall within a range of 750–5000 mm in order to grow.	India, Hawaii, Australia, Malaysia, Indonesia, The Philippines
Neem oil (Non-edible)	Neem is an evergreen tree that is endemic to the Indian subcontinent. This tree can be found in various countries within Asia, Africa as well as Central America and South America. It grows in tropical and sub-tropical regions	India, Burma, Bangladesh, Malaysia, Sri Lanka, Cuba
Karanja oil (Non-edible)	Karanja grows in the Indian subcontinent and has been introduced successfully to humid, tropical regions of the world. This plant grows quickly and it is drought-resistant with high tolerance to salinity.	Northern Australia, Fiji, India
Castor oil (Edible)	This plant is a tropical crop and the seed is sown in hot weather. Consistent rainfall is required for good growth. The soil should be well-drained, deep and moderately fertile.	Cuba, Brazil, China, India, Italia, France

Sun flower oil

Sunflowers grow in fertile, moist, well-drained soils containing heavy mulch. Sunflower oil is extracted from sunflower seeds and this oil is commonly used for cooking as well as to produce margarine and biodiesel. Sunflower oil is cheaper compared to olive oil. Sunflower varieties vary in their fatty acid content, some "high oleic" types contain a higher level of monounsaturated fatty acids in their oil compared to olive oil. High oleic sunflower oils has many qualities that render it suitable for lubricants such as good oxidation stability and lubricity. One study showed that high oleic sunflower oil (HOSO) can be used to substitute for mineral oils in textile and tannery applications without technical problems or modification of facilities. A properly formulated sunflower is comparable to that of mineral oil and it is therefore a promising alternative lubricant for chain saws.

Rapeseed oil

Rapeseed is a bright yellow flowering member of the mustard family and it contains high levels of erucic acid (~ 45%). Rapeseed oil was first produced in the 19th century as a base for steam engine lubricant. Rapeseed contains four major components (i.e. oil, water, protein and fibre) but it also contains several minor constituents for lubricating applications such as free fatty acids, phosphatides (gum), enzymes (particularly myrosinase) and glucosinolate. Rapeseed oil is not suitable for human and animal consumption because it has a bitter taste which is due to the high levels of glucosinolates. However, there are new varieties of rapeseed with lower glucosinolate content and therefore, they are more edible.

Canola oil

Canola is a genetically modified variant of rapeseed which has gained prominence commercially due to its nutritional quality (lowerucic acid and low-glucosinolate rapeseed oil). Both canola and rapeseed oils are primarily composed of unsaturated fats, there is a significant difference in the composition of these oils, whereby the amount of erucic acid in canola oil is nearly negligible (< 1%).

Soybean oil

Soybean is a species of legumes which is native to East Asia. It is widely cultivated for its edible beans, which have numerous uses. The cultivation of soybean is successful during hot summers in which the optimum mean temperature is within a range of 20°C to 30°C. Soybean can be grown on a wide range of soils but the optimum growth is achieved on moist, muddy soils with good organic content. Soybean oil has been successfully used to produce dielectric liquids for transformers, since it increases the fire point and service life of the transformer by extending the life of the insulating paper. Soybean-based oil has also been used as the hydraulic fluid for the lift of the famous Statue of Liberty in New York Harbour.

Palm oil

Palm oil is an edible oil which is derived from the mesocarp of the oil palm fruit. Oil palm thrives in hot, humid tropical regions with an annual rainfall within a range of 1500 mm – 2000 mm. Oil palm will grow well provided that there is no more than three months of drought. The optimum temperature range is 26°C – 32°C, and 5 – 7 hour of direct sunlight per day is beneficial. One hectare of oil palm is sufficient to produce almost 10 times as much oil compared to other vegetable oil. Hence, palm oil has great potential to fulfil the demand for vegetable oil-based lubricants. A large number of experiments have been carried out on the use of palm oil as an additive in engines as well as a lubricant for cold forward extrusion and minimum quantity lubrication (MQL).

Coconut oil

It is rare to find coconut trees in dry regions because these trees are unable to grow without frequent irrigation. These trees are mostly found in tropical regions. The fruits of coconut trees are light, buoyant and highly water-resistant and these fruits have evolved to disperse at significant distances via sea currents. Coconut oil is rich in saturated fatty acids (91%) and therefore, it does not oxidize easily. Coconut oil has been widely used as a lubricant in rickshaws and scooters in Southern India. This oil has been shown to improve vehicle mileage, engine pick up and operations. In addition, coconut oil produces less smoke when it is burned.

Jatropha oil

Jatropha curcas is a drought-resistant shrub or tree which belongs to the family Euphorbiaceae and it is widely cultivated in Central America and South America, as well as Southeast Asia, India and Africa. Even though, Jatropha oil is one of the common feedstocks for biodiesel production, its function as a lubricant is not really known. Jatropha oil has potential for lubricant production due to its high fatty acid content (61% – 64%). The production techniques and optimum parameters needed to produce high yields of lubricant from Jatropha oil are still investigated to date.

Castor oil

Ricinus communis (castor) is a fast-growing, suckering perennial shrub which can reach the size of a small tree (around 12 m) and it is not a cold-hardy plant. This plant also known as castor beans. The seeds contain around 40% – 60% of oil that is rich in triglycerides, particularly ricinolein. Castor oil has better low-temperature viscosity and high temperature lubrication properties compared to most vegetable oils. Therefore, castor oil is desirable to be used as a lubricant in jet, diesel and race car engines. Castor oil, with its 80% ricinoleic acid content, has unique characteristics and it is the only source of C18:1OH. This gives the oil a unique combination of physical properties such as relatively high viscosity and specific gravity as well as solubility in alcohol in any proportions. However, castor oil has limited solubility in aliphatic petroleum solvents.

Calophyllum inophyllum L

Calophyllum inophyllum L. is commonly known as polanga or honne, and this plant can be found largely in abundance along the seashores of The Philippines. This plant is native to tropical Asia. This medium to large-sized tree has a height within a range of 8 m – 20 m (25ft – 65 ft) with a broad spreading crown of irregular branches. Calophyllum inophyllum L. is an evergreen sub-maritime tree which grows best on deep soils or exposed sea sands. The seeds of Calophyllum inophyllum L. contain a high percentage of oil within a range of 65% – 75%. Calophyllum inophyllum oil is not only used for medicinal purposes and as hair grease, but this oil is also used to produce biodiesel with physicochemical properties which fulfil ASTM D 6751 and EN 14214 standards.

Karanja oil

Pongamia pinnata L. is medium-sized evergreen tree which belongs to the Millettieae family. This plant takes 4 to 7 years to reach maturity and it is regenerated through direct sowing, transplanting and root cutting. Karanja oil has been used for traditional medicines, timber, pesticides and fuel in India as well as neighbouring regions. The seeds are rich in oleic acid with an oil content within a range of 30–40 wt%.

Physicochemical properties of bio-based lubricants

It is imperative to gain an understanding on the physicochemical properties of bio-based lubricants. The properties of vegetable oils are closely associated with the structural parameters of the fluid particles.

In general, vegetable oils possess low toxicity, high biodegradability, high lubricity, high flash point and good viscosity index, as well as low friction and wear characteristics compared to mineral oils. Even though vegetable oils have many advantages compared to mineral oils.

They also have a few disadvantages such as low pour point and poor oxidation stability. The effect of unsaturation, chain length and branching on the viscosity index, low-temperature properties and oxidation stability of vegetable oils are shown in Table 2.

Table 2: Effect of chain length, chain branching and degree of unsaturation on the viscosity index, low-temperature properties and oxidation stability of vegetable oils.

	Viscosity index	Kinematic viscosity	Low temperature properties	Oxidation stability
Increase of chain length	Positive	Positive	–	–
Increase of chain branching	Negative	Viscosity	Positive	Positive
Higher degree of unsaturation	Positive	Negative	Positive	Negative

Viscosity

Viscosity is a measure of the substance's resistance to flow and it corresponds to the informal concept of "thickness" or "fluidity". High viscosity means that the substance has high resistance to flow and low viscosity means low resistance to flow and vice versa.

Viscosity plays a vital role in the lubricant's ability to reduce friction and wear. A very high viscosity will increase the oil temperature and drag whereas a very low viscosity will increase the metal-to-metal contact friction between the moving parts. The carbon chain length is one of the factors which affects the viscosity of the lubricant. It is believed that the degree of random intermolecular interactions increases when the length of the fatty acid chain increases, which increases the viscosity.

However, in chemically modified vegetable oils, the introduction of branching results in a more compact molecular configuration.

The degree of unsaturation is also another factor which affects the viscosity of the lubricant. One double bond will increase the viscosity, but two or more double bonds will decrease the viscosity of the lubricant. Epoxidized soybean oil has high viscosity compared with commercial lubricants and therefore, it is suitable for high-temperature applications.

Viscosity index

Viscosity index (VI) is a measure of the change in the substance's viscosity with a change in temperature.

A high VI indicates a small variation in the viscosity with respect to a change in temperature and vice versa. A high VI is an essential characteristic of good lubricant since it is an indication that the lubricant can be used over a wide range of temperatures by maintaining the thickness of the oil film. In contrast, a low VI indicates that the viscosity of the lubricant is less stable at high temperatures and hence, the film thickness of the oil tends to be thinner and becomes less viscous at elevated temperatures.

Vegetable oil-based lubricants generally have higher VI than mineral oils. For instance, it was shown that castor oil has good VI with very high viscosity compared to super-refined mineral oil, which can be attributed to the hydrogen bond of the hydroxyl monounsaturated triglycerides.

In addition, it was shown that a bio-based lubricant produced from canola biodiesel has a high VI of 204, which is due to the polyunsaturated fatty acid chains of the canola biodiesel.

Since vegetable oils contain triglycerides that sustain intermolecular interactions when temperature is increased, the VI of palm oil-based lubricant is higher than that for mineral oils.

Flash point

The flash point refers to the lowest temperature at which lubricant must be heated before it vaporizes. Lubricants will ignite (not burn) when they are mixed with air.

This property is useful to determine the volatility of a lubricant. Lubricants should have high flash point to ensure safe operation and minimum volatilization at the maximum operating temperature.

Low temperature properties of bio-based lubricants

Low-temperature performance is the main constraint when it comes to using vegetable oils as lubricants. Even though vegetable oils have strong intermolecular interactions which provide a durable lubricating film, these interactions also result in poor low-temperature properties.

The pour point is the most vital low-temperature property for lubricants since it is the lowest temperature at which the lubricant becomes semi-solid and loses its flow characteristics. In general, lubricants with low pour points are desirable since these lubricants provide good lubrication at extremely low temperatures as well as during cold starts.

If the pour point is not sufficiently low, the lack of lubricant flow will lead to excessive friction, wear and heat in the system, which will lead to equipment damage or failure. The risk of equipment failure is significantly greater if the lubricant does not flow properly during start-up.

Several studies have been carried out over the years to determine the low-temperature properties of vegetable oils and these studies revealed that most vegetable oils will become cloudy as well as precipitate and solidify at −10°C upon long-term exposure to cold temperatures, resulting in poor flow and pumpability.

This is due to the fact that vegetable oils tend to form macro-crystalline structures at low temperatures through uniform stacking of the "bend" triglyceride backbone. These structures restrict the ease of flow of the system through the loss of kinetic energy of the individual molecules during self-stacking. The pour point of vegetable oils decreases with an increase in the number of double bonds in the molecules.

Vegetable oils that have a high percentage of unsaturated fatty acid chains will have lower pour points because the fatty acid chains in a bent configuration prevents close packing of the molecules during cooling. It was shown in that rapeseed oil has lower pour point (−21°C) compared to olive oil (−15°C) which is clearly due to the high unsaturated fatty acid content of rapeseed oil.

However, the introduction of branched or aromatic hydrocarbon molecules with high molecular weight can generally reduce the pour point of vegetable oils by preventing of molecule packing during cooling.

In general, a high degree of unsaturation is favourable for low-temperature properties of the lubricant but it is unfavourable for the oxidation stability.

Oxidation stability

Oxidation is a chemical reaction that occurs when the lubricant combines with oxygen. Oxidation stability indicates the ability of the lubricant to withstand oxidation. The rate of oxidation of lubricants is influenced by several factors such as temperature, pressure as well as the presence of water and contaminants.

In addition, the service life of lubricants decreases with an increase in temperature. High oxidation stability is an important criterion for lubricants since a low oxidation stability will cause the lubricant to oxidize rapidly if it is untreated.

Consequently, the lubricant thickens and polymerizes into a plastic-like consistency. The oxidation stability of vegetable oils is generally lower than that for synthetic esters because of higher degree of unsaturation in vegetable oils.

Oxidation is undesirable since it results in polymerization and degradation of the lubricant. Polymerization of vegetable oil increases the viscosity and decreases the functionality of the lubricant.

Degradation results in breakdown of the product, which is undesirable since the lubricant becomes volatile and corrosive, and its structure and properties weaken. The oxidation stability is determined based on the dominant fatty acids in the vegetable oils.

The main factor that affects the oxidation of vegetable oils is the presence of unsaturated fatty acids particularly polyunsaturated compounds such as linoleic and linolenic acids. The double bonds in the alkenyl chains easily react with oxygen to form free radicals which then degrade to form peroxides and acids. This leads to polymerization and fragmentation.

Therefore, oxidation is dependent on the degree of unsaturation of the fatty acid chains. Linolenic, linoleic and oleic acids are the main fatty acids with double bonds and the oxygen absorption rate is 800:100:1. Thus, a higher degree of unsaturation leads to higher rate of oxidation.

Rapeseed oil, which is rich in polyunsaturated fatty acids, is less resistant to the action of oxygen as well as high temperature. It has been shown that the kinematic viscosity of Jatropha oil increases drastically due to its poor oxidation stability. The presence of the β-CH group removes easily from the molecular structure and this weakens the middle carbon-oxygen bond. This results in the formation of carboxylic acid which will degrade the lubricant.

Chemical modification of vegetable oils

The low-temperature fluidity and chemical stability (oxidation and thermal stabilities) of vegetable oils are due to their fatty-acid structure, as shown in Figure 2. The unsaturated structural "double bond" elements in the fatty acid component and the β-CH group of the alcohol components results in oxidation and thermal instability since the double bonds in the alkenyl chains are reactive and readily react with oxygen in the air.

The β-hydrogen atom in glycerol removes easily from the molecular structure, cleaving the esters into acid and olefin.

However, it shall be noted that some unsaturation is necessary in order to maintain the low-temperature properties of the lubricant.

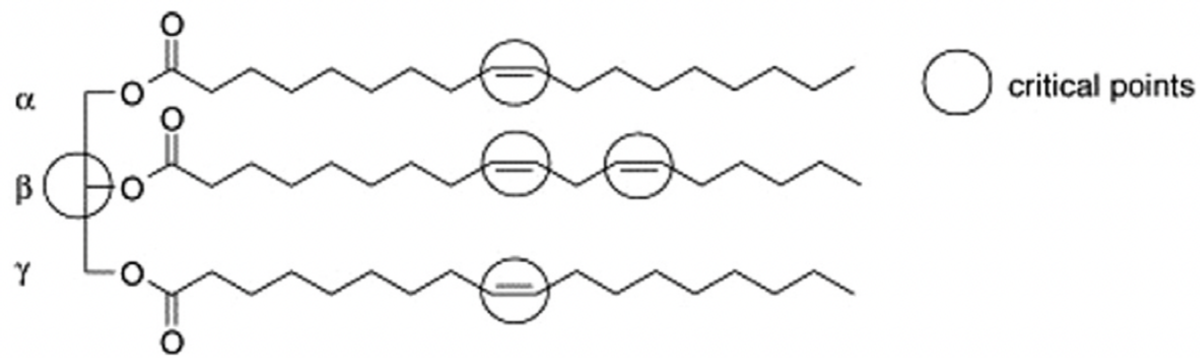

Figure 2: Plant oil-glycerine ester which consists of different fatty acids. The critical points are β -CH group and unsaturated fatty acid residues.

Attempts to improve the low-temperature properties and oxidation stability of vegetable oils include transesterification of trimethylolpropane and methyl ester from vegetable sources, selective hydrogenation of polyunsaturated C=C bonds of fatty acid chains and conversion of C=C bonds into oxirane rings via epoxidation.

There are a number of advantages of modifying vegetable oils chemically which include stability of the lubricant over a wide temperature range as well as excellent wear and friction characteristics.

Transesterification

Transesterification is a reaction whereby the triglyceride molecule reacts with three moles of methanol in the presence of an acid or base catalyst, resulting in glycerol and mixtures of fatty acid methyl esters, as shown in Figure 3.

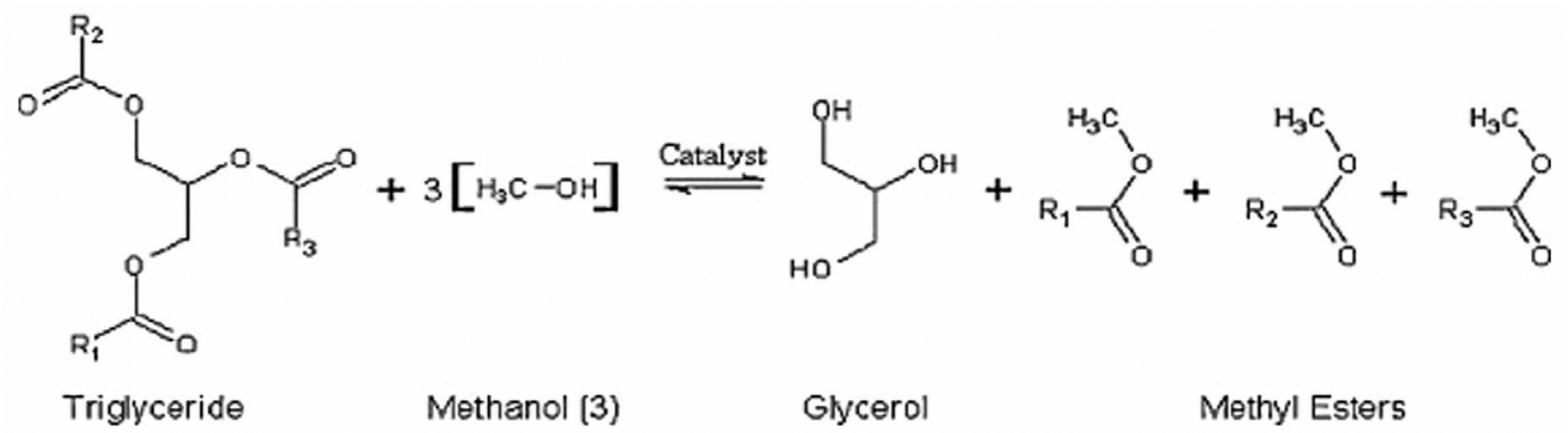

Figure 3: Chemical reaction of the transesterification process.

The presence of hydrogen atoms in position β relative to the hydroxyl group in the glycerol molecule can be solved using transesterification. In this process, glycerol is replaced with polyol which does not contain β-hydrogen atoms, namely neopentyl glycol (NPG), trimethylolpropane (TMP), or pentaerythritol (PE).

This enhances the thermal stability of the lubricant at high temperatures by preventing self-polymerization to form free fatty acids. Polyol esters usually contain more ester groups compared to others and the added polarity further reduces volatility and enhances lubricity of the lubricant. Gryglewicz discovered that polyol esters have better thermal stability compared to other vegetable oils.

Transesterification has been carried out on various vegetable oils including soybean oil, canola oil, olive oil, Jatropha oil, palm oil and palm kernel oil and rapeseed oil in order to produce fatty acid methyl esters (FAME).

Point to ponder:
Different between transesterification and esterification.

Esterification is any reaction (typically between an fatty acid and an alcohol) that results in the production of an ester, while transesterification is the reaction of an ester with an alcohol in order to replace the alkoxy group; it is used in the synthesis of polyesters and in the production of biodiesel.

Hydrogenation

Hydrogenation is a process in which hydrogen is added to the C=C bonds in the triglycerides of an oil molecule. The hydrogenation process of vegetable oils involves three simultaneous chemical reactions:
(1) saturation of double bonds
(2) geometric (cis-trans) isomerization and
(3) positional isomerization.

The quality and physical properties of hydrogenated oils are greatly influenced by the number of double bonds present and the cis-trans-isomers of fatty acids.

In industrial processes, hydrogenation is conducted in the presence of a support or Raney Ni catalyst within a temperature range of 150°C – 225°C and pressure range of 69 kPa – 413 kPa. However, the toxicity of the Ni traces remaining in the oil raises concerns and this leads to the development of a new catalyst, i.e. palladium (Pd).

The use of Pd catalyst is attractive due to the higher catalytic activity of Pd compared to Ni. Moreover, Pd catalyst can be used in softer conditions. The selectivity of a catalyst refers to the ability of the catalyst to favourably reduce linolenic acid before linoleic acid and oleic acid.

Selectivity also refers to the ability of a catalyst to reduce by hydrogenation only to form monoenes, without reducing to full saturation. This is called partial hydrogenation, which is important to prevent deterioration of the low-temperature properties of the lubricant such as the pour point.

Epoxidation

Epoxidized vegetable oils are produced by the reaction of double bonds by peroxy acids and removal of the C=C bonds.

Conventional epoxidation methods include acid ion exchange resins, enzymes and metal catalyst. In general, alkene is reacted with peroxy acid in order to synthesis epoxide groups or oxirane rings, as shown in Figure 4.

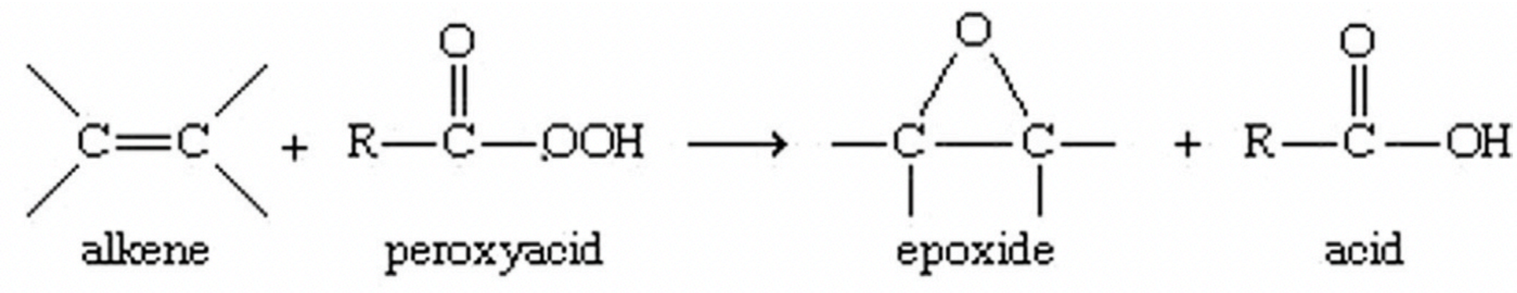

Figure 4: Reaction of double bonds with peroxy acids

Epoxidized rapeseed oil using the conventional epoxidation method (i.e. in situ peracetic acid generation), whereby carboxylic acid is reacted with concentrated hydrogen peroxide. It is found that the oxidation stability of the epoxidized rapeseed oil enhances significantly in the presence of antioxidants. The epoxidized rapeseed oil has better friction-reducing characteristics and extreme pressure capabilities compared to the rapeseed oil. This is due to the formation of a polyester or polyether material film by the three-member ring of oxirane created by tribo-polymerization.

Epoxidation has received much attention because a wide range of reactions can be performed in moderate conditions by modification of the C=C bonds to the oxirane ring. The epoxidation reaction is followed by ring-opening of the epoxidized oil as well as the esterification process.

Hwang and Erhan used sulphuric acid as the catalyst during the ring-opening reaction of epoxidized soybean oil with various linear and branched alcohols. This was followed by esterification of the resulting hydroxyl group with acid anhydride. The results showed that there is improvement in the oxidation stability and the pour point is reduced significantly by the introduction of branching.

A one step process was used to prepare a bio-based lubricant, which involves simultaneous epoxy ring-opening and esterification of epoxidized canola oil in the presence of acetic anhydride using a novel sulphated TiSBA-15 catalyst.

The results revealed that the epoxidized canola oil has good tribological properties and therefore, it is a promising bio-based lubricant.

Comparison of technologies for various lubrication applications

Despite the lubrication properties of natural oils, direct use of vegetable oils is not suitable for prolonged use in IC engines because of their low thermal and oxidation stability. Research has shown that chemically modified vegetable oils-based biolubricants exhibit excellent oxidation stability and low-temperature flow properties.

Such chemically functionalized esters are produced from relatively pure raw materials to produce predetermined molecular structures formulated for high performance lubrication. Synthetic esters have improved thermo-oxidative stability, high viscosity indices, and advantage of absence of the undesirable impurities found in conventional petroleum based oils.

Similar to neat natural oils, synthetic esters maintain an affinity for metal surfaces due to their high degree of polarity which affords them the ability to establish monolayers that minimize the surface contact and enhance the tribological properties. Due to their sensitivity towards hydrolysis and thermal degradation, thermal properties of esters have been improved by replacing the glycerol with other polyols such as neopentylglycol (NPG), pentaerythritol (PE), trimethylolpropane (TMP), trimethylolhexane (TMH), and trimethyoloethane (TME).

Esters such as the NPG were originally developed for the lubrication of aircraft jet engines whereas PE esters have found use in gas turbines.

TMP esters have attained considerable importance in applications which include engine lubricants, gear oils, hydraulic oils, compressor oils, pump and turbine oils.

For engine use in automotive and marine engine lubrication, TMP esters have found widespread use. High viscosity index (VI) with moderate thermo-oxidative stability make TMP esters attractive lubricants for reciprocating engine applications.

Lubrication characteristics of bio-based lubricant

Examining the effects of tribological system parameters on the chemistry of the lubricant can help one to identify the lubrication requirements for a given application. It is known that vegetable oils provide good lubrication through their ester functionality.

The polar head of the fatty acid chain attaches to the metal surface by a chemical process which results in the formation of a monolayer film. The non-polar end of the fatty acid chain sticks away from the metal surface, which reduces the coefficient of friction.

The performances of vegetable oils commonly affected by the fatty acid unsaturation, chain length and branching on the lubrication characteristics of vegetable oils. Most studies have shown that even though the crude vegetable oils improve the coefficient of friction, the surface wear increases.

The triglyceride structure provides desirable qualities for boundary lubrication because of their long polar fatty acid chains. This results in a high-strength lubricating film. The film interacts strongly with the metal surface, reducing friction and wear.

Carbon chain length

In general, studies have shown that the boundary friction coefficient decreases with an increase in the carbon chain length. A long hydrocarbon chain of fatty acids provides a great molecular barrier.

The increase in the adsorbed film thickness is contributed by the length of the fatty acid chains, which increases the protected surface area. The friction transition temperature increases for fatty acids with an increase in molecular weight and the minimum chain length for effective lubrication is $n = 9$ (pelargonic acid).

However, it has been shown that short fatty acid chains with $n \leq 8$ does not improve lubrication.

For instance, it was shown that the viscosity and flash point of polyol ester decrease by the introduction of short chain fatty acids into the synthesis of esters. The lubricity can also be improved by decreasing the degree of branching (to be more linear) in the base oil.

The steady-state wear rate of TMP and PE linear chain acids decreases as the chain length increases. In contrast, the steady-state wear rate is higher for branched-chain acids compared to linear-chain acids having the same carbon number. The polyol ester with a longer linear structure shows better scuffing resistance.

Types of fatty acids

The presence of fatty acid chains in vegetable oil-based esters facilitates the formation of a monolayer film on the sliding surfaces.

The boundary lubrication mechanism by the vegetable oil may have some impact on the effectiveness of various fatty acids. It is possible that the stearic acid molecules will align themselves as a straight chain since they do not contain double bonds. The stearic acid is closely packed on the surface, which contributes towards a strong protective layer.

However, a couple of studies have shown that increasing the degree of unsaturation has a negative effect on the performance of fatty acids as boundary-wear reducers.

Unsaturated acids, in the "cis" form, unable to establish straight chains and therefore, it is more difficult for these fatty acids to pack themselves close together, resulting in a weak protective layer.

Polarity

Polarity means that a molecule is asymmetrical with a different chemical affinity at either end of the molecule. Polarity is particularly important for lubrication.

It is believed that the existence of a polar structure, which disperses the non-polar molecules or base lubricant, provides a great boundary layer. Fatty acid has a carboxyl group at one end (i.e. COOH), which is strongly attached to a metallic surface. The other end is an alkyl group (i.e. CH3) which has no affinity for almost all of its molecules.

It shall be noted that different molecular species have different polarities and there is a hierarchy for its adsorption onto a surface.

The polar functional groups in the molecule create physical contact and interact chemically with a metal surface, with the non-polar end forming a molecular layer or barrier that separates the rubbing surfaces and thereby preventing direct contact.

For this reason, vegetable oils have good boundary lubrication properties. The high degree of polarity in chemically modified vegetable oils is due to the ester linkage in the molecules, and therefore, these oils are more effective than mineral oils.

The wear protection is improved by increasing the polar functionality of the vegetable oil structure, which results in stronger adsorption on the metal surface as well as greater lateral interaction between the ester chains.

Vegetable oils have high solubilizing power for polar contaminants and additive molecules. However, this causes competition between the additive molecules and other molecules.

The presence of additives may interfere with the ability of the ester to attach to the metal surface. Such interactions can lead to synergistic and antagonistic effects.

Since most of the additives contain oxygen and nitrogen (each having its own polarity), these additives will compete with the surface-active compounds. Choosing a suitable additive will have a positive effect on the lubricity of the lubricants. However, an incompatible boundary lubricity agent sticking will significantly reduce lubricity.

Additives used in bio-based lubricants

The limitations of vegetable oils such as poor thermo-oxidative stability and cold flow behaviour may also be enhanced by the use of additives.

The manufacturers of various vegetable oils can use the same base stock for each formulation and choose different additives in order to fulfil the requirements of a specific application. Additives may constitute up to 5% (by weight) for some oils.

The presence of additives help improves the properties of lubricants and bio-based lubricants in terms of corrosion inhibition as well as friction and wear characteristics.

In general, esters with biodegradable additives are more superior compared to pure oils or vegetable oil blends in terms of its wear resistance.

Antioxidants

Antioxidants are additives that are used to delay or prevent the oxidation process by slowing down the lubricant from oxidative degradation while ensuring that the lubricant fulfils industrial requirements.

These additives interfere with the autoxidation process in many ways according to their structure and mechanism. Most of these additives act as primary antioxidants (chain-breaking radical scavengers) or secondary antioxidants (oxygen scavengers and peroxide decomposers) or through a combination of the functionalities of these antioxidants.

The chain breaking antioxidants react with the radicals to form stable compounds and prevent propagation of the oxidation reaction. Commonly used chain-breaking antioxidants include butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), mono-tert-butyl-hydroquinone (TBHQ), propyl gallate (PG) and the naturally occurring tocopherol (TCP).

Secondary antioxidant are essentially oxygen scavengers. The main difference between chain breaking radical scavengers and oxygen scavengers is that the latter does not convert free radicals into stable molecules.

Ascorbyl palmitate (AP) is an example of an antioxidant showing this type of mechanism. Several studies have reported the application of antioxidants in vegetable oils in order to improve their oxidation stability. It was shown that zinc diamyl dithiocarbamate (ZDDC) has the best antioxidant activity when it is added into soybean oil, followed by BHT and alkylated phenol/dithiophosphoric acid ester/diphenylamine (APDD).

ZDDC shows better performance than diphenylamine, whereby it hinders phenol in vegetable oils since it acts as both a radical scavenger and hydroperoxide decomposer. This reduces the hydroperoxides formed during the oxidation process into non-radical products such as alcohol while the oil is oxidized in a sacrificial manner, which prevents chain propagation.

α-TCP has been widely used as an antioxidant in vegetable oils with varying degrees in its performance. It was shown in one study that the use of TCP on its own as well as the combination of TCP with butylated hydroxyanisole enhances the stability of trimethylolpropane fatty acid triester (TFATE).

Since conventional additives such as zinc dialkyldithiophosphate (ZDDP) contain harmful substances such as phosphorus, chlorine and some heavy metals , eco-friendly additives such as acylated chitosan schiff base have been developed as substitutes and these additives are used as antioxidants in N-butyl palmitate/stearate bio-based lubricant.

Detergents and dispersants

Detergent and dispersant additives (DDA) are essential to improve engine efficiency, prolong the lifespan of the lubricant, as well as ensure cleanliness of the engine.

Carbonaceous sludge forms in the combustion chamber due to incomplete combustion and this sludge accumulates, forming an oil-insoluble substance. In such cases, detergents are very effective to prevent the accumulation of sludge particles.

Dispersant additives disperse the sludge particles and keep them suspended in the oil. Multi-functional additives are presently in use, acting both as detergents and dispersants. The DDAs commonly used are: metal sulfonate, ash-less sulfonate, overbased sulfonate, salicylates, alkyl phenolates, overbased carboxylate, polyisobu-tylene succinimides, glycidol modified succinimides, Mannich adducts, polyethylene glycol esters, polyol poly- (12-hydroxy stearic acid), phosphates and phosphonates.

However, vegetable oils have a high level of solvency and therefore, they act as detergents in various applications. Biodegradability and toxicity are the main properties which need to be considered when it comes to choosing detergents for vegetable oils.

Phenates and sulfonates should be avoided since they are toxic and therefore, they are not for environmentally safe. However, low amounts of phosphates and phosphate esters are acceptable for vegetable based oils since these detergent additives give desirable performance without compromising the environmental benefits of vegetable based oils.

To date, most of the dispersants are formulated to act in the presence of mineral base oil. However, several studies have been conducted to evaluate the performance of dispersants in vegetable oils.

The use of dispersant polymers in vegetable oils has been shown to improve the dispersant characteristics of the lubricant without compromising other significant properties of the lubricant. The dispersant polymers keep the amount of non-biodegradable products to a minimum level.

Viscosity modifiers / Viscosity improvers

Vegetable oils typically have a high viscosity index (VI), which indicates that these oils maintain their designed viscosity over a wider range of temperatures compared to the mineral oils.

Viscosity modifiers contain polymers which help lubricants maintain their lubrication capabilities at high temperatures. These additives increase association with the oil by increasing their molecule size so that they do not flow away from the surface.

Viscosity modifiers increase both the low-temperature and high-temperature viscosity of the oil. Formulated engine oils using blends of triglyceride base oil, synthetic ester and mineral oil.

Ethylene-vinyl acetate (EVA) copolymer was tested previously as a viscosity modifier for vegetable oils and the results showed that this additive increases the viscosity of vegetable oils, particularly those with a low viscosity such as sunflower oil, high-oleic sunflower oil and soybean oil.

The EVA copolymer increases the viscosity up to 420% with respect to the base oil at 40°C. Other commonly used polymers include polymethacrylates, styrene-diene copolymers, and styrene-ester copolymers.

Nanoparticles

It has been reported extensively in the literature that nanoparticles are great additives for lubricants and bio-based lubricants in order to reduce friction and wear. Nanoparticles are regarded as attractive candidates compared to conventional extreme pressure and anti-wear additives due to their environmental properties. The properties of bio-based lubricants are dependent on the properties of the nanoparticles such as the size, shape and concentration of the nanoparticles.

The effects TiO 2, CuO and ZnO nanoparticles on the properties of bio-based lubricants have been investigated in several studies. It was shown in one study that the coefficient of friction of a chemically modified rapeseed oil is reduced by 15.2% upon the addition of TiO_2 nanoparticles. This may be due to the fact that spherical TiO_2 act as ball bearings, which reduce contact between frictional surfaces.

In addition, the wear scar diameter (WSD) is reduced by 11% and the wear scar is observed to be smoother. In another study, the results showed that the tribological properties of coconut oil are enhanced upon the addition of CuO nanoparticles at the optimum concentration (0.34 wt %).

There is also less scuffing on the surface of the pin subjected to sliding during the pin-on-disk tribometer tests. The zinc borate ultrafine powder ($2ZnO$-$3B_2O_3$-$3.5H_2O$) shows outstanding friction reduction and anti-wear properties when it is used as a lubricant additive in sunflower oil, particularly at a concentration of 0.5% which reduces the coefficient of friction and WSD by 14 and 10%, respectively.

This is due to the formation of tribofilms resulting from tribochemical reactions on the worn surface, as well as increased hardness of the substrate. However, both ZnO and CuO do not show good anti-wear characteristics when they are used as additives in epoxidized sunflower oil and soybean oil.

This is due to the chemical nature of these vegetable oils, whereby the polar groups adhere to the surface and they have a third body behaviour, which in turn, increases friction.

Corrosion inhibitors

Corrosion inhibitors are additives that help protect metal from oxygen, water, acid, base and salt attacks.

Corrosion inhibitors act by physically adsorbing on the metal surfaces via their polar functional groups and maintaining a resilient protective film on the surface by associating with the lubricant. Several studies have been carried out over the years in order to determine the effects of corrosion inhibitors on the corrosive effect of bio-based lubricants.

One study showed that boron-containing additives increase the corrosion of steel, but these additives are less corrosive on copper. This is due to the chemical reaction between boron monoethanolamine (BMEA and 2,5-dimercapto-1,3,4-thiadiazol (DMTD), which forms dust-preventing solids that adsorb onto the copper surface.

This adds weight to the copper surface. The performance of borated and non-borated overbased carboxylates as corrosion inhibitors has been studied and the results showed that both borated and non-borated carboxylates are good corrosion inhibitors, particularly in the presence of borate.

Pour point depressants (PPD)

Pour point depressants (PPD) are developed to overcome the formation of large crystals during solidification and ensure oil flow at low temperatures.

PPD function as wax-crystal modifiers and they work by altering the crystal size either by absorption onto the surface of the newly formed crystals or crystallizing with the precipitating wax. Commercial PPD are generally composed of a polymethacrylate backbone with a certain type of branching, which permits inclusion of the PPD molecules into the growing crystals.

In general, the pour point of the lubricant decreases with an increase in the chain length of the ester branching. It has been shown that ester branching groups with a chain length of at least six carbons are the most effective to impose the desired molecular spacing, resulting in the most desirable pour point properties.

The addition of 1% PPD (i.e. Lubrizol TM 7670 made from sunflower and mineral oils) reduces the pour point of soybean oil-based lubricant from −9°C to −45°C.

Besides PPD, diluents such as 2ethylhexyl oleate, isobutyl oleate, trimethylolpropane trioleate, pentaerythritol tetraoleate and diisodecyl adipate have also been used and the effect of their dilution on the pour point of vegetable oils have been determined.

Extreme pressure and anti-wear additives

Friction is primarily dependent on the shearing forces necessary to divide the adhering asperities.

Friction and wear can be reduced by the addition of anti-wear and extreme pressure additives into the lubricant. These additives create a durable, protective films over the metal surface by reacting thermo-chemically with the metal surface.

Extreme pressure and anti-wear additives typically contain chlorine, phosphorus and sulphur. These elements protect the metal surface with easily sheared layers of sulphides, chlorines or phosphides, which forbid severe seizure and wear.

However, it should be noted that the use of these "active" elements are controlled due to environmental concerns since these elements lead to corrosion of metal specimens as well as pollution. Dermawan et al. found that dibutyl phosphite reduces wear on rubbing bodies. However, 2,5-dimercapto-1,3,4-thiadiazol (DMTD) needs to be added at extreme pressure conditions in order to obtain the same result as that for normal conditions.

In another study, used fourball test to test lubricants with boron-containing additives. They concluded that dibutyl phosphite is a better additive than DMTD in the absence of boron monoethanolamine (BMEA) at extreme pressure conditions.

However, DMTD is a better additive in the presence of BMEA.

However, the dibutyl phosphite + DMTD + BMEA additive mixture is less effective compared to the DMTD + BMEA additive mixture, which may be due to the insignificant amount of phosphorus. Phosphorus plays a vital role in reducing greenhouse gas (GHG) emissions to the environment.