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REVIEW

A Review on Tribological Characterization of Lubricants with Nano Additives for Automotive Applications

P.D. Srivyas[a], M.S. Charoo[a]

[a] *Mechanical Engineering Department, NIT Srinagar, Jammu and Kashmir, India.*

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Corresponding author:

Pranav Dev Srivyas
Mechanical Engineering Department,
National Institute of Technology,
Srinagar-190006,
JandK, INDIA.
E-mail: devpranav.srivyas_17@nitsri.net

ABSTRACT

Automotive manufacturers made significant efforts to achieve an overall increase in the energy efficiency and to reduce the toxic emission level. In the way to achieve these goals, non-conventional engine technologies were brought to the market with improved efficiency and controlled emission system. Numerous other supporting technologies which include biofuels and newly improved lubricants were also involved to contribute in automotive engine system improvement. The problem of friction and wear being inbred to the automotive application, further raise environmental hazards by way of more fuel consumption and wear debris. For several years there have been numerous efforts to reduce the amount of fuel consumed by automotive engines. Many of the solutions been strictly mechanical based. Other efforts have revolved around finding the lubricants that reduce the overall friction in the engine. Lubricants perform an anti-friction media which facilitate smooth operation, reduce friction, wear and risk of frequent failure. Due to this ever-increasing demand for lubricant, a considerable amount of work has been done to modify the lubricating oils with additives to enhance their overall properties. This review paper is aimed to highlight the research carried out in the field of lubricating oil with nano additives for the automotive applications.

1. INTRODUCTION

Improving environmental friendliness, reliability, durability and energy efficiency is of significant interest in the field of automotive industries. New techniques are being developed which include introducing new lightweight materials, less harmful along with controlled combustion of fuels, effective lubrication which controls the environmental problems brought by the vehicles [1-3]. Effective lubrication of the relative parts in the automobile is required for smooth sliding over each other and to reduce friction and wear in order to decrease the emission and energy losses from the engine. To meet these challenges and to open up the new possibilities, new lubricants, and improved additives must be developed constantly [4-6]. Lubricants are important as they reduce the wears mechanism, protect the surface against the corrosion and also sometimes serve as the coolant. Most of the lubricants that are produced don't have all the tribological properties. It was found that various additives are used along with the lubricants in order to improve its tribological properties [7-11]. In the current scenario, most of the lubricants have reached their performance limit. The most significant is now to develop lubricants that can achieve energy efficiency across various fields and can be used even under severe conditions. This hunt for energy efficiency has led the current research toward the use of the nanoparticles as the lubricant additive. From the development history of the lubricants additive, nanoparticles are relatively the latest class of lubricant additives. It involves the colloidal solid particles within the lubricating oil [12-16]. The main component of nano lubricants is; the lubricant/base oil; nano additive and surfactant. Nano-additives in the lubricating oil improve the anti-wear properties; extreme pressure properties; and also enhance the friction properties of the lubricants. The role of the surfactant is to inhabit the interface area between the lubricating oil and the nanoparticles. Use of the nanoparticles in the lubricating oil has some potential advantages as lubricating additives [17]. Most important one is the small size that enables the nanoparticles to enter the contact area which helps in positive lubrication effect. The other possible advantages are insolubility in nonpolar base oils, low reactivity with other additives, high possibility of film formation which helps to withstand high temperature and are more durable [18]. But the effectiveness of the nano-additives depends on certain factors i.e. their compatibility with base oils; their size and morphology; their concentration and their dispersion stability [19,20]. In order to determine the suitable nanoparticles and lubricants, a comprehensive review is required which also focuses on these parameters. This review provides an overview of the tribological performance of nanoparticles, their performance parameters and their applications in automotive industries.

Table 1. Summary of the development of lubricants additives [21].

Year	Development in Lubricants Additives
2020	Nanoparticles Additives as Friction Modifiers, Extreme Pressure, and Anti-Wear Additives.
2000	Polymers Friction Modifiers
1980	Soluble Moly Friction Modifiers.
1960	Dispersants.
1940	Pour Point, Extreme Pressure, Viscosity Modifiers, Antioxidants, Anti-wear, Corrosion Inhibitors.
1920	Organic Friction Modifiers.

2. OVERVIEW OF LUBRICATION AND LUBRICANTS

Liquid lubrication is the earliest method to reduce friction and wear in the sliding contact bodies. Lubricant separates the contacting mating surfaces by forming a fluid film between the rubbing surfaces. The fluid film reduces metal-to-metal contact. There are some other factors which affect the lubricant performance are viscosity index, pour point, flash point thermal stability and oxidation resistance. Moreover, the operating characteristics depend on the lubrication regimes which include boundary lubrication, hydrodynamic lubrication, and elasto hydrodynamics lubrication [22-25]. However, in the case of boundary lubrication, it becomes more important because in that case a thin film of the lubricant can only be maintained and direct contact between the asperities play a dominant role. The right selection of lubricants plays an important role to reduce friction and wear of materials. Depending upon the source and properties lubricating oils have been classified into different types.

Table 2. General classification of the lubricants [26].

Lubricants Classification		
Mineral Oil		
Paraffinic	Naphthenic	Aromatic
Synthetic Oil		
Synthetic Hydrocarbon	Silicon Oil	Organohalogens
Bio-Lubricants		
Animal Fat	Vegetable Oil	

2.1 Mineral oil

These oils were derived from the fractional distillation of crude oil. The most important constituents of the mineral oils are hydrocarbons. Hydrocarbons used in lubricants have three basic chemical structures: paraffinic, naphthenic and aromatic, and their distributions in the chemical structures giving them unique properties. Paraffinic base oils consist of about 45-60 % paraffinic structure. Paraffinic is made of the ith straight chain hydrocarbons. They have good lubrication and additive response properties and can be used up to a 200 ˚C temperature in the absence of oxygen and 150 ˚C in the oxygen atmosphere. They have an inherently high viscosity index and can be used from full film to boundary lubrication regimes. Naphthenic oils consist of 65-75 % of the naphthenic structure and 24-35 % of the paraffinic structure. It includes a cyclic carbon atom structure with no unsaturated bond. The naphthenic structure allows good additive solubility. Aromatic base oils include compounds having benzene-like structure. Mineral oils are economical and easily available but it comes from the non-renewable source of energy and is non-ecofriendly in nature, oxidized at high temperature, the chance of explosion and loss of viscosity are some of the factors which crease its use [27].

2.2 Synthetic oil

These oils are the alternatives for the petroleum-based oils and made from the chemical modification of petroleum-based instead of using completely crude oil. They are artificially made with uniform hydrocarbon molecules which help them to work under extremely low to high temperature. In synthetic base oils, the chemical structure is tailor-made based on the particular applications. Polyalphaolefins (PAO'-s) is the synthetic oil synthesized from linear paraffin and shows superior performance as compared to mineral base oils but its ability to absorb the additives is low due to its well-defined molecular structure. Esters or naphthenic base oils are commonly added to the PAOs base oil to improve the additive solvency of the PAOs base oils. Some other synthetic base oils are phosphate esters, polyalkalene glycols, polyisobutylene, silicone oil [28, 29].

2.3 Bio-lubricant oil

Bio-lubricants include animal fats and vegetable oils. As of now, we are facing hydrocarbon depletion. Bio-lubricants (Environmentally adapted lubricants) are the best alternative to mineral-based lubricants [30]. Vegetable oils are mainly triglycerides (i.e. glycerol with three fatty acids). They have excellent lubricating properties, inherent high viscosity-index, and high flash point, biodegradable, renewable and low/nontoxic in nature [31]. Vegetable oils are generally extracted from the plants by the solvent method as well as the pressing method [32]. Vegetable oils are further classified into four main classes on the basis of the dominance of fatty acid. These are lauric acid, erucic acid, ricinoleic acid and oleic-linoleic acid [33-35]. Lauric oil consists of about 51 % of lauric acid, 7 % monounsaturated fatty acid and 2 % of polyunsaturated fatty acid [36]. Coconut oil belongs to the class of lauric oil. Eurcic oils are the type of long chain fatty acids. They contain fatty acid as erucic acid (C22). The percentage of erucic acid varies from 20-50 %. These include rapeseed oil and mustard oil [37, 38]. Canola oil is another type of Erucic oil but it is low in erucic acid oil category. In this oil, the percentage of erucic acid is less than 2 %. It consists of 58 % oleic acid and 36 % of polyunsaturated acid. Due to the presence of an unsaturated bond, it has low oxidation stability [39]. Ricinoleic oil is those which are having 89 % of the ricinoleic acid in them. Castor oil belongs to the category of ricinoleic oil. The other fatty acid present in this oil is linoleic acid 4 %, oleic acid 3 %, stearic acid 1 % and palmitic acid 1 % [40-42]. Oleic-Linoleic oils are the class of the vegetable oil which include palm oil, olive oil, soyabean oil, peanut oil, cottonseed oil and sunflower oil. These oils contain a high percentage of unsaturated fatty acid [43].

Table 3. Summary of the constituents and characteristics of different Bio-Lubricants [30-43].

Oleic-Linoleic Oil	**Constituents**	**Characteristics**
Palm Oil	Monosaturated Fatty Acid [36%]	Exhibit good anti-wear properties Reduce poisonous gases to the environment
	Linoleic Fatty Acid [9 %]	
	Saturated Fatty Acid (Palmitic acid) [43 %]	
Olive Oil	Oleic Acid [55-83 %]	Resistant to oxidation
	Linoleic Acid [3.5-21 %]	
Cotton-Seed Oil	Linoleic Acid [40-55 %]	More susceptible to oxidation (Anti-oxidant are used to make them more stable) Exhibit good anti-wear properties.
	Oleic Acid [18-30 %]	
	Palmitic Acid[20-25 %]	
	Stearic Acid [2-7 %]	
Soyabean Oil	Linoleic Acid [54 %]	A large percentage of polyunsaturated acid
	Oleic Acid [24 %]	
Sunflower Oil (High Linoleic)	High Unsaturated Fatty Acid [59 %]	Better oxidation stability Better additive solubility Exhibit good anti-wear properties
	Monosaturated Fatty Acid [30 %]	

Sunflower Oil (High Oleic)	A Large amount of Olice Acid Concentrated Monosaturated fatty acid [80 %]	

Table 4. Summary of the comparative studies done by various researchers on lubricating oil [44-62].

Lubricant/ Reference Lubricant	**Test Method / Summary**
Coconut Oil/ SAE 20W50	Four-ball tester rig/ Better lubrication is achieved Lower Coefficient of Friction and higher anti-wear properties were achieved
Palm Oil/ SAE 20W50	Ball on disc high-frequency reciprocating tribometer / Good lubrication properties, Lower COF, higher oxidation and corrosion properties were achieved
Palm Oil/ SAE 20W40	Pin on disc tribometer/ Lower volatility, lower COF, good lubrication properties for boundary lubrication.
Palm Oil with TMP ester/ SAE 40	High-frequency reciprocating tribometer/ Better tribological properties were achieved and reduction in wear scar diameter
Waste Palm Oil/ SAE 40	Four-ball tester rig/ High viscosity and lower COF was achieved
Soyabean Oil/ 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/ Commercial Synthetic Lubricating oil	High-frequency reciprocating tribometer/ High viscosity
Castor Oil/ SAE 20W40	Pin on disc tribometer/ Lower volatility, higher viscosity index, higher lubrication properties.
Castor Oil/ Super refined mineral oil	Four-ball tester rig/ Higher antioxidation properties, lower volatility, higher viscosity index
Pongamia Oil/ SAE 20W40	Four Stroke, Single cylinder, Direct injection diesel compression ignition engine/ Minimum brake specific energy consumption and highest brake thermal efficiency at high load were achieved. Less frictional losses, completely eliminate emission problem
Jatropha Oil/ SAE 20W40	Pin on disc tribometer/ Lower wear loss and lower COF was achieved
Modified Rapeseed Oil/ SAE 20W40	High-frequency reciprocating tribometer/ Improved cold flow property, better oxidation stability, lower COF.
Neem Oil, Olive Oil, Sunflower Oil, Mahua Oil/ 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.

3. NANO-PARTICLES LUBRICATION MECHANISM

Nowadays, nanoparticles are added to the lubricating oils to enhance its tribological properties. So it is important to understand the lubrication mechanism of the nanoparticles in lubricants to reduce the friction and wear mechanism. Many researchers have proposed various lubrication mechanisms using various surface analysis techniques. These lubrication mechanisms are mainly categorized into two types that include direct as well as indirect lubrication mechanism. Direct lubrication mechanism includes ball bearing mechanism and protective film mechanism whereas the indirect mechanism includes mending and polishing mechanism.

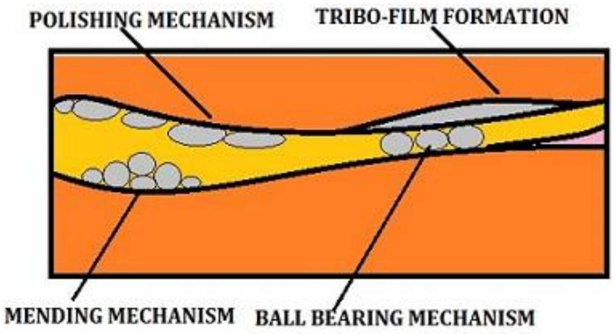


Fig 1. Different lubrication mechanism of Nano-particles [26].

3.1 Ball Bearing/ Rolling Mechanism

In this mechanism, the nanoparticles act like the ball bearing and roll between the mating surfaces. The nanoparticles are generally spherical or quasi-spherical in shape. This lubrication is better for the tribological application having low load conditions so that the shape and rigidity of the nanoparticles can be maintained [63-65]. Peng et al. [100] demonstrated the ball bearing mechanism on the addition of diamond nanoparticles to the liquid paraffin. As the experimentation time increased, the spherical nanoparticles behaved as small ball bearings and rolling mechanism takes place.

3.2 Protective Film an / Tribo-Film Formation Mechanism

In this mechanism, an amorphous layer of the nanoparticles formed on the friction surface and thus reduce the actual area of contact. The reaction between the nanoparticles and the substrate cause the formation of tribo-film under the provided environment [66,67]. Yu et al. [85] made a comparative study of two oils mixed with 0.2 % surface modified copper nanoparticles. The researchers have reported a soft protective film of copper was formed on the steel balls after performing the tests on four ball tester. Hu et al. [156] demonstrated Protective film formation capability by adding Magnesium borate in 500-SN base oil and it was reported that an amorphous film was formed between the rubbing surfaces. As a result, there was a decrease in the COF and an increase in the wear resistance.

3.3 Polishing Effect Mechanism

It acts as the surface enhancement mechanism and is also called a smoothing effect. In this mechanism, nanoparticles smoothen the rubbing surface. They may fill up the gaps of the rough asperities which help to reduce the friction and wear mechanism [68,69]. Lee et al. [74] demonstrated the polishing mechanism by adding fullerene nanoparticles in the refrigeration mineral oil. Xu et al. [96] have reported that upon the use of diamond particles as additives in paraffin oil, the rubbing surface at the start of the tribotest got smoother as compared to the pure paraffin.

3.4 Mending Effect Mechanism

This mechanism is also called as a self-repairing effect. During this lubrication mechanism, the nano-particles get deposited and accumulate on the grooves, which form on the rubbing surfaces to reduce the abrasion. A number of the surface characterization techniques were used by the researchers, in order to investigate the nanolubrication mechanism. Liu et al. [70] conducted an experimental investigation using a pin on disk set-up. The disks of 20CrMnTi steel and pins of H62 bronze were used. After analyzing SEM, and STM it was found that the copper particles underwent mending mechanism in the wear area. Ahmadi et al. [155] also reported mending mechanism in their study on sliding bearings used in the I.C engine.

Table 5. Summary of the effect of the nanoparticle as a lubricant additive on lubrication mechanism and tribological properties [44-62].

Base Oil/ Nanoparticle Additive/ Role	**Lubrication Mechanism/ Surface Analysis Techniques**	**Tribological Effect/ (Friction and Wear)**
PAO/ MoS_2/ [AW, EP, FM]	Tribo-Flim Formation SEM, EDS	Reduction in COF/ Enhancement of Wear properties
PAO/ ZnO, CuO/ [FM, AW]	Mending Effect, Tribo-Flim Formation SEM, EDS	Reduction in COF/ Enhancement of Wear properties
PAO6/ Ca/ [AW, EP]	Tribo-Flim Formation SEM, EDS	Enhancement of Wear properties
PAO6/ Ni/ [AW, EP, FM]	Tribo-Flim Formation SEM, EDS	Enhancement of Wear properties
PAO6/ ZnO, ZrO_2, CaO/ [AW, EP]	Mending Effect SEM, EDS	Enhancement of Wear properties
PAO10/ MoS_2, BN/ [FM, AW]	Tribo-Flim Formation Raman spectroscopy	Reduction in COF/ Enhancement of Wear properties
SuperGear/ EP220/ Gr/ [FM, AW]	Polishing Effect SEM, EDS	Reduction in COF/ Enhancement of Wear properties
TBA, Liquid Paraffin/ Pb/ [FM, AW]	Ball Bearing, Tribo-Flim Formation SEM, EDS	Reduction in COF/ Enhancement of Wear properties
Liquid Paraffin/ Al/ [FM, AW]	Tribo-Flim Formation SEM, EDS	Reduction in COF/ Enhancement of Wear properties
Liquid Paraffin/ CuO/ [FM, AW]	Ball Bearing SEM, EDS	Reduction in COF/ Enhancement of Wear properties
Liquid Paraffin/ MoS_2/ [FM, AW, EP]	Tribo-Flim Formation SEM, EDS	Reduction in COF/ Enhancement of Wear properties
Liquid Paraffin/ MoS_2, TiO_2/ [FM, AW]	Mending Effect, Tribo-Flim Formation XPS	Reduction in COF/ Enhancement of Wear properties
SAE 10/ Fe, Cu, Co/ [FM, AW]	Tribo-Flim Formation SEM, EDS	Reduction in COF/ Enhancement of Wear properties
SAE 30/ CuO/ [FM, AW]	Ball Bearing, Mending Effect SEM, EDS	Reduction in COF/ Enhancement of Wear properties
SAE 20W50/ Carbon Nanoball/ [AW]	Mending Effect SEM	Enhancement of Wear properties
SAE 20W40/ MoS_2/ [FM, AW, EP]	Mending Effect SEM, EDS	Reduction in COF/ Enhancement of Wear properties
SE 15W40/ Al / Sn/ [AW, EP]	Mending Effect SEM, EDS	Reduction in COF/ Enhancement of Wear properties

SAE 15W40/ h-BN/ [FM, AW]	Ball Bearing, Polishing Effect SEM	Reduction in COF/ Enhancement of Wear properties
SAE 15W40/ Al_2O_3 [FM, AW]	Plowing Effect SEM	Increase in the COF/ Enhancement in Wear Rate
SAE 10W-30 /TiO2 [FM, AW]	Ball Bearing, Deposition SEM, EDS	Reduction in COF/ Enhancement of Wear properties
60 SN Base Oil ZnO [FM, AW]	Mending Effect SEM	Reduction in COF/ Enhancement of Wear properties
500 SN Base Oil $B_2Mg_3O_6$ [FM, AW, EP]	Deposition, Tribo-Film Formation SEM, XPS	Reduction in COF/ Enhancement of Wear properties
Mineral Oil CuO [FM, AW]	Deposition, Polishing Effect SEM, EDS	Reduction in COF/ Enhancement of Wear properties
Mineral Oil ZnO [FM, AW]	Deposition, Tribo-Film Formation SEM, EDS	Reduction in COF/ Enhancement of Wear properties
Lubricating Oil $ZnAl_2O_4$ [FM, AW]	Mending Effect SEM, EDS	Reduction in COF/ Enhancement of Wear properties
Palm TMP Ester CuO, MoS_2 [AW, EP]	Mending Effect, Tribo-Flim Formation SEM, EDS, Raman spectroscopy	Enhancement of Wear properties
Jatropha TMP Ester WS_2 [AW, EP]	Tribo-Flim Formation SEM	Enhancement of Wear properties
Sunflower Oil ZnO, CuO [FM, AW]	Tribo-Flim Formation SEM	Reduction in COF/ Enhancement in Wear Rate
Soyabean Oil ZnO, CuO [FM, AW]	Tribo-Flim Formation SEM	Reduction in COF/ Enhancement in Wear Rate

AW: Anti Wear; EP: Extreme Pressure; FM: Friction Modifier

4. NANOPARTICLES PERFORMANCE PARAMETERS

4.1 Role of nanoparticles size

The size of the nanoparticles has a direct effect on the tribological performance of the nano lubricant in many ways. The small size of the nanoparticles helps them to penetrate the rubbing surface which helps to reduce the friction and wear mechanism [70-72]. The mechanical properties of the particles such as hardness can be determined by its size which ultimately effects the tribological properties of the nano-fluid. For the material having a size of the nanoparticle greater than 100 nm, the hardness increases with decreasing particle size. If the hardness of the nanoparticle additive is more as compared to the hardness of the tribopair it leads to scratching and indentation [73-75]. While selecting the size of the nanoparticles material, it is important to consider the root mean square roughness of the lubricated surface. If the particle size is too big as compared to the gap between the asperities it would lead to low lubrication as the bid particles get deposited on the contact surface [76,77]. Nano-particles size can also affect the homogeneity of the lubricant. It was reported that the dispersion of the nanoparticles can be increased by decreasing the size of the particles. It was also stated that the tenfold increase in the particle size decreases the sedimentation time by a hundredfold [78].

4.2 Role of nanoparticle morphology

For tribological applications, the role of nanoparticles shape and structure plays a very vital role. Basically, there are five different types of shape of the nanoparticles i.e. spherical, onion, granular, tube and sheet shape [79]. The surface energy of the nanoparticles is large and in order to achieve equilibrium, the spherical shape is preferred. The surface energy is homogeneous in all directions for spherically shaped particles. Spherical shape particles are having ball-bearing effect as they roll between the rubbing surfaces. Spherical shape particles show extreme pressure characteristics and also have high load carrying capacity. Spherically shaped nanoparticles have point contact with the counter body [80-82]. Onion shape nanoparticles are another type of nanoparticle shape. It is characterized by having an externally spherical shape but the internally laminar shape. It has an advantage as this type of shape lacks dangling bond which leads to less interaction between the particles and the surface [83]. Lamellar Sheet shape was observed in the graphene and MoS_2 structure, which makes them better lubricant. In these types of lubricants, the exfliotaion will occur between the adjacent layers under the applied shear stress and hence reduces wear [84].

Table 6. Summary of the size and morphology of the nanoparticles used by various researchers as lubricant additives.

Nanoparticles/ Classification	Average Particle Size (nm)/ Morphology	Morphology Analysis Technique
Cu Metal	25 Nearly Spherical	TEM
Ni Metal	20 Nearly Spherical	TEM
Al Metal	65 Spherical	SEM
Pb Metal	2.2 Spherical	TEM
CuO Metal Oxide	40 Spherical	TEM, XRD
CuO Metal Oxide	5 Spherical	TEM
CuO Metal Oxide	4.35 Nearly Spherical	SEM
ZnO Metal Oxide	11.7 Nearly Spherical	SEM
ZnO Metal Oxide	20 Nearly Spherical	TEM
TiO_2 Metal Oxide	80 Spherical	TEM
MoS_2 Transition Metal Dichalcogenide	90 Layered lamellar flaky	FESEM
MoS_2 Transition Metal Dichalcogenide	350 Layered	TEM
MoS_2 Transition Metal Dichalcogenide	150 Layered	TEM
MoS_2 Transition Metal Dichalcogenide	100 Rectangular, Oblate Spheroid	SEM, TEM
WS_2 Transition Metal Dichalcogenide	100 Spherical	AFM
WS_2 Transition Metal Dichalcogenide	120 Polyhedral	SEM, TEM
Diamond Carbon Based	10 Sphere	TEM
Graphite Carbon Based	55 Spherical	TEM
Carbon Nanohorns Carbon Based	80 Dahila (Rounded ball shape with the double flat spiral on the surface)	SEM
Graphene Carbon Based	10 Spheroidal	TEM
Boron Nitride Nitrides	70 Spherical	SEM
Boron Nitride Nitrides	114 Nonspherical	SEM,XRD
Aluminum oxide Ceramics	78 Spherical	SEM
SiO_2 Ceramics	30 Spherical	FESEM, TEM
SiO_2 Ceramics	365 Spherical	FESEM
SiO_2 Ceramics	215 Spherical	FESEM
SiO_2 Ceramics	140 Spherical	FESEM
SiO_2 Ceramics	58 Spherical	FESEM
Al2O3/SiO2 Nanocomposites	70 Elliptical	TEM
ZrO2/SiO2 Nanocomposites	50-80 Nearly spherical	TEM
Polytetrafluoroethylene (PTFE) Polymer	30-50 Spherical	FESEM

4.3 Role of nanoparticles dispersion stability

Nanoparticles have high surface energy due to the high surface area by volume ratio. In order to achieve the equilibrium state, the particles in suspension may stick to each other to form agglomerates. This phenomenon is called as agglomeration / flocculation [85,86]. Agglomeration of the nanoparticles affects the sedimentation rate and also there is a loss of wear and friction protection ability. That is why the dispersion stability of the nanoparticles is important. In the case of poor dispersion stability, sedimentation and clogging may occur. Stability means that the particles do not accumulate at a significant rate. The stable suspension is a prerequisite for an effective nano lubricant formulation. As suspension stability is vital issues that affect the performance of the lubricant, it is important to understand these influencing factors: (a). method of nanoparticle dispersion in the lubricant (b). dispersion stability analysis methods (c). methods to enhance dispersion stability.

In order to achieve stable dispersion and to reduce the agglomeration of the nanoparticles, various techniques such as ultrasonication, homogenizing, magnetic force agitation, probe sonication, ball milling and high shear mixing are done [87]. For the proper dispersion of the nanoparticles, it is important to select the method which governs proper dispersion. After selection of the dispersion method, another key factor is the time duration for dispersion in order to reduce the chance of agglomeration. To investigate the dispersion stability, a number of methods have been used which include sedimentation, zeta potential, spectral absorbency and metallographic micrograph stability test [88-90]. Sedimentation method is the simplest method to evaluate the dispersion stability of the nanolubricants. It is also called as observation stability test. But the main disadvantage of this mechanism is that it is a time taking the process and also precautions must be taken to maintain the same volume, temperature and other conditions for all the samples. The movement should be avoided to ensure reliability. The sedimentation rate of the particles can be calculated using Stokes' law [138].

(1)

v_2 = Settling Velocity
ρ_{NP} = Nanoparticles Density
ρ_F = Fluid Density
g = Gravity
r = Nanoparticle Radius
μ = Viscosity

Particle suspension in a liquid medium is subjected to the different type of forces: gravitational force particles to fall down; viscosity of fluid decrease the speed of their displacement; Archimedes force opposite to gravitational force. By applying the fundamental relation of dynamics, the expression of steady-state sedimentation speed of the dispersion particles is obtained [138].

$$V = \frac{2}{9}\left[\frac{R^2(\rho\_\rho')}{\eta}g\right] \tag{2}$$

R = Radius of the Particles
η = Dynamic Viscosity of the Fluid
ρ = Density of the Particles
ρ' = Density of the Fluid

It is important to notice that the speed varies is proportional to the square of the radius of the particle. Particles with large radius will sediment much faster than the small one, due to the flocculation process. Fortunately, some other effects can also allow for the better dispersion stability of the dispersed particles suspension. Brownian Motion is an interesting one which corresponds to the chaotic movement of the dispersion particles due to shocks of liquid molecules on its surface. For small dispersion particle, the relation of strokes-Einstein gives the average distance ‘x’ by particles, during a certain time ‘t’ [138].

$$X = \sqrt{\frac{2kTt}{6\pi\eta R}} \tag{3}$$

R = Radius of the Particles
η = Dynamic Viscosity of the Fluid
T = Temperature
t = Time
k = Boltzman Constant (1.38×10^{-23} J/K)

By using 2nd and 3rd equation the distance covered by one particle in 1 second can easily be compared by sedimentation and the Brownian motion respectively. The sedimentation force is oriented vertically whereas the distance covered by Brownian movement has no preferential direction.

Spherical absorbency is another method in which ultraviolet-visible spectrophotometry absorbance measurements are used to characterize the colloidal stability of the dispersion particles. Zeta Potential shows the dispersion stability of the dispersion by measuring the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersion particles. This value helps us to determine the dispersion tendency of the nanoparticles in the oil. It was reported that higher the value of zeta potential higher the tendency of stability of the dispersion.

Table 7. Summary of the dispersion properties and sedimentation time for different nanoparticles at 20 °C.

Nano-particle	**APS /nm**	**Sedimentation (Distance covered in 1 sec)**	**Brownian movement in 1 sec**	**Sediment Time (Hours)**
IF-MoS_2	40	0.01	282	10
IF-WS_2	140	0.2	150	5.5
IF-WS_2	90	0.1	188	6.5
IF-NbS_2	60	0.02	230	8
2H- MoS_2	2000	140	28	---
2H- WS_2	1000	55	39	---
3R-NbS_2	1000	29	13	---

There are certain methods for improving the dispersion stability of the nanoparticles in the oils. The dispersion stability can be enhanced either by surface modification of nanoparticles or by using the surfactants. In the method of surface modification, the surface properties of the nanoparticles are tailored to the use of organic modifying agents [89]. The most commonly used modifying agent is oleic acid which absorbs around the nanoparticles reducing their surface energy which prevent the agglomeration. Surfactants are another method which is used for the dispersion stability of the dispersion particles. They are also called as dispersants that are added to the nano lubricants to enhance the dispersion stability. It is an easy and economical method. The most commonly used surfactants are oelic acid, sodium dodecyl sulfate (SDS), TRITON TMX102, Benzalkonium chloride, benzethonium chloride [90]. It was reported that the use of the surfactants not only enhance the dispersion stability but also reduce the friction and wear on its own.

Table 8. Summary of the commonly used dispersion methods, dispersion duration, a technique to achieve dispersion stability and dispersion stability measuring technique.

Lubricant / Nanoparticles	**Dispersion Method/ Dispersion Duration/ Surfactant/ Surface-Modifying Agent**	**Dispersion Stability Measuring Technique**	**Effect on Dispersion Stability**
Machine Oil ZrO_2/SiO_2 (Surface Modified)	Ultrasonic Dispersion 30 min Aluminium Zirconium coupling agent	Ultraviolet-Visible Spectrophotometry Absorbance, Zeta Potential	Improved dispersion stability [108]
Machine Oil Al_2o_3/SiO_2 (Surface Modified)	Ultrasonic Dispersion 30 min Silane coupling agent	Sedimentation	Improved dispersion stability [71]
Machine Oil Al_2O_3 (Surface Modified)	Ultrasonic Dispersion 30 min Silane coupling agent (KH-560)	Ultraviolet-Visible Spectrophotometry Absorbance, Sedimentation, Zeta Potential	Improved dispersion stability [71]
Servo 4T synthetic 10W-30 Oil TiO_2	Chemical Shaker Agiation 30 min ---	Ultraviolet-Visible Spectrophotometry Absorbance	[78]
Liquid Paraffin TiO_2 (Surface Modified)	--- 30 min Tetrafluoro benzoic Acid	Ultraviolet-Visible Spectrophotometry Absorbance	[99]
Lubricating Oil $ZnAl_2O_4$	--- 30 min Oelic Acid	Ultraviolet-Visible Spectrophotometry Absorbance	Improved dispersion stability [94]
Multigrade Engine Oil CuO	Ultrasonic Agitation 30 min ---	Ultraviolet-Visible Spectrophotometry Absorbance	[83]
SAE-40 CuO	Ultrasonic Dispersion 40 min ---	Ultraviolet-Visible Spectrophotometry Absorbance	[83]
Coconut Oil CuO	--- 40 min ---	Ultraviolet-Visible Spectrophotometry Absorbance	[83]
Machine Oil ZrO_2 (Surface Modified)	Ultrasonic Probe Sonicator 30 min Silane coupling agent (KH-560)	Ultraviolet-Visible Spectrophotometry Absorbance	---
PAO CuO, ZnO	Ultrasonic Probe Sonicator 30 min ---	Ultraviolet-Visible Spectrophotometry Absorbance	[94]
Vegetable Oil CuO,ZnO	Ultrasonic Probe Sonicator 30 min Oelic Acid	Ultraviolet-Visible Spectrophotometry Absorbance	[94]
60SN Base Oil ZnO (Surface Modified)	Ultrasonic Bath/ megnatic stirrer 30 min/ 20 min Oelic Acid	Sedimentation	Improved dispersion stability [94]
Palm TMP ester CuO, MoS_2 (Surface Modified)	Ultrasonic Bath 60 min Oelic Acid	Ultraviolet-Visible Spectrophotometry Absorbance	Improved dispersion stability
Coconut Oil MoS_2 (Surface Modified)	Ultrasonic Shaker 60 min with an intermediate gap of 3 min Sodium Dodecyl Sulfate (SDS)	Ultraviolet-Visible Spectrophotometry Absorbance	Improved dispersion stability [91]
Mineral Oil MoS_2 (Surface Modified)	Ultrasonic Shaker 60 min with an intermediate gap of 3 min Sodium Dodecyl Sulfate (SDS)	Ultraviolet-Visible Spectrophotometry Absorbance	Improved dispersion stability [97]
Liquid Paraffin SiO_2 (Surface Modified)	Ultrasonic Stirrer 60 min Oelic Acid	Sedimentation	Improved dispersion stability [90]

Liquid Paraffin PbS (Surface Modified)	--- --- Oelic Acid	Sedimentation	Improved dispersion stability
SAE 15W40 h-BN (Surface Modified)	Ultrasonic Homogenizer 20 min Oelic Acid	Sedimentation	Improved dispersion stability [98]
PAO100 Silica	Magnetic Stirrer --- Amino Functionalized	Sedimentation	Improved dispersion stability
PAO6 Cu	Ultrasonic Probe Sonicator 30 min ---	Sedimentation	[94]
PAO6 Ni	Ultrasonic Probe Sonicator 30 min ---	Sedimentation	[94]
PAO6 ZnO, ZrO_2	Ultrasonic Probe Sonicator 2 min ---	Sedimentation	---
PAO Carbon Onion Graphite	Ultrasonic Bath 300 min ---	Sedimentation	[102]
PAO Carbon Nano-onions	Ultrasonic Bath 300 min ---	Sedimentation	[105]
EOT 50 SiO_2, MoS_2	Ultrasonic Shaker 120 min ---	Sedimentation	---

4.4 Role of nanoparticle concentration

Particle concentration is another important factor in reducing the friction between the mating surfaces. Suitable optimum concentration is important; adding an excess of nanoparticles does not necessarily means it is going to reduce the friction and wear [91]. Suitable nanoparticles concentration for lubricating oil depends on some critical factors which include dispersion method, dispersion duration, the role of nanoparticles and tribo test conditions [92]. Besides this, some other parameters, such as the type of base oil, counter surface roughness etc. also affect the tribological properties.

5. NANOPARTICLES AS OIL ADDITIVES

Nanoparticles can be generally categorized into different types based on its applications. Since in this review the main focus is on the tribological properties of the nanoparticles as additives. Because of the excellent properties of nanoparticles due to their high surface to volume ratio, the role of the nanoparticles as additives in lubricating oil has gained much focus. Different nano-additives have different characteristics of extreme pressure, anti-wear, friction modifier, antioxidant, an anti-corrosion additive which can be used in various tribological applications.

5.1 Classification of nanoparticles

Based on chemical composition the nanoparticles additives are classified as Metals nanoparticles additives, Metal Oxide nanoparticles additives, Sulphide nanoparticle additive, Nitride nanoparticle additive, Carbon-based nanoparticle additive and Nanocomposite based additives. Metal nanoparticles additives include Au, Ag, Cu, Ni, Fe, Zn. These nanoparticles are used in the base oils to enhance the properties of the lubricating oils. These nano-metallic particles lead to the formation of the adsorbed film between the mating surface and then these particles generate the ball bearing effect which helps in reducing the friction and wear. Another class of nano-additives are metal oxides, they also have the same lubrication mechanism similar to that of metal. Sulfides are another class of nanoparticles additives. The most commonly used sulfides nanoparticles are MoS_2, WS_2, CuS. They exhibit protective film mechanism. Tribofilm formation is due to the heat generated because of the friction between the rubbing surfaces.

Carbon-based nanoparticles are the other class which includes diamond particles, carbon nanotubes, and graphene. There are some hybrid multiphase solids nanoparticles which is another class of additives in the lubricating oil. They include Cu/ SiO_2, Al_2O_3/SiO_2, Cu/ graphene oxide, Al_2O_3/TiO_2 etc. these multiphase particles shows excellent results due to the presence of different phases. To investigate the tribological performance of the lubricating oil with nanoparticles additive various research studies were carried out using different tribo-geometries which include four-ball tester, ball on the disc, pin on the disc, the cylinder on a flat plate, piston ring on cylinder liner and block on the ring. Here is the detailed literature regarding the experimental studies of the nanoparticles as an additive in various lubricant oils. Kanagasabapathi et al., [93] in their research of pure soyabean oil, soybean methyl ester (SBME), soybean methyl ester + 1.5 % of copper nanopowder and mineral oil (4T). It was reported that the introduction of the copper nanopowder decreases the wear scar diameter by 12 % as compared to the SBME as well as mineral oil. Asakauskas et al. [94] conducted a comparative study between the different type of oils i.e. mineral oil, synthetic oil and vegetable oil. Different nanoparticles i.e. copper, iron, nickel, zinc were investigated in different oils. Various oxidation modifiers and other additives are also added to the oils. After the experimentation, it was reported that the synthetic oils show the minimum wear scar diameter as compared to the other oil used. Nallusamy et al. [142] in this research work studied the various performance and emission characteristics of a single cylinder direct injection diesel engine by using an alternative fuel of the biofuel mixed with pine oil and its blends. The results were compared with standard diesel fuel. From the results, it was found that there is a slight increase in brake thermal efficiency and a decrease in brake specific fuel consumption in all pine blended fuels when compared with regular diesel fuel. The use of pine oil resulted in lower emissions of carbon monoxide, hydrocarbons and increased emissions of nitrogen oxides. 5% of pine oil showed significantly comparable thermal efficiency and consumption of specific fuel with diesel.

Arumugum et al. [74] studied the behavior of the micro and nano TiO_2 particle in the chemically modified rapeseed oil. it was reported that by using TiO_2 nanoparticles there is a decrease in the wear scar by 15 % when compared to the microparticles. Baltez et al. [73] used different nanoparticles i.e. CuO, ZnO, and ZrO_2 in PAO6 oil as the nano additive. It was reported that 0.5 % is the optimum concentration for the reduction in the COF. It was reported that the ZnO nanoparticles exhibit best tribological performance. Xu et al. [96] in their investigation used the micro as well as nano MoS_2 particles (1.25 µm, 100 nm, and 2 nm) with varying concentration (0.5, 1, 1.5, 2 wt%) as the additive. It was reported that the nano additive enhances the friction and wear properties by forming the protective film between the mating surfaces as compared to the micro additive particles. Optimum results come from 100nm and 1 wt% of MoS_2 particles. Gulzar et al. [83] in their research study the tribological behavior of CuO and MoS_2 nanoparticles in the palm oil. It was reported that 1 wt% of MoS_2 particles showed better results as compared to CuO particles. Kogovsek et al.[97] in their studies make a comparative analysis by using micro, nano MoS_2, WS_2 and carbon nanoparticles and it was reported that nano MoS_2 give the best result in tribological aspects. Zhang et al. [169] studied and reviewed the recent developments, structural and physical properties of 2-D few layered MoS_2. Altavilla et al. [149] investigate a new kind of hybrid organic-inorganic nano-composite, made by an inorganic core of CNT/MoS_2 coaxial nano-tubes coated by oleylamine molecules as an anti-friction and anti-wear additive for grease lubricants. Feranandes et al. [150] studied the electronic structure of a hetro-junction made of two monolayers of MoS_2 & WS_2. Tannous et al. [151] experimentally investigate the Inorganic Fullerene (IF-MoS_2, IF-WS_2) as anti-wear and friction modifier additive under boundary lubrication. It was reported that lubrication properties are attributed to a gradual exfoliation of the external sheets of the particles during the friction process leading to their transfer on to aspirates of the reciprocating surface. Different rubbing surfaces (steel, alumina, DLC) were investigated in this research. Lahouij et al. [152] investigated Inorganic Fullerene nano-particles (IF-MoS_2, IF-WS_2) as anti-wear and friction modifier additive. It was reported that exfoliation and third body transfer of molecules sheet on to the asperities constitute the prevalent mechanism for the improved tribological behavior of IF nano-particles. It was also reported that rolling friction process could also play a role for well crystallized and spherical particles. Yadgarov et al. [154] studied the tribological properties of Rhenium- Doped Inorganic Fullerenes like MoS_2 nano-particles in PAO's oil as compared to the IF-MoS_2 and 2H-MoS_2 platelets in the lubricating oil. The tribological tests were performed in different lubrication regimes. A reduction in friction and wear was reported. Re-doped MoS_2 nano-particles exhibit best results due to their reduced tribo-charging and agglomeration. The reduction is about 40 % in the COF was observed compared to the base lubricant value. Xie et al. [157] studied the effects of the base lubricant with and without nanoparticles on the tribological behavior of magnesium alloy/steel contacts using reciprocating sliding ball-on-flat tribometer. It was reported that as compared with the SiO2 nanolubricants, the positive effect of the MoS2 nanolubricants is more pronounced in terms of the load carrying capacity and the lubrication film stability. The optimal concentration of nano-MoS2 is 1.0wt% and that of nano-SiO2 is 0.7wt%. Nano-SiO2 is deposited on to the wear track during the sliding, which helped to reduce the friction coefficient due to the rolling action of billions of nanoparticle between the rubbing surfaces. The advanced lubricity of MoS2 platelets could be attributed to friction chemical reaction which led to the formation of the tribo film on the mating metal contact. Reeves et al. [98] studied the behavior of h-BN (Hexagonal Boron Nitride) nanoparticles of different size (70 nm, 0.5 µm, and 5µm) in canola oil. It was reported that the nanoparticles show improved friction and wear properties as compared to the microparticles. Shaari et al. [99] studied the behavior of TiO_2 particles in the palm oil with TiO_2 in different concentration varying from 0.1wt% to 0.5wt%. It was reported that 0.1wt% of the concentration which improves the friction and wears properties. Thottackkad et al. [78] studied the behavior of CuO nanoparticles with different concentration varying from 0.2wt% to 0.6wt% in the coconut oil. After experimentation, it was concluded that 0.34wt% is the most optimum nanoparticle concentration in the lubricating oil for the best tribological properties. Nallusamy et al. [143] experimentally optimize the machining parameters for face milling of EN 31 steel workpiece using a tungsten carbide tipped tool under minimum coolant flow requirement. Aluminum Oxide (Al_2O_3) nanoparticles with 60 nm are added in the coolant for improving the face milling process. Material removal rate was found maximum with 3 % concentration of nanoparticles in the coolant. Nallusamy et al. [144] experimentally studied the nano-fluid consists of water & 1 % volume concentration of Al_2O_3. Nanofluid flowing through parallel and counter flow shell and tube heat exchangers. About 50 nm diameter of Al_2O_3 nanoparticles were used in this analysis and found that the overall heat transfer coefficient and convective heat transfer coefficient of nano-fluid were slightly higher than those of the base liquid at a same mass flow rate and inlet temperature. Sendilvelan et al. [145] in their research calculate various emission factors in a diesel engine using cerium oxide nanoparticles. The experimental result reveals that the influence of cerium oxide in the form of nano-particles for oxides of nitrogen, hydrocarbon, and carbon monoxide levels in a diesel engine. The cerium oxide increases the conversion rate due to the oxygen content for the oxidation process of carbon monoxide and hydrocarbon in the catalytic converter. It was also observed that the cerium nano-particles reduce the oxides of nitrogen effectively. Nallusamy et al. [146] in their research studied the overall heat transfer coefficient by doing an experimental investigation of the convective heat transfer and flow characteristics of a nanofluid. Nanofluid consisting of water and 1 % volume concentration of Al_2O_3/ flowing in a parallel flow, counter flow in shell and tube heat exchanger under laminar flow condition. It was reported that that the overall heat transfer coefficient and convective heat transfer coefficient of nanofluid to be slightly higher than that of the base liquid at a same mass flow rate and inlet temperature.

Peng et al. [100] in their studies used the diamond nanoparticles in the paraffinic oil to reduce the friction and wear mechanism. Yusu et al. [101] studied the behavior of graphene nanoplatelets (GNP) in the vegetable oil. It was reported that the GNP leads to reduce the COF and wear considerably. Zhang et al. [102] experimentally studied the behavior of graphene and multi-wall carbon nanotubes as an additive in diamond-like carbon, ionic fluid. Hybrid film in high vacuum condition. It was reported that different lubrication mechanism is produced using different nanomaterials. Lin et al. [103] studied the behavior of chemically modified graphene platelets. The mixing process was done by sonication and magnetic stirring and then the tribotest was conducted on the four-ball tester at 1200 rpm speed under load 147 N at the temperature of 75 °C. It was reported that adding the nano graphene platelets increase the load carrying capacity of the oil. The optimum concentration is 0.075 wt.% to reduce the friction and wear. Also, Lin et al. studied the behavior of surface modified graphene and it was reported that there was a reduction in the wear and friction of the mating surface. Micrographic studies revealed that this might be due to the thin laminated structure of the graphene which help him to easily enter between the rubbing surface. Senatore et al. [104] studied the behavior of graphene oxide nanosheet in lubricating oil. They added 0.1 % of graphene oxide. It was reported that the average COF is decreased by 20 % within the temperature of 25-80 ˚C. the wear scar diameter was also reduced up to 30 % with graphene oxide additive based oil as compared to the base oil. Choudhary et al. [105] first performed alkylated graphene with variable length of alkyl chain by coupling alkylamine with the carboxylic group of graphene oxide and then disperse them in different organic solvents. The tribological test was performed on a four-ball tester at 392 N load, 1200 rpm speed at temperature 75˚C. the friction and wear were reduced by 20%. It was reported that the lubrication properties were because of the graphene nanosheet between the rubbing surface which prevent the direct contact. Wei et al. [106] studied the tribological ˚behaviour of liquid phase exfoliated graphene modified (0.02-0.06%0 as an additive in oleic acid. It was reported that the graphene as a nano additive enhance the friction and wear properties of the lubricating oil and there is a reduction in wear scar diameter by 17%. Kinoshita et al. studied the behavior of graphene oxide nanoparticles in the water-based coolant. It was reported that the COF is reduced to 0.05 after using nanoparticle in the coolant. Nallusamy et al. [140,141] experimentally investigate different samples with a varied composition of the nano-materials copper-multiwalled carbon nanotubes-graphene hybrids. The hybrid composite was made by stir casting process. It was also found that the addition of carbon nanotubes and graphene into copper leads to lower surface roughness values better surface finish compared to pure copper. In another research, they experimental investigated the heat transfer of nanofluids using carbon nanotubes. It was reported that the thermal conductivity enhancement of nanofluids depends on the particle volume fraction, size and shape of nanoparticles, type of base fluid/nanoparticles, pH value of nanofluids and type of particle coating.

Li et al. [92,108] studied the multiphase ZrO_2/SiO_2 nanocomposite with Aluminium zirconium as an additive. It was reported that the COF is lower by 16.24% with 0.1 wt.% of the Nano additive. Al_2O_3/ TiO_2 multiphase nanocomposite was added to the lubricating oil. Xie et al. [158] experimental investigated, the SiO2/MoS2 hybrid nanoparticles with different mass ratios as lubricant additives in the base oil, and their tribological properties were evaluated using a reciprocating ball-on-plate tribometer for magnesium alloy-steel contacts. The results demonstrate that the SiO2/MoS2 hybrid nano-particles exhibit superior lubrication performances than individual nano-SiO2 or nano-MoS2 even in high load and diverse velocity cases. The optimal SiO2/MoS2 mixing ratio and the concentration of SiO2/MoS2 hybrid nanoparticles in the base oil are 0.25:0.75 and 1.00–1.25 wt%, respectively.

Table 9. Summary of the tribotest conditions for lubricating oil with nano-additives.

Lubricant/ Nanoparticles Additives/ Concentration	**Geometric Configration/ Tribopair (Material/ Counter body)**	**Tribo-Test Conditions**
		Test Duration/ Temperature /Normal Load (N)/ Frequency (Hz) Speed (RPM)
PAO 6 Cu	Block on Ring --- ---	3066 sec/---/165 N/ 1 m/s [115]
PAO 10 MoS_2	Piston Skirt Cylinder Liner --- ---	10,800 sec/ 20°C, 40 °C, 100 °C/ 250 N/ 120 RPM [131]
PAO 10 BN	Piston Skirt Cylinder Liner --- ---	10,800 sec/ 20 °C, 40 °C, 100 °C/ 250 N/ 120 RPM [131]
Chemically Modified Rapeseed Oil CuO	Piston Skirt Cylinder Liner	7200 sec/ 60 °C/ 80 N/ 600 RPM [83]
Mineral Oil CuO	Pin on Disc --- ---	400, 600, 1200 sec/ ---/ 40 N, 60 N/ 0.5m/s, 1 m/s, 1.5 m/s. [83]
Coconut Oil CuO	Pin on Disc --- ---	178-714 sec/ ---/ 49-98 N/ 1.4-5.6 m/s [83]
PAO CuO	Ball on Disc --- ---	3600 sec/ 50 °C/ 10 N/ 1200 RPM [83]
Sunflower CuO	Ball on Disc	3600 sec/ 50 °C/ 10 N/ 1200 RPM [83]

Soybean CuO	Ball on Disc --- ---	3600 sec/ 50 °C/ 10 N/ 1200 RPM [83]
SAE 30 WS$_2$	Piston Ring Cylinder Liner	27,000 sec/ 70 °C/ 160 N/ 2.29 m/s [8]
Paraffin Oil WS$_2$	Pin on Disc --- ---	24,000 sec/ ---/ 100-500 N/ 0.6 m/s [8]
Mineral Oil C60	Disc on Disc	600 sec/ 26-28 °C/ 1000-1500 N/ 1000 RPM
Paraffin Oil Pb	Pin on Disc --- ---	5000 sec/ ---/ 7 N/ 1 m/s [115]
Chemically modified Palm Oil CuO	Piston Ring Cylinder Liner --- ---	21,600 sec/ 70 °C / 160 N/ 1.1 m/s [83]
Chemically modified Palm Oil MoS$_2$	Piston Ring Cylinder Liner	21,600 sec/ 70 °C/ 160 N/ 1.1 m/s [118]
SAE 40 Cu	Ball on Flat --- ---	120 sec/ 25 °C/ ---/ 0.001-1.8 m/s [115]
SAE 40 TiO$_2$	Ball on Flat --- ---	120 sec/ 25 °C/ ---/ 0.001-1.8 m/s [120]
SAE 40 Carbon Horns	Ball on Flat --- ---	120 sec/ 25 °C/ ---/ 0.001-1.8 m/s [116]
PAO 6 CuO	Block on Ring --- ---	1533 sec/ ---/ 165 N/ 2 m/s [115]
PAO 6 ZnO	Block on Ring --- ---	1533 sec/ ---/ 165 N/ 2 m/s
PAO 6 ZrO$_2$	Block on Ring	1533 sec/ ---/ 165 N/ 2 m/s
SAE 10W BN	Ball on Disc --- ---	160 sec/ 20 °C/ 10 N/ 0.25 m/s[12]
Vegetable Based Oil Graphite	Pin on Disc --- ---	3600 sec/ 24 °C/ 2,10 N/ 100 RPM
Commercial Mineral Oil Graphite	Disc on Disc --- ---	600 sec/ 35 °C/ 500-3000 N/ 1000 RPM
PAO Cabron	Pin on Flat	1000, 20,000 sec/ 25 °C/ 2,5,10 N/ 0.25 m/s
PAO Nano Onions	Pin on Flat --- ---	1000, 20,000 sec/ 25 °C/ 2,5,10 N/ 0.25 m/s
PAO Graphite	Pin on Flat	1000, 20,000 sec/ 25 °C/ 2,5,10 N/ 0.25 m/s
Engine Oil MoS$_2$	Ball on Flat --- ---	1800, 4500 sec/ 25 °C/ 1,3,5,8 N/ 0.03, 0.08 m/s [131]
Engine Oil SiO$_2$	Ball on Flat --- ---	1800, 4500 sec/ 25 °C/ 1,3,5,8 N/ 0.03, 0.08 m/s
SE 15W40 BN	Disc on Disc --- ---	180 sec/ 25 °C/ 500 N/ 500 RPM[131]
PAO4 + PAO 40 MoS$_2$	Ball on Flat	144,000 CYCLES/ 80 °C/ 10 N/ 600 RPM [131]
PAO8 CuO	Ball on Disc --- ---	7200 sec/ 50 °C/ 200 N/ 3000 RPM [99]
PAO8 Al$_2$O$_3$	Ball on Dsc --- ---	7200 sec/ 50 °C/ 200 N/ 3000 RPM [20]
SAE 75W85 CuO	Ball on Disc --- ---	7200 sec/ 50 °C/ 200 N/ 3000 RPM [99]
SAE 75W85 Al$_2$O$_3$	Ball on Disc --- ---	7200 sec/ 50 °C/ 200 N/ 3000 RPM [92]
Machine Oil ZrO$_2$/SiO$_2$	Thrust Ring --- ---	1800 sec/ 75 °C/ 200 N/ 1200 RPM [129]
Machine Oil Al$_2$O$_3$/SiO$_2$	Thrust Ring --- ---	1800 sec/ 75 °C/ 200 N/ 1200 RPM [113]
60 SN Base Oil ZnO	Four-Ball Wear Tester Steel Steel	1800 sec/ 25 °C/500 N 1000 RPM [115]
150 N Group II Base Oil PTFE	Four-Ball Wear Tester Steel Steel	3600 sec/ 75 °C/ 392 N/ 1200 RPM [108]
SAE 15W40 h-BN	Four-Ball Wear Tester Steel Steel	10 stages till weld/ 25 °C / variable load till weld/ 1760 RPM [119]
Liquid Paraffin MoS$_2$/TiO$_2$	Four-Ball Wear Tester Steel Steel	1800 sec/ 25 °C/ 300 N/ 1450 RPM [120]
SAE 10 Fe	Four-Ball Wear Tester Steel Steel	3600 sec/ 25 °C/ 150 N/ 1400 RPM [115]
SAE 10 Cu	Four-Ball Wear Tester Steel Steel	3600 sec/ 25 °C/ 150 N/ 1400 RPM [115]
SAE 10 Co	Four-Ball Wear Tester Steel Steel	3600 sec/ 25 °C/ 150 N/ 1400 RPM [115]
Chemically Modified Jatropha Oil WS$_2$	Four-Ball Wear Tester Steel Steel	10 stages till weld/ 25 °C/ variable load till weld/ 1770 RPM [8]

Chemically Modified Palm Oil TiO_2	Four-Ball Wear Tester Steel Steel	300 sec/ 25 °C/ 392, 784, 1176, 1568 N/ 1200 RPM [120]
PAO + 5%^Chemically Modified Palm Oil $CaCO_3$	Four-Ball Wear Tester Steel Steel	3600 sec/ 25 °C/ 392 N/ 1200 RPM
HC Base oli 0.5wt% GO	Reciprocating Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel ball	---/ 50 ºC/ 50 N, 100 N, 150 N/ 50 Hz [125]
HC Base oli 0.5wt% GO	Reciprocating Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel ball	---/ 100 ºC/ 50 N, 100 N, 150N/ 50 Hz [125]
HC Base oli 0.5wt% GO	Reciprocating Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel ball	---/ 150 ºC/ 50 N, 100 N, 150 N/ 50 Hz [125]
HC Base oli 0.5wt% GO	Reciprocating Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel ball	---/ 50 ºC/ 100 N/ 10- 50 Hz [125]
PAO40 0.05wt% GO	Reciprocating Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel ball	---/ ---/ 100 N, 200 N, 300 N, 400 N, 500 N/ 30 Hz [126]
PAO40 0.5wt% GO	Reciprocating Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel ball	---/ ---/ 100 N, 200 N, 300 N, 400 N, 500 N/ 30 Hz [126]
PAO40 0.1wt% GO	Reciprocating Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel ball	---/ ---/ 100 N, 200 N, 300 N, 400 N, 500 N/ 30 Hz [126]
PAO40 1wt% GO	Reciprocating Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel ball	---/ ---/ 300 N/ 10- 50 Hz [126]
PAO4 0.01 wt% τ-GO	Rotary Universal Tribometer ALSI52100 Steel disc M50 steel ball	---/ ---/ 10 N/ 10 mm/s [126]
PAO4 0.1 wt% τ-GO	Rotary Universal Tribometer ALSI52100 Steel disc M50 steel ball	---/ ---/ 10 N/ 10 mm/s [126]
PAO 10 0.01wt% GNP	Rotary Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel	---/ ---/ 392 N/ 1200 rpm [122]
PAO 10 0.03wt% GNP	Rotary Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel	---/ ---/ 392 N/ 1200 rpm[122]
PAO 10 0.05wt% GNP	Rotary Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel	---/ ---/ 392 N/ 1200 rpm [122]
PAO 10 0.1wt% GNP	Rotary Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel	---/ ---/ 392 N/ 1200 rpm [122]
PAO 10 0.2wt% GNP	Rotary Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel	---/ ---/ 392 N/ 1200 rpm [122]
PAO 10 0.5wt% GNP	Rotary Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel	---/ ---/ 392 N/ 1200 rpm [122]
PAO 10 1wt% GNP	Rotary Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel	---/ ---/ 392 N/ 1200 rpm [122]
PAO 10 3wt% GNP	Rotary Universal Tribometer ALSI 52100 Steel ALSI 52100 Steel	---/ ---/ 392 N/ 1200 rpm [122]
SN 350 0.075wt% MGP	Rotary Universal Tribometer ALSI 52100 Steel ALSI 52100 steel ball	---/ 75 ºC / 147 N/ 1200 rpm [127]

SN 150 0.1 wt% GO	Rotary Universal Tribometer X155CrVMo12-1 steel disc X45Cr13 steel ball	---/ 25 ºC / 60 N/ 1 m/s, 1.5 m/s, 2 m/s [127]
SN 150 0.1 wt% GO	Rotary Universal Tribometer X155CrVMo12-1 steel disc X45Cr13 steel ball	---/ 50 ºC / 60 N/ 1 m/s, 1.5 m/s, 2 m/s [127]
SN 150 0.1 wt% GO	Rotary Universal Tribometer X155CrVMo12-1 steel disc X45Cr13 steel ball	---/ 80 ºC / 60 N/ 1 m/s, 1.5 m/s, 2 m/s [127]
SN/CF20W50 Additive + G60	Rotary Universal Tribometer Steel Ball Steel Ball	---/ ---/ 40 N/ 1200 rpm [133]
SN/CF20W50 G60	Rotary Universal Tribometer Steel Ball Steel Ball	---/ ---/ 40 N/ 1200 rpm [133]
SN/CF20W50 G12	Rotary Universal Tribometer Steel Ball Steel Ball	---/ ---/ 40 N/ 1200 rpm [133]
SN/CF20W50 G8	Rotary Universal Tribometer Steel Ball Steel Ball	---/ ---/ 40 N/ 1200 rpm [133]
SJ/CF20W50 Additive + G60	Rotary Universal Tribometer Steel Ball Steel Ball	---/ ---/ 40 N/ 1200 rpm [134]
SJ/CF20W50 G60	Rotary Universal Tribometer Steel Ball Steel Ball	---/ ---/ 40 N/ 1200 rpm [134]
SJ/CF20W50 G12	Rotary Universal Tribometer Steel Ball Steel Ball	---/ ---/ 40 N/ 1200 rpm [134]
SJ/CF20W50 G8	Rotary Universal Tribometer Steel Ball Steel Ball	---/ ---/ 40 N/ 1200 rpm [134]
10W40 0.1wt% GO	Rotary Universal Tribometer GCr15 steel ball GCr15 steel ball	---/ ---/ 343 N/ 1200 rpm [135]
10W40 0.1wt% Ag/GN	Rotary Universal Tribometer GCr15 steel ball GCr15 steel ball	---/ ---/ 343 N/ 1200 rpm [135]
10W40 0.1wt% Sc-Ag/GN	Rotary Universal Tribometer GCr15 steel ball GCr15 steel ball	---/ ---/ 343 N/ 1200 rpm [135]

Table 10. Summary of the tribological studies of base lubricating oil [136-146].

Base Lubricating Oils	Geometrical Configuration/ Tribopair	Summary
Palm Oil	Reciprocating Universal Tribometer Grey Cast Iron/ Chromated Grey Cast Iron	For palm base oil the COF is 0.092 and wear scar diameter is 25.6mm.
Mineral Oil	Reciprocating Universal Tribometer Grey Cast Iron/ Chromated Grey Cast Iron	For mineral base oil the COF is 0.075 and wear scar diameter is 19.1mm. It was reported that mineral oil shows better tribological properties than compared to palm oil.
Rapeseed Oil	Four Ball Tester Steel/ Steel	Wear scar diameter of the base rapeseed oil is 0.63 mm.
Epoxy Rapeseed Oil	Four Ball Tester Steel/ Steel	Wear scar diameter of the base Epoxy rapeseed oil is 0.72 mm.
Epoxidised Soyabean Oil	Ball On Disc Steel/ Steel	Epoxidised Soyabean Oil exhibit lower COF due to the formation of polymeric Film on Metal Surface.
Hexadecane Oil	Ball On Disc Steel/ Steel	COF of Hexadecane Oil is reported to be 0.5
Jojoba Oil	---/---	COF of Jojoba Oil is reported to be 0.1
Safflower Oil	Ball On Disc Steel/ Steel	COF of Safflower Oil is reported to be 0.11
High-Oleic Safflower Oil	Ball On Disc Steel/ Steel	COF of High-Oleic Safflower Oil is reported to be 0.10
Methyl Palmitate	Ball On Disc Steel/ Steel	COF of Methyl Palmitate is reported to be 0.11
Sunflower oil (stearic acid, oelic acid, linoleic acid)	Reciprocating Universal Tribometer Steel/ Steel	It was reported that the addition of Linoleic acid in the sunflower oil hardly affect the wear, whereas the addition of Oelic acid improves the wear properties. It was reported that 0.5 wt% of the nano additive reduced the wear rate by 20% and for 5 wt% the wear rate is decreased by 30%. By the addition of 1 wt% stearic acid in the lubricating oil reduce the wear by 90%.
Soyabean Oil	Sequential Four Ball Tester Steel/ Steel	It was reported that with an increase in the temperature the oxidation of the lubricating oil increases.
High Oelic Sunflower Oil	Sequential Four Ball Tester Steel/ Steel	It was reported that High Oelic Sunflower Oil exhibit better tribological properties than Soyabean Oil and Epoxidised Soyabean Oil

Epoxidised Soyabean Oil	Sequential Four Ball Tester Steel/ Steel	Epoxidised Soyabean Oil exhibit better wear properties than compared to Soyabean Oil
Lubricating Oil (Glycerol+oelic acid)	Four Ball Tester Steel/ Steel	Wear scar diameter decreases from 0.84 mm to the range of 0.34-0.75 mm.
Benzotriazole Sulphur	Four Ball Tester Steel/ Steel	It was reported that sulfur based oil exhibit minimum improvement in wear scar diameter.
Dibutyl Phosphite	Four Ball Tester Steel/ Steel	Dibutyl Phosphite showed better performance by reducing the wear scar diameter to 0.53 mm
Oleic Acid Triester Lubricant	Four Ball Tester Steel/ Steel	Improvement in the anti-wear properties and pour point was reported. Improvement in the low-temperature properties due to ti increase in chain length of the midchain ester.
Stamping Oil	Four Ball Tester Steel/ Steel	It was reported that the Stamping oil exhibit m, minimum wear scar diameter of about 0.9 mm.
Commercial Hydraulic Oil	Four Ball Tester Steel/ Steel	It was reported that under extreme conditions the commercial hydraulic oils exhibit minimum COF.
Jatropha Oil	Four Ball Tester Steel/ Steel	Jatropha oil exhibit good tribological properties. It was reported that the wear scar diameter is about 3.1 mm.
RBD Palm Oil	Four Ball Tester Steel/ Steel	The wear scar diameter is about 3.9 mm in case of RBD Palm Oil
Lesquerella	Four Ball Tester Steel/ Steel	Lesquerella oil sample had the lowest COF of about 0.045.
Cuphea	Four Ball Tester Steel/ Steel	Cuphea oil is having maximum COF of about 0.096 but having lowest wear scar diameter of 0.530 mm.
Mewod Form Oil	Four Ball Tester Steel/ Steel	It was reported that Mewod Form Oil is the most oxidation stable oil.
[Blend] Jatropha Oil, SAE 40 (10, 20, 30, 40, 50%)	Pin On Disc Aluminum/ Cast Iron	It was reported that the maximum wear occurred with SAE 40 blend with 40% OF Jatropha Oil and minimum wear with 10% blend of jatropha oil. It was reported that the COF may remain almost the same for 10-40% bio-lubricant which is about 0.15, afterward it will increases to 0.225 for 50% blend.

Table 11. Summary of the tribological studies of lubricating oil with nano-additives[136-146].

Lubricant/ Nanoparticle Additive/ Particle Size/ Particle Concentration	**Geometric Configration / Tribopair**	**Summary**
Coconut Oil 20-150 nm 0.1-0.4 wt%	Four ball tester Steel/ Steel	COF decreases with an increase in the concentration of unmodified CuO up to 0.3 wt%. Coconut oil with CuO. Nanoparticles offer better tribological properties.
Coconut Oil Modified and Unmodified MoS_2 90 nm 0, 0.25, 0.50, 0.75, 1 wt%	Four ball tester Steel/ Steel	COF for unmodified MoS_2 nanoparticles is 0.052. Minimum COF for modified MoS_2 nanoparticles is 0.049 at a concentration of 0.52 wt%
Coconut Oil Cu 20-150 nm 0-0.6 wt%	Four ball tester Steel/ Steel	Minimum COF is obtained at 0.34 wt%.
Rapeseed Oil Micro MoS_2 Platelets, Nano MoS_2 Vesicles, Nano MoS_2 Platelets 1.25µm, 100 nm, 20 nm 0, 0.5, 1, 1.5, 2 wt%	Four ball tester Steel/ Steel	Nano MoS_2 Vesicles gives the best results with minimum COF which is around 0.06 at 1 wt%. It was reported that there is a decrease in the tribological properties while using Micro MoS_2 Platelets and Nano MoS_2 Platelets.
Rapeseed Oil TiO_2 20 nm 0-4 wt%	Four ball tester Steel/ Steel	Minimum COF and better anti-wear properties were obtained at 0.25 wt% concentration.
Rapeseed Oil Cerium-Doped Anatase 20 nm 0-4 wt%	Four ball tester Steel/ Steel	Beter tribological properties were obtained.
Chemically Modified Rapeseed Oil CuO 40-70 nm 0, 0.1, 0.5, 1 wt%	Four ball tester Steel/ Steel	Optimal COF and Wear rate is obtained at 0.5 wt% of the nano-additives. It was reported that there is an increase in the COF and wear rate beyond this limit.

Chemically Modified Rapeseed Oil CuO, WS$_2$, TiO$_2$ 70 nm, 40-80 nm, 30-35 nm 0.5 wt%	Four ball tester Steel/ Steel	It was reported that there is a decrease in the frictional torque by 21, 14 and 14.5 % for CuO, WS$_2$ and TiO$_2$ nanoparticle additives. Wear scar diameter is reduced by 39, 36 and 34 % for CuO, WS$_2$ and TiO$_2$ nanoparticle additives.
Chemically Modified Rapeseed Oil CuO CeO$_2$ <50 nm <50 nm 0.1-1 wt%	Four ball tester Steel/ Steel	COF is reduced by 40% as compared to the base oil. It was reported that 0.5 wt% of CuO gives the optimal value for the COF. For CeO$_2$ nano additive, the reduction in the COF is about 54% at the concentration of 0.1 wt%.
Palm Oil TiO$_2$ 22.97 nm 0, 0.05, 0.1, 0.2, wt%	Four ball tester Steel/ Steel	Minimum COF was obtained at 0.1 wt% of the TiO$_2$ nanoparticles.
Chemically Modified Palm Oil CuO, MoS$_2$ 127 nm 1048 nm 1 wt%	Four ball tester Steel/ Steel	Wear scar diameter is reduced by 1% , 4.95% and 6.65 % for CuO, 1% MoS$_2$ and 1% MoS$_2$ + 1% Surfactant respectively.
Palm oil based trimethylpropane (TMP) ester s TiO$_2$ --- 0.1 wt%	Four ball tester Steel/ Steel	COF and wear scar diameter is decreased by 15% and 11% with the addition of TiO$_2$ nanoparticles in the base oil.
Soyabean Oil Cu --- 1.5 wt%	Four ball tester Steel/ Steel	Soybean oil with Cu nano additive improves the tribological properties of the lubricating oil.
Soyabean Oil ZnO CuO 11 nm 4 nm ---	Four ball tester Steel/ Steel	It was reported that the minimum COF is for soyabean oil + ZnO nano additive followed by soyabean oil + CuO and than for epoxidized soyabean oil.
Soybean Methyl Ester Cu --- 1.5 wt%	Four ball tester Steel/ Steel	It was reported that the soybean oil had the least wear scar followed by Soybean Methyl Ester + 1.5 wt%
Rapeseed Oil, Stearic Acid TiO$_2$ 20 nm 0-4 wt%	Four ball tester Steel/ Steel	Rapeseed Oil + stearic Acid exhibited lower COF as compared to the Rapeseed Base oil.
Sunflower Oil ZnO CuO 11 nm 4 nm ---	Four ball tester Steel/ Steel	Epoxidised Sunflower oil exhibits minimum COF.
Canola Oil BN 70 nm 0.5, 1.5, 5 µm 5 wt%	Four ball tester Steel/ Steel	Maximum COF of 0.19 was reported for 5 µm particles and wear rate of 0.9mm^3.
Karanja Oil ZDDP --- 1-5 wt%	Four ball tester Steel/ Steel	2 wt% od ZDDP exhibit minimum wears scar diameter and COF. COF is 0.0424 for 2 wt% of ZDDP additive. It was reported that 2 wt% of ZDDP improve the pour point from -6˚C to 1˚c.
Rapeseed Oil, Oleic Acid Lanthanum doped TiO$_2$ 20 nm 0-4 wt%	Four ball tester Steel/ Steel	0.25wt% with rapeseed oil + oleic acid+ Lanthanum doped TiO$_2$ improved the friction and anti-wear capability of the lubricating oil.
LB2000 Vegetable Oil Graphite 35, 80 nm 0-0.25 vol%	Four ball tester Steel/ Steel	Minimum COF was obtained for 0.25 wt% of graphite particles of size 35 nm. It was also reported that the wear rate decrease with an increase in the concentration of the graphite particles.
Di Octyl Sebacate Micro MoS$_2$ Nano MoS$_2$ 500, 250, 125, 100, 10 nm 0, 0.25, 0.50, 1.0, 1.5, 2.0 wt%	Four ball tester Steel/ Steel	It was reported that the addition of MoS$_2$ particles in the Di Octyl Sebacate improved the tribological properties. Hence reduce the COF and wear rate.
Synthetic Oil ZnO CuO 11 nm 4 nm ---	Four ball tester Steel/ Steel	Improvement in the friction and wear properties.

Mineral Oil ZnO CuO 11 nm 4 nm ---	Four ball tester Steel/ Steel	It was reported that the addition of the nanoparticles in the mineral oil increases the wear scar diameter of the balls.
SAE 20W40 ZDDP --- 1-5 wt%	Four ball tester Steel/ Steel	Improvement in the COF, Wear properties, pour point and cloud point was reported.

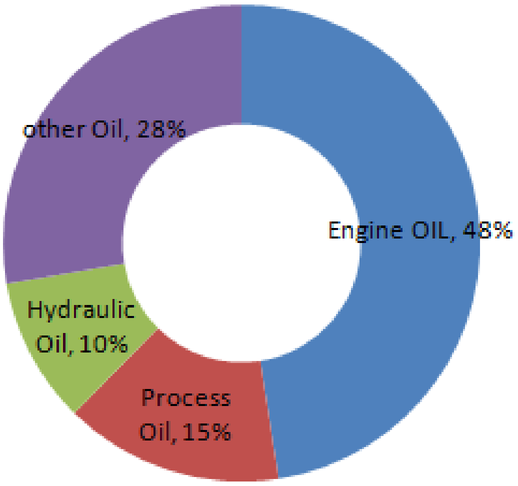
5.2 Lubricants and nanoparticles additives for automotive application

Eswaraiah et al. [114] studied the tribological properties of graphene as the antiwear, antifriction and extreme pressure additive in the engine oil. It was reported that there is an enhancement in all the three above-mentioned properties, attributed to the ball bearing lubrication mechanism by the nano-particles. Maleque et al. [126,127] experimentally studied the tribological behavior of palm oil methyl ester blended lubricant for steel cast iron tribopair for cylinder liner piston ring assembly. It was reported that the corrosion wear and pit are the main reason for the wear on the mating surfaces. It was observed that more than 5 % of the palm oil methyl ester in the lubricant causes oxidation and corrosion. Zulkifi et al. [52] studied the tribological behavior of Palm oil based trimethylpropane (TMP) esters, as an engine lubricant. Four-ball tester configuration was used for a boundary, hydrodynamic, elastic-hydrodynamics lubrication regimes. The blended lubricant consists of (5, 10, 15, 20 and 100 %) palm oil TMP ester. It was reported that the lubricant oil with palm oil TMP ester gives better performance as compared to the ordinary oil. Bekal et al. [55] studied the behavior of the Pongamia oil as the alternative for the mineral oil for the Internal Combustion Engine (ICE) application. In their study, three oil samples are prepared i.e. pure Pongamia oil, pure mineral oil and a blend of both the oils. Their samples were tested on the commercial four strokes, single cylinder, direct injection diesel engine. It was reported that in the Pongamia oil lubricant friction losses were less and it eliminates the emission of metal traces unlike in the mineral oil lubricant. Bhale et al. [62] studied the wear characteristics of a cylinder liner rings with diesel and biodiesel on a pin on disc tribometer. The pins and the disc are prepared from the actual cylinder liner and the top ring of the piston. The lubricating oil used in the blend of lube oil, jatropha oil methyl ester, and diesel. The lube oil with jatropha oil exhibit good friction and wear properties as compared to the lube oil blended with diesel. It was reported that the jatropha oil is having methyl ester double bond which led to the improvement in the lubricity of that lubricating oil sample. Suhane et al. [46] studied the behavior of non-edible vegetable coil as an alternative for the automotive applications. It was reported that bio lubricants used as the alternative for the automotive applications help in reducing the emission problem and also they are biodegradable in nature. Ting et al. [128] studied the tribological behavior of soyabean oil lubricant as the alternative for engine lubricant. Viscosity analysis was also reported so that it can fit the viscosity as required for the engine oil lubricant. It was reported that the soyabean oil seems to be good as the base oil for engine application. Nagendramma et al. [129] worked on the development of eco-friendly lubricants. It was reported that synthetic lubricating oil and vegetable oil based ester offer the best choices in formulating environmental friendly lubricant for automotive transmission fluids or automotive gear lubricants.

Charoo et al. [130] studied the friction and wear behaviors of different concentration of IF-MoS_2 nanoparticles additive in SAE 20W40 lubricating oil. The research experimentation was conducted at different operating condition parameters to ascertain the influence of nano additive on friction and wear of cylinder liner and piston ring trio pair. Tribometer test revealed that Individual Fullerence-MoS_2 as additive reduces the wear loss when compared to the lubricant without the nanoparticle additive. It was also reported that the reduction of friction and wear of cylinder liner and piston ring assembly is essential not only for increasing life of the IC Engine but it also beneficial for reducing fuel consumption and emission in an IC Engine. In another study, the tribological behavior of lubricant containing a different concentration of h-BN nano-particles into SAE20W50 engine oil was conducted. Charoo et al. [139] in another research studies, observed that the addition of nanoparticles to engine oil significantly improve the tribological performance in ICE applications. Arumugam et al. [131,132] studied the effect of bio-lubricants and biodiesel contamination lubrication on the tribological behavior of cylinder liner piston ring tribopair by using a pin on disc tribometer. The disc and pin material is white cast iron from the actual engine liner and piston ring. Four different lubricant samples were taken i.e. 10% bio-lubricant with SAE 20W40, 10 % B_2OR with SAE 20W40, 10 % diesel with SAE 20W40 and SAE 20W40. 10 % bio-lubricant with SAE 20W40 gives the best results for friction and wear as these lubricating oil samples exhibit better lubricity than other samples. It was observed that the engine's oil generated from the vegetable oil is eco-friendly biodegradable renewable and exhibit low volatility. It was reported that the COF is reduced by 23 % but the wear rate is increased by 12 % when compared to commercially synthetic oil lubricant. Sgroi et al. [153] experimentally investigate the anti-friction and anti-wear properties of MoS_2 and WS_2 in the fully formulated engine oil (SAE 5W30) to improve the performance of the lubricants. It was reported that MoS_2 nano-particles integrated into the additive package of engine oil showed a reduction of 50% in COF. The characterization was done on a bench test to simulate the real tribological conditions in the valve train diesel engine. Reduction in COF is reported in all the lubrication regimes. Lubrication mechanism was reported to the mechanical exfoliation action of a tribo-film on the contact surface. It was also reported that the engine head bench test was an unfired apparatus so it is difficult to account the effect of nanoparticles in an oxidizing atmosphere commonly present in Internal Combustion Engine. Nallusamy et al. [147] in their study reported that the nanoparticles are extensively used to increase the thermal conductivity, heat transfer rate and tribological properties of the engine lubricant by adding nano-additives to form nanofluids. In order to reduce the friction and wear, lubricants are used, but still, the fuel consumed for frictional losses is about ten to twenty percentages of the total fuel supply. In this study, they prepare nanolubricants by selecting suitable commercial engine oil, biodegradable oil, and nanoparticles based on tribological performance for multi-cylinder petrol engine applications. The copper oxide nanoparticles and SAE15W40 commercial engine oil and punga oil as biodegradable oil used. The nanolubricants were prepared by adding nanoparticles to the base oils with 0.1 % concentrations. It was found that, at working temperature between 60-80 ^{0}C, CuO with 0.1 % based nano lubricant has performed better than commercial engine oil for multi-cylinder petrol engine and hence the friction and wear of engine was found reduced. SAE15W40 with CuO nano lubricant have good anti-wear properties with wear scar diameter of 0.13 mm. But punga oil with CuO has better anti-friction properties than SAE15W40-CuO lubricant.

6. GLOBAL STATUS OF LUBRICATING OILS

During the last decade, there is a continuous rise in the demand for lubricant in the global market. It was reported that the global demand of lubricant in the year 1991 is approximately 35 million tons per year which rose up to 37.4, 37.9 and 41.8 million tons for the year 2004, 2005 and 2007 respectively [133]. The main contributors to lubricant consumption were automotive lubricants with 53 % followed by 32 % industrial lubricants, 10 % process oils, and 5 % marine oil. In the year 2014, the global market of the lubricants was 88,230.8 million dollar and it is expected to grow by 2.6 % by 2020 [134]. It was observed that the rapid industrialization in the Asia-Pacific region leads to the growth in the demand for lubricants. In the year 2017, the demand of the lubricant increases by 2.3 % and reach 43.9 million metric tons [135]. In the global market, it was also observed that the demand of biolubricants as an alternative for engine oils, hydraulic oils, marine oils are growing at the rapid pace. In the year 2015, 56 % of the demand for bio-lubricant comes from the engine oil and commercial automotive demand was about 43 % [136].



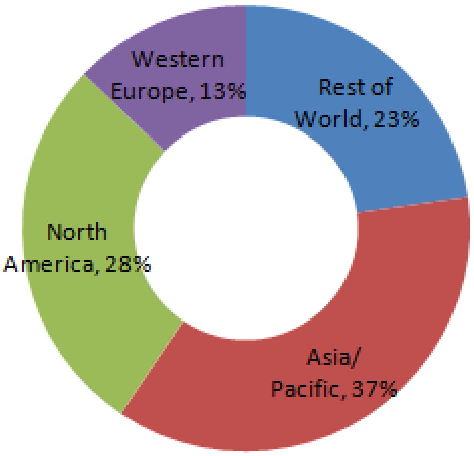


Fig 2. Classification of lubricating oil on the basis of applications and world market segmentation by geographical area [22].

Table 12. Summary of the lubricant demand growth by region based on the application area (2005-2015) [22].

Region/ Manufacturers	**Consumer-able Automobile %**	**Commercial Automobile %**	**Indust-rial %**
United States/ Exxon Mobil, Chevron, Valoviline, Conoco Phillips	0.25	0.5	0.5
China/ Petro China	10	6.5	7
Russia/ Lukoil	4	3	3
Japan/ Nippon Oil	1	-2	-1.75
India/ Servo, Max, Castrol, Shell, Gulf, Valvoline	4	3.5	3
Germany/ Fuchs	-3	-4	-2
Canada/ Petro Canada	1	2	1
United Kingdom/ BP, Shell	-2.25	-2.1	-2

India is an emerging global economy to the rapid growth of the industrialization. India placed fifth in the lubricant market after the United States, China, Russia, and Japan. In India, research on bio lubricants as an alternate for automotive applications is becoming the top priority as eco-friendly lubricants are nowadays gaining importance in the global market. The increasing demand of the lubricating oil in India will be aided by the ongoing expansion in the industrial manufacturing and automotive sector [137].

6.1 Current status of nano-additives in commercial lubricants

Lubricants Oil Additives (LOA's) are used to enhance the performance of the lubricants as well as functional fluids. Each additive is selected as per the specific or functional requirement. Selected additives are formulated into packages for use with specific lubricant base oil and for a specified application. The largest use is in the automotive engine applications. Some other applications are hydraulic fluid additives, gear oil additives, coolant and machining additives. In addition to this LOA's also presents in the industrial metalworking oils/ lubricants. The major functionally used additives types are dispersants, detergents, oxidation inhibitors, anti-wear agents, extreme pressure additives and viscosity index improvers. Some of the nano-material additives currently used in the commercial lubricants are fullerenes; carbon-based nano additives; ceramics; sulfides; oxides; polymers, etc. Current advances in using nanomaterials additives in engine oil, industrial lubricants, and grease are discussed below. Fullerenes are the cyclic molecules that are claimed to enable rolling lubrication mechanism. Inorganic Fullerenes (IF) comprises another class of nano-additives with fullerenes. IF is marked as the extreme pressure/ anti-wear additives for engine oils, gear lubricants, and greases, yet their applications so far are very limited. Nano-diamond and carbon-based additives are another class of the additives that are claimed to embed into the sliding surfaces rendering them more resistant to wear, enable rolling lubrication, micro-polishing effect between the surfaces, thus reducing friction and wear. Oxides, sulfides, polymers are also the commonly used additives in metalworking fluids, engine oil, and other commercial lubricants because of their extreme pressure/ anti-wear additives properties. By replacing sulfur phosphorous and ZDDP by boric acid and PTFE as nano additive, it is hoped to eliminate the main source of environmental hazardous emission and waste. PTFE- fortified oils and greases are known to exhibit higher welding loads, higher load wear index and reduced stick-slip. Results of numerous studies combined with formulation experiences strongly suggest that nanomaterials do indeed have the potential for enhancing certain lubricant properties. Nano-additives are used in a number of aftermarket engine treatment products, yet there is a long way to go.

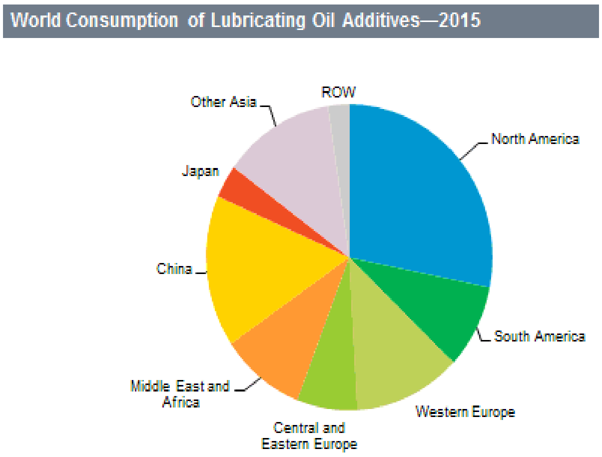


Fig 3. Summary of the world consumption of lubricating oil additives [26].

7. SUMMARY AND FUTURE SCOPE

The paper presents the state of art related to the tribological behavior of lubricants with nano-additives, performance parameters for nanoparticles additives and lubrication mechanism of nanoparticles additives. The majority of the research conducted claimed that the nanoparticles as additives in lubricating oils enhance the performance of lubricants. The lubrication mechanism of nanoparticles was also reported in this paper. The lubrication mechanism seems to be much complex to understand, as there is a large number of nanoparticles as each nanoparticle work in a different manner for different applications. Nano-particles performance (as an additive in lubricating oils) parameters were also reported in this paper. Dispersion stability of the nanoparticles is the most important performance parameters which are to be maintained for better performance of the lubricants. It was reported that various dispersion techniques, surface modification of nanoparticles and surfactants are used for uniform dispersion of the nanoparticles in the lubricants. Another important issue of biodegradability and the global energy crises were also reported in the paper which focuses on the development of biodegradable bio lubricants as the alternative for mineral oils. Biolubricants seems to be the potential alternative for automotive and industrial applications. Moreover, for the future scope, it is important for the researchers to find the sustainable solution to reduce the frictional and wear. Future studies must be directed toward the development of new nano additives, chemically modified lubricants, hybrid lubricants for various automotive and industrial applications, new lubrication mechanism and other various performance parameters which affect the tribological properties of the lubricants and nanoparticles additives are needed to be investigated.

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