Chapter-2

Literature Review

This chapter summarizes the past work done by the various researchers in the field of lubrication. It includes the oil composition, properties of the base oils and their synergistic effect with additives in tribological prospects. Evolution of the lubricant additive gives an insight into the transition from SAPS (sulfated ash, phosphorus, and sulfur) containing additive (hazardous) to nanoparticles (non-hazardous), considering environmental issues. The role of different types of additives and a hypothetical mechanism to improve tribo-performance creates an explicit background of the work. At last objective of the thesis work ends this chapter.

2.1. Background

Worldwide increasing industrialization and motorization has increased the petroleum product demand. Petroleum based stocks are limited and concentrated in specific regions in the world. These are non-biodegradable and affect our environment in every state. Therefore, alternatives to this petroleum base-stock are necessary to explore. On considering environmental health aspect, the researcher focused to develop the biodegradable, non-toxic and renewable lubricants to replace the mineral oil base stock (Gnanasekaran and Chavidi 2018; Honary and Richter 2011). The environment is being negatively affected directly or indirectly by the large use of lubricant in industries and commercial applications. Lubricant loss contaminates the water and soil directly while volatile lubricant or lubricant miasma influences the air indirectly (Rizvi 2009). Therefore, all the concerns regarding environment protection must consider at every stage (i.e. production, application, and disposal) of the lubricants. Vegetable oils are the potential source of lubricant regarding biodegradability, renewability, non-toxicity, eco-friendly and lubrication performance, except the limitation of poor thermo-oxidation and low temperature performance (Adhvaryu et al. 2004; Kumar et al. 2016). A big question is; can vegetable oil be a good base stock to replace petro-product? Numerous researchers carried out to overcome its inferior thermo-oxidative properties, fulfilling all the requirements for ideal and economic lubricants (Kashyap and Harsha 2016). It includes modification of the vegetable oils by chemical method or the use of low/zero SAPS (sulfated ash, phosphorus, and sulfur) additive (Rastogi et al. 2013).

Vegetable oils have a long hydrocarbon chain along with the polar group, which makes it amphiphilic surfactant. It helps in proper adherence of the lubricant with the metal surface forming a monomolecular layer, thus suitable for both boundary and hydrodynamic lubrication situation (Jahanmir and Beltzer 1986; Jain and Suhane 2012). Various researchers reported the improved thermo-oxidative stability of vegetable oils i.e. rapeseed oil (Wu et al. 2000), soybean oil (Doll and Sharma 2012; Castro et al. 2006), coconut oil (Mannekote and Kailas 2011), sunflower oil (Campanella et al. 2010), jojoba oil (Bisht et al. 1993). However, tribological properties of the vegetable oil depending on the variation of the fatty acid compositions. It affects lubricating properties, the formation of protective film thickness, friction, and wear (Biresaw and Bantchev 2008). The vegetable oils alone are not capable of performing at par with the mineral or synthetic oil without additives. Thus additives are essential for achieving the intended function. This is because of additives may behave in different and/or complex way between the mating surfaces that result in protective film formation capability thus friction and wear (Biresaw and Bantchev 2008).

2.2. Base oils: Composition and properties

2.2.1. Petroleum based oils

Petroleum base stock is a natural substance and produced by the decomposition of plants, animals and other living organisms inside the earth crust with the passing of the time. According to the crude oil source, oil composition varies distinctly, and it is categorized as, i.e. paraffinic, aromatic and naphthenic compounds (Shahnazar et al. 2016). Crude petroleum base stock consists of a majority of covalently linked hydrocarbon molecule (e.g., paraffin, aromatic, etc.) and low amount of sulfur, nitrogen, metal trace, etc. Many refining procedures are performed to remove the minor elements such as sulfur and nitrogen along with average molecular weight reduction (called as cracking) of paraphenes to prevent wax deposition during lubrication. Most commonly used petro-product, e.g. mineral oils are also produced by fractional distillation and refining. The mineral oil consists of numerous positive properties like availability, excellent oxidation stability, low cost including some shortcomings like low temperature solidification, viscosity loss.

2.2.2. Synthetic oil

Synthetic oils are artificially-made which possess predicted lubricating properties with unique molecular structure. These oils consist of high molecular weight compounds formed by chemical modification of petroleum products rather than crude oil. Synthetic oil exhibits superior thermal and oxidation stability, viscosity index and biodegradability as compared to mineral oils. Therefore the worldwide application of synthetic oil is increased undeviatingly where mineral oil cannot sustain. From chemical composition, synthetic oils are classified as synthetic hydrocarbon (polyalphaolefins, ester, polyalkylene glycols), silicon analogues hydrocarbon (silicones, silahydrocarbons), organohalogen, polyether oils, etc. (Shahnazar et al. 2016). The properties of the synthetic oil can vary according to the applications, but production cost is very high.

2.2.3. Vegetable oil based biolubricants

Environmental concern focused on exploring such oil that degrades after use with the passing of time. Biolubricants are lubricants based on natural resources like plants and animal fats. Bio means anything that touches natural material and lubricant implies oil used to reduce the friction and wear. Biodegradability is defined as the susceptibility of a substance to undergo degradation under the influence of biological agents such as bacteria, fungi, yeast etc. Vegetable oils are considered in the category of biolubricant. The fact that vegetable oils are renewable, degradable and non-hazardous, therefore concentrated attention is being made to use as biofuels, industrial and commercial lubricants (Honary 2001). Biodegradability of few base oils shown in Table 2.1, shows that vegetable based oils are mostly degradable than the other oils (Gnanasekaran and Chavidi, 2018). Mostly used vegetable oils- soybean, olive, cottonseed, sunflower, castor, rapeseed, coconut, palm, canola and less commonly used vegetable oils-rice bran oil, tiger nut oil, niger seed, piririma oil, and much more (Aluyor et al. 2009). The main constituents of oils and fats are mixture of fatty acid esters of trihydroxy alcohol (Nwobi et al. 2006). In other words, the significant content of vegetable oil is triglycerides. These triglycerides are simply glycerol molecules with three long chain fatty acids attached to hydroxyl group through ester linkages (Shashidhara and Jayaram 2010).The minor contents are mono and diacylglycerols, free fatty acid, phosphatides, sterols, fatty alcohol, fat soluble vitamins, etc. Different fatty acids combined in ester have different chemical structure causes variation in bonding forces, which are responsible for different melting points of fats. These differences are also accountable for various chain length, the presence or otherwise unsaturation.

Table 2.1. Biodegradability of different base oil (Gnanasekaran and Chavidi, 2018).

Base oil	Biodegradability (%)
Mineral oil	20-40
White oil	30-55
Polyols	70-100
Poly Alpha Olefin	30-55
Esters	75-100
Vegetable oil	90-100

Table 2.2. Composition of common vegetable oils (Honary and Richter 2011).

Base oil	Mono-unsaturates (%)	Poly-unsaturates (%)	Saturates (%)
Olive	75	11	14
Canola	58	36	6
Peanut	49	34	18
Palm	39	10	51
Corn	25	62	13
Soybean	24	61	15
Safflower	13	78	9
Coconut	6	2	92

If the fatty acids have single carbon-to-carbon bond it is termed as saturated, whereas one or more carbon-to-carbon double bond is termed as unsaturated. If there is one double bond present in fatty acid then it is known as monounsaturated, while more than one double bond called as polyunsaturated. The composition of most commonly used vegetable oils presented in Table 2.2.

2.3. Characteristic of biolubricants and approach to improve thermo-oxidative stability

2.3.1. Effect of fatty acid composition on tribological properties

Triglyceride structure plays a vital role in vegetable oil as a lubricant. On one hand, triglyceride helps in formation of high strength tribo-film on the metallic surface to reduce friction and wear. On the other hand, triglyceride structure limits the vegetable oil as a lubricant. In fatty acids, unsaturated double bonds act as active sites where various desired or undesired reactions take place. It includes oxidation of biolubricants that lowers the thermo-oxidation stability and causes hydrolysis. The strong intermolecular interactions are also responsible for inferior low temperature performance of vegetable oils (Fox and Stachowiak 2007). Since fatty acids have different chain length and number of double bonds, therefore the fatty acids compositions are evaluated by the position of carbon-carbon double bond. Mostly the vegetable oil comprise one, two or three double bond (termed as oleic, linoleic, and linolenic fatty acid components respectively) in long hydrocarbon chain (Mongkolwongrojn and Arunmetta 2002; Orsavova et al. 2015). Chemical compositional structure, physico-chemical properties, and application of different vegetable based oils presented in Table 2.3.

Reeves et al. (2017) studied the antiwear and antifriction behavior of different vegetable oils viz. safflower, corn, soybean, sesame, peanut, canola, olive and avocado oil. They reported that different vegetable oils have distinct tendency to form the protecting film depending upon its fatty acid composition, which reflects the tribo-performance.

Table 2.3. Structure of fatty acid, physico-chemical properties and application of different vegetable oils.

Common name	C:D	Base oil						
		Coconut	**Rapeseed**	**Palm**	**Avocado**	**Linseed**	**Soybean**	**Jatropha**
Saturates								
Lauric acid	12:0	57.18	-	-	0.09	-	-	-
Myristic acid	14:0	18.7	-	1.5	0.15	-	-	-
Palmitic acid	16:0	4.82	9.8	43.0	30.91	5.0	1.5	12-17
Stearic acid	18:0	0.82	1.6	5.0	1.17	3.0	4.3	6.7
Arachidic acid	20:0	Traces	9.2	0.5	0.25	-	-	-
Behenic acid	22:0	Traces	-	-	0.12	-	0.5	-
Unsaturates								
Palmitoleic	16:1	-	-	-	10.06	-	10.4	-
Oleic acid	18:1	0.56	18.4	40.0	34.79	22.0	24.4	37-63
Linoleic acid	18:2	2.84	16.8	10.0	8.67	17.0	51.6	19-41
α-Linolenic acid	18:3	0.1	6.5	-	0.82	52.0	7.7	-
Erucic acid	22:1	-	37.7	-	-	-	-	-
Physico-chemical Properties								
Viscosity (@40˚C, mm^2/s)		28.56	4.45	5.72	36	3.74	4.05	4.82
Density (kg/m^3)		924	880	875	903	890	885	878
Oxidation stability 110˚C (h)		30 (at 185˚C)	7.5	4.0	-	0.2	4.05	2.3
Flash point (˚C)		278	240	260	271	222	240	240
Application								
		Biodiesel engine fuel	Chain saw bar lubricant	Steel industries	Automotive lubricants	Paints, varnishes	Biodiesel fuel	Greases
Reference		Koshy et al. 2015; Ghazali et al. 2009	Joseph et al. 2007	Krishna et al. 2014; Leslic et al.2006	Indriyani et al. 2016	Popa et al. 2012	Siniawski et al. 2007	Pramanik 2003

2.3.2. Improvement in oil stability

2.3.2.1. Modification of the base oil

- *Chemical modification of vegetable based oil*

- Modification of carboxyl group

  Esterification

  Transesterification

- Modification of fatty acid chain

Esterification is the reaction in which a carboxylic acid combines with an alcohol in the presence of an acid catalyst to form an ester. Little concentrated sulfuric acid usually selected as a catalyst. The esterification reaction is both slow and reversible, given in equation:

$$RCO_2H + R'OH \leftrightarrow RCO_2R' + H_2O$$

Transesterification is a process in which interexchange between organic group R'' of an ester and organic group R' of alcohol takes place. And in this organic reaction ester is transformed into another through alcohol moiety interchange (Schuchardt et al. 1998). The generalized transesterification reaction is given by:

$$RCOOR' \quad + \quad R''OH \xleftrightarrow{catalyst} RCOOR'' + \quad R'OH$$

Modification in fatty acid chain improves the biolubricant properties. It leads to the formation of C-C and C-O bonds to enhance oxidation property. Since the double bond is the most prone location in the fatty acid chain to act as the reactive site, therefore it can be functionalized by epoxidation. In this process, three membered oxirane ring or epoxides are being formed by combining of an oxygen atom with an olefinically unsaturated molecule. By epoxidation oxygen stability of vegetable based oil is improved (Saurabh et al. 2011).

- *Genetic modification of oilseed crops*

Genetic engineering helps to modify the oilseed crop by inserting additional DNA. One or two genes are added in crop to modify the particular characteristics to improve their existing property. There are two types of genetic modification of crop, first, to alter the input trait (like herbicide tolerance) called as a first generation genetically modified crop. And second, to change the output traits (such as structure, fatty acid chain length etc) resulting in different composition compared to non genetic modified crops called as a second generation genetically modified crop. To produce a wide range of modified oil for industrial application new kind of crop, breeds developed by various methods like genetic engineering, backcrossing, inbreeding, hybrid breeding etc. (Cahoon and Kinney 2005; McKeon 2005). High oleic soybean oil and sunflower oil produced from genetically modified plants showed improved oxidation stability, higher load carrying capacity and excellent antiwear property (Adhvaryu and Erhan 2002).

2.3.2.2. By using chemical reagent in base oil

Literature shows that the tribo-chemical properties of vegetable oil improved significantly with the small amount of chemical compound additive. In internal combustion engine test rig, the blend of 2%w/v of zinc dialkyldithiophosphate (ZDDP) in base coconut oil enhanced the tribological property significantly by lowering the friction and wear (Jayadas et al. 2007). Rapeseed oil with functional additives such as triethanolamine oleic acid and triethanolamine oleate enhanced both tribo-performance and thermal stability (Dmitrieva et al. 2001). Soybean oil in three modes, i.e. soybean 25% oleic, soybean 85% oleic and epoxidized soybean with organosulfur phosphorous, phosphorodithioate, and amine phosphate was used to study the effect on tribological properties. Organosulfur phosphorous and phosphorodithioate reveals well antiwear behavior with soybean 25% and 85% oleic but not much useful with epoxidized soybean oil. While amine phosphate shows improved properties in all condition (Castro et al. 2005).

2.4. Additive evolution

2.4.1. Low SAPS lubricant additive

Modern engine lubricant limits the use of sulfur, phosphorus, and sulfated ash either present as an active element or generated during the application. This is because of sulfur and phosphorus oxides along with metallic ash produced from additive, hazardous to the environment. Also, in the automobile application, it blocks the exhaust after treatment filter that used to suppress the engine exhaust and to reduce air pollution.

Zinc dialkyldithiophosphate (ZDDP) is one of the multifunctional low SAPS additive used in the lubricant to improve mainly antiwear property along with antioxidant and corrosion inhibitor. ZDDP contains four sulfur atoms, two phosphorus and one zinc atom in each molecule. Zinc tends to form ash. Although ZDDP has a substantial negative impact on the environmental health, in spite of this it is being used to date. This is because no other lubricant additive can perform in a multifunctional way with the minimum addition in the lubricant. Researchers are exploring the alternative to ZDDP that can perform at least at par with ZDDP and environment friendly. Spikes (2008) suggested the alternative of ZDDP with the presence and/or absence of the sulfur, phosphorus and metal and these presented in Table 2.4.

Table 2.4. Possible ZDDP substitutes by low- and zero- SAPS additives (Spikes; 2008).

Phosphorus	Sulfur	Metal	Lubricant additive
Y	Y	Y	Metal dialkyldithiophosphates (here metal is not Zn)
Y	Y	N	Thiophosphate
Y	N	Y	Metal dialkylphosphates
Y	N	N	Phosphates, amine phosphates
N	N	Y	Organometallics (e.g. Ti, Sn compounds)
N	N	N	Organoboron compounds
N	N	N	Halide Compounds
N	N	N	Zero SAPS
N	N	N	N and O Heterocyclics
Y: Present and N: Absent atoms			

Concerning antiwear property, only environment hazardous metals, i.e. lead and cadmium containing metal dialkyldithiophosphates (MDDP) is capable of performing like ZDDP (Born et al. 1992). Phosphorous and sulfur free organometallic additives also show good antiwear performance. Moreover, lead naphthenate and organocadmium additives have superior antiwear and extreme pressure properties, but not acceptable due to hazardous exhaust impact (Didziulis and Fleischauer 1991, Spikes 2008).

2.4.2. Zero-SAPS lubricant additive

Table 2.4 also represents SAPS free lubricant additives. Boron containing compounds as a lubricant additive widely studied in boundary lubrication (Choudhary and Pande 2002). Liu et al. (1993) studied the tribo-performance of tri-borate ester series having $(R^1O)(R^2O)(R^3O)B$ structure. They found improved antiwear and antifriction properties with all the esters. However, superior performance observed with the esters with longer chain length. Jaiswal et al. (2014) examined the tribo-performance of SAPS free and schiff bases of 4-aminoantipyrine with benzaldehyde, salicylaldehyde, *p*-chlorobenzaldehyde and *p*-methoxybenzaldehyde and their synergistic interaction with borate ester in paraffin oil. They reported that all the Schiff bases with borate ester show good tribological properties; however, *p*-methoxybenzaldehyde exhibits the best results. Also, the synergy of donor–acceptor complex between nitrogen and boron results in improved performance by forming a durable protective film.

2.4.3. Nanoparticles as a lubricant additive

Due to the variation in severity of the operating conditions and correspondingly equipment development, it requires to explore new kind of additives. It should also be optimized in concentrations so that lubricants must be effective and economical. In this prospect nanoparticles are most effective additives to meet these demands. The nanoparticle application in base oil improves the antiwear property and reduces the friction as well. But the effectiveness of nanoparticle in the base oil strongly depends upon parameters such as size, shape, and concentration. Surface modification of the nanoparticles may also help in indirect tribological improvements. The nanoparticles, e.g. ceramic, metallic or polymeric, etc. blended in base oil by using various methods like mechanical or magnetic stirring, ultrasonication to formulate the nanolubricants. The tribo-performance of some nanolubricants containing different nanoparticles is discussed in subsequent sections.

2.4.3.1. Metallic nanoparticles

Various authors studied with metallic nanoparticles in different types of the base oils and reported the distinct results of formulated nanolubricants (Table 2.5). They also observed a significant variation in the tribological results with all the nanoparticles parameter.

Table 2.5. Summary of tribo-performance for nanolubricants with metallic nanoparticles.

Base oil	Nanoparticle	Operating/Variable parameter	Test rig	Findings	Ref.
500SN (Mineral oil)	Ni; 10 nm	0.25 to3.0wt% concentration	Four ball	Weld load ↑ 67 %. AW improved by 33 % μ ↓ by 26 %	Qui et al. (2001)
Paraffin	Pd ; 2 nm	5wt% concentration, RT, Relative humidity 40%	Pin-on-disc	• 97% Contact electrical resistance↓ • μ ↓	Kolodziejczyk et al. (2007)
50CC oil	Cu	T: 50, 80, 110 and 140°C, Concentration: 0.2wt%	Four ball	AW and AF↑ at 140°C	Yu et al. (2008)
Raw oil	Cu; 25 and 60 nm	L 500-3000N 0.1%w/v	Disc-on-disc	μ↓ by 44 % for 25 nm and 39 % for 60 nm.	Choi et al. (2009)
PAO6	Ni; 20nm	0.5-2.0 wt% concentration	Block-on-ring and four ball	μ ↓ by 30%, wear↓ by 45% load-wear index↑ by 30.8%	Chou et al. (2010)
PAO6	Cu; 25nm	0.5-2.0wt% concentration	Block-on-ring	0.5wt% optimum AW and EP↑	Viesca et al. (2011)
SAE 10	Fe, Cu, Co and combination	0.5wt% concentration kept constant either separate or in combination	Four ball	• 1.5 times reduction in friction and wear. • Cu combination show good tribo-performance	Padgurskas et al. (2013)
Liquid paraffin	Cu; 3.5 nm	L 200-400N 0.2-1.0wt%	Four ball	AW and AF improved	Zhang et al. (2015)
SAE 40	Cu; 50 & 130 nm	RT(25°C) 0.001 to 1.8m/s	Ball-on-flat	μ ↓ by 17% with 130 nm while no effect with 50 nm	Zin et al. (2015)
SAE 10 and Rapeseed	Fe	Size variation 50-340 nm 0.1wt% concentration	Four ball	At 0.1wt% μ ↑ but AW↓; 50-140 nm was optimum.	Maliar et al. (2015)
PEG	Ag	1.5 to 4.5mM concentration	Pin-on-disc	μ ↓ by 35% and AW↑ 4.5mM optimum.	Ghaednia et al. (2016)
Glycerol	Al	0-1wt% concentration,	Thrust collar	At 0.6667wt% concentration, friction and wear minimum.	Le et al. (2017)
AW: antiwear, AF: antifriction, μ: COF, L: load, RT: room temperature, T: temperature, ↑: increase/improve, ↓: decrease/impair					

2.4.3.2. Metal oxide nanoparticles

Numerous metal oxide nanoparticles were also used in different base oils to investigate the tribo-performance in different contact configurations. Various authors reported both improved and impaired properties for the oxide nanoparticles based nanolubricants. It is not necessarily to improve all the tribological properties (either antiwear, or extreme-pressure) with one kind of nanoparticle in the same oil. For example, Battez et al. (2006) worked out with ZnO nanoparticles up to 3wt% in PAO6. They used two dispersing agents (OL100 and OL300) along with ZnO nanoparticles and found that OL300 is better dispersant. From the experimental results, they argued that ZnO nanoparticles are not good as an antiwear additive, however good extreme pressure additive with PAO6 at 0.3% concentration in presence of 3% OL300. Moreover, rest of other concentration of OL300 and ZnO impaired the tribo-properties. In a further study, Battez et al. (2007) also performed a comparative extreme pressure study for PAO6 containing CuO, ZnO and ZrO_2 nanoparticles in 0.5, 1.0 and 2.0wt% concentration separately using four-ball tester. CuO showed better tribological behavior while ZrO_2 performed worst. ZrO_2 nanoparticles behave similar regardless of the concentration.

For the development of nanolubricants, it may be interesting questions that; (i) how same nanoparticles having different morphology can behave in the same oil, (ii) what may be the possibility to influence the tribological behavior. Gao et al. (2013) worked out with similar queries and observed the morphology effect (hexagonal, octahedral, and irregular shape) of magnetic nanoflakes in base oil and reported hexagonal shape of the nanoparticle shown superior antifriction properties. The summary of some key literature of oxide based nanolubricants and tribological performance has been presented in Table 2.6.

Table 2.6. Summary of tribo-performance for nanolubricants with oxide based nanoparticles.

Base oil	Nanoparticle	Variable parameter	Test rig	Findings	Ref.
SAE 40CD	a. CeO_2 b. $CaCO_3$	0.2, 0.4, 0.6, 0.8 and 1.0wt% concentration	Four ball	• EP↑ by 40.25% • 0.6wt%, mixture of a and b is optimum • AW↑ 33.5& µ↑32%	Caixiang et al. (2008)
20[#] mineral machine oil	ZrO_2	0.1 to1.0 wt% concentration	Thrust-ring	0.5wt% optimum µ↓ by 27.34%	Ma et al. (2010)
Liquid paraffin	SiO_2 ; 58nm	0.0125, 0.025, 0.05, 0.1 , 0.2, 0.5, 1, 2, 4 wt% concentration	Ball-on-ring	0.0.05 to 0.5wt% improved AW and AF.	Peng et al. (2010)
Mineral oil	Composite Al_2O_3/SiO_2 ; 70 nm	0.05,0.1,0.5,1 %	Four ball & thrust-ring	In four ball tester with 0.5 % NP, µ↓ by 20 % & AW↑ by 22 %.	Jiao et al. (2011)
20[#] mineral machine oil	ZrO_2/SiO_2	Time 30 min (constant) 0.05 to 1.0wt% concentration	Thrust-ring	0.1wt% optimum µ↓ 16.24%	Li et al. (2011)
Liquid paraffin	MoS_2/TiO_2	Time 30 min L 100-650N Speed 0.2-0.8m/s	Four ball	AW↑	Hu et al. (2011)
Liquid paraffin	Y_2O_3	0.05, 0.1, 0.25, 0.5 and 1.0wt% concentration	Four ball	Weld load↑ by 25% Sintered load↑ 26.9%	Yu et al. (2012)
Base oil	a.TiO_2 (P25) b. TiO2 (anatase)	L 14.715 & 0.05 m/s (constant)	Pin-on-disc	Anatase phase TiO_2 is superior than commercial TiO_2 (b) AF↑	Ingole et al. (2013)
Modified palm oil	TiO_2	Time 10 min. RT L 40, 80, 120, 160 kg	Four ball	At 160 kg AW↑ by 11% and µ↓ 15%	Zulkifli et al. (2013)
Mineral oil(#40)	Fe_2O_3	0-2.0wt%	Four ball	AF↑	Xiang et al. (2014)
Lubricati-ng oil	Al_2O_3	0.05-1.0wt% concentration	Four ball & thrust-ring	0.1wt% optimum AF↑ 23.92 and AW↑ 41.75% (maximum)	Luo et al. (2014)
a.PAO8 & b.SAE75 W -85	CuO and Al_2O_3	0.5, 1.0 and 2.0wt%	Ball-on-disc	AW↑ 18% AF↑ 14% EP↑ 14 (a) & 273% (b) with CuO	Peňa-parás et al. (2015)
AW: antiwear property, AF: antifriction property, EP: extreme pressure property, µ: COF, L: load, RT: room temperature, T: temperature, ↑: increase/improve, ↓: decrease					

2.4.3.3. Polymeric nanoparticles

Some researchers also used polymeric particles in the base oils to evaluate the antiwear and friction characteristics using various test rigs. For example, Rico et al. (2007) used polytetrafluoroethylene (PTFE) nanoparticles in different concentrations (1.0-10 wt%) in SN350 and Bright Stock as mineral base oil having different viscosity. They examined wear scar, LWI and weld point with varying compositions of the oil. They reported that with a gradual increase in the concentration wear scar reduced as well as LWI and weld point (from 160 to 630 kgf) increased. They also recognized the effect of contact angle for different test oils on their performance and found in line relation of concentration increment and contact angle which is directly proportional to improvement in tribological properties. Dubey et al. (2013) studied PTFE based nanolubricants with four ball tester and compared the results with Optimol-SRV III oscillating friction and wear tester. They used four different sizes 50, 150, 400 nm and 12μm and three concentrations viz. 4, 8 and 12wt% in 150 N API Group II base oil. They reported that lower size is more efficient to improve tribo-performance with increase the PTFE concentration. Maximum 40% reduction in COF was reported with 12wt% of PTFE while wear scar reduced by 20% for 50 nm particle size.

2.4.3.4. Carbon allotropes

Carbon allotropes like a diamond, carbon sphere, graphene, single and multiwall carbon nanotubes, etc. are also a recent trend to use as a lubricant additive. Among all, graphene is a nascent carbon allotrope. Song et al. (2016) studied two forms of carbon allotropes i.e. carbon sphere (CS) and flaky graphene oxide (GO) as an additive in sunflower oil to correlate suspension stability and tribo-performance. They found flaky structure exhibits good suspension, thus better tribological results. In brief, Table 2.7 represents a summary of tribo-performance for carbon allotropes based nanolubricants.

Table 2.7. The summary of tribo-performance of different lubricants with carbon allotropes as an additives.

Base oil	Nanoparticle	Operating/ variable parameter	Test rig	Findings	Ref.
API-SF engine oil	Nano-diamond; 10nm & CuO	1.0wt% concentration L 200N, speed 0.12 m/s	Recipro-cating tester	AF ↑ but CuO better than nanodimond.	Wu et al. (2007)
Poly-alpha-olefin	Ni-CNT	Speed 2.5 m/s, RT, 0.1wt% concentration (const.) L 2, 5, 10N	Pin-on-flat	Significant AW↑ Mild AF↑	Joly-Pottuz et al. (2008)
Industrial gear oil	Graphite; 55nm	L 0-3000N, speed 1000rpm & concentration 0.1 and 0.5 vol% and	Disc-on-disc	0.5wt% is optimum, AF↑ AW↑	Lee et al. (2009)
Mineral oil	Carbon nanocapsule; 40-80 nm	0.1-1.0wt% concentration & Speed 0.55-1.65 m/s	Ball-on-ring	Friction improved at 0.05wt% and 1.65m/s.	Jeng et al. (2014)
Mineral oil	Nano-diamond	L 391N, &speed 1200 rpm (constant) 0-0.01wt% concentration	Four-ball	AW and AF↑ at 0.01wt%.	Marko et al. (2015)
Engine oil (SAE 40)	Carbon nanohorns (SW); 80nm	RT(25°C) 0.001 to 1.8m/s	Ball-on-flat	µ↓ by 12%	Zin et al. (2015)
LB2000 vegetable oil	Graphite; 35 and 80 nm	L 2, 10N; Speed 100 rpm, 0.05 & 0.25wt% concentration	Pin-on-disc	• 35 nm better than 80 nm. • At both loads 0.25wt% improved AW and AF↑	Su et al. (2015)
Sunflower oil	a. carbon sphere (1.8-2.2 µm) b. flaky graphene oxide	L 5N and speed 300 rpm (constant) 0.5-3.0wt% for a 0.1-1.0wt% for b	Ball-on-disc	• 0.3wt% optimum for graphene oxide. • AF↑ • Flaky structure better than sphere.	Song et al. (2016)
Marine engine oils	Nano-diamond	L 300N and speed 0.216 m/s (constant) & 0.1, 0.3, 0.5, and 1.0% concentration	Ball-on-disc	• 0.3 wt% optimum • AW and AF↑ • High concentration cause high wear	Kim et al. (2016)
Oil, and water	single- and multi-walled CNT	p 0.8 and 1.1 GPa, 0.01 and 0.05wt% concentration	Twin-disc	0.01wt% for multi-walled CNT in oil and 0.05wt% for single-walled CNT optimum in water	Cornelio et al. (2016)
AW: antiwear property, AF: antifriction property, µ: COF, L: load, RT: room temperature, T: temperature, ↑: increase/improve, ↓: decrease, p: pressure					

2.4.3.5. Other nanoparticles

Excluding the metal, metal oxide, polymer, and carbon allotropes, other nanoparticles have also been explored by the various researchers to evaluate the tribo-performance of the base oil. Also, a substantial improvement reported in terms of wear resistance antifriction properties of different lubricant as presented in Table 2.8.

Table 2.8. The summary of tribo-performance of other types of nanoparticles as a lubricant additive.

Base oil	Nanoparticle	Operating/ variable parameter	Test rig	Findings	Ref.
Liquid paraffin	ZnS (4 nm)	Concentration 0.05-0.4wt%; L: 100,200,300,400 ; N:1450, t:30	Four ball	0.1wt% is optimum. Antiwear↑ Load carrying capacity↑	Liu and Chen (2000)
Paraffin oil	WS_2 (100 nm)	v: 0.6 L:100-500	Pin-on-disc	Friction↓ Rougness↑	Rapoport et al. (2003)
Poly-alpha-olefin	Mo–S–I nanowires	Concentration 0.5-2.0 wt%; L: 1, 2, 5, 10 T: 25 v: 2.5	Pin-on-flat	Friction↓ 1.0wt% is optimum.	Joly-Pottuz et al. (2005)
Diesel engine oil (50CC)	Serpentine (1μm)	Concentration 0.5-2.0wt%; L: 100,200,300,400 v: 1.51 t: 120	MM-10W sliding friction tribotester	Wear↓ Friction ↓ 1.5wt% is optimum.	Yu et al., (2010)
Base oil	Cerium borate (50 nm)	L: 390 N: 1450, t: 30	Four ball	Friction ↓	Lingtong et al. (2011)
Engine oil (API SM grade 5W-30)	Talc (1μm)	0.05-1.5wt% L: 5 v: 0.04 p: 0.75 s:2000 T: RT to 120	ball-on-plate	100°C and 0.15wt% optimum. Friction and wear↓ at high temperature, not at RT.	Rudenko et al. (2013)
SAE 20W40	MoS_2 (≤ 150 nm)	Concentration 0.25-1.0wt%; L: 392, N:1200 t: 60, T: 75	Four ball	Load-wear index↑ Weld load↑ Friction and wear↓ 0.25 to 0.5wt% optimum.	Srinivas et al. (2017)
SAE 20W50	h-BN (50 nm)	1.0-3.0wt% L: 392, N:1200 t: 60, T: 75	Four ball	Wear loss↓ by 30-70%. Friction and wear is function of nano-additive concentration	Charoo and Wani; (2017)
L: Load (in N), t: time (min.), v: velocity (m/s), P_B: maximum non-seizure load (N), N: speed (rpm), T: temperature (°C), p: contact pressure (GPa), s: sliding distance (m), RT: room temperature (°C)					

2.4.4. Biolubricants with different nanoparticles in tribological contact

It reported that vegetable oils are suitable in the boundary lubrication conditions because of its unique intrinsic property. However the addition of nano-additive substantially changes its performance. Any of the tribo-performance can be improve or impair depending on the nanoparticles parameters (shape, size or concentration). Table 2.9 shows the tribo-performance of some bio-based nanolubricants, which indicates that optimality condition varies for different nanolubricants in different test conditions.

Table 2.9. Summary of some nanoparticles as a biolubricant additive in tribological contacts.

Base oil	**Nanoparticle**	**Operating/Variable parameter**	**Test rig**	**Findings**	**Ref.**
Coconut oil	CuO	s: 1000 m speed: 1.4 to 5.6 m/s concentration 0.1, 0.2, 0.3, and 0.4%	Pin-on-disc	0.34% concentration and 3.7 m/s speed is optimum. AF↑	Thottackkad et al. (2012)
Rapeseed oil (chemical modified)	TiO_2 a. 20 nm b. 45 μ m	Speed: 1, 2, 3, 4 m/s; Concentration 0.05wt% (constant)	Pin-on-disc	µ↓ by 15.2% with a; AW↑ by 11% with a. µ↓ by 6.9% with b. AW↑ by 6.1% with b.	Arumugam et al. (2013)
Palm oil-based ester	TiO_2	L 40, 80, 120, 160 kg Time 10 min	Four ball	Max. AW↑ by 11% and AF↑ by 15% at 160 kg.	Zulkifli et al. (2013)
Soybean and sunflower oil	ZnO (11.71nm); CuO (4.35 nm)	Concentration 0.5wt% (separately in each oil)	High frequency reciprocat-ing rig	Sunflower oil was better. No significant improvement in AW and AF.	Trajano et al. (2014)
Modified Palm oil	CuO (50-300 nm); MoS_2 (50-2000 nm)	Concentration 0.25, 0.5, 0.75, 1.0, 1.25 and 1.5wt%	Four ball	MoS_2 better than CuO. 1wt% was optimum. AW/EP↑ by 1.5 times.	Gulzar et al. (2015)
Coconut oil	MoS_2	T 30 and 120°C L 100 - 200N	Pin-on-disc Four ball	0.53wt% optimum. AW↑	Koshy et al. (2015)
Pyrolysis bio-oil	La_2O_3	L 100N, Speed 1250 rpm, RT, time 30 min Concentration 0.6-2%	Four ball	0.6 to 1 wt% better, AW and AF↑	Xu et al. (2015)

Rapeseed oil	CuO (70nm), WS_2 (40-80 nm), TiO_2 (30-50 nm)	Concentration 0.5wt%	Four ball	Better AW and AF property for CuO than other nanoparticles.	Baskar et al. (2015)
Palm oil	TiO_2	Concentration 0-0.2wt% L 40 kg, speed 1200rpm, time 15 min.	Four ball	Slight improvement in AW.	Shaari et al. (2015)
Rapeseed oil	Fe	Size variation 50-340 nm 0.1wt% concentration	Four ball	At 0.1wt% μ ↑ but AW↓; 50-140 nm was optimum.	Maliar et al. (2015)
Rice bran oil	TiO_2 CeO_2 ZrO_2	Concentration 0.1 to 2wt% L: 400N	Four ball	TiO_2 at 0.3wt% was best composition.	Rani (2016)
Sunflower oil	Carbon sphere (CS; 1.8-2.2 μm); and Graphene oxide (GO; flake)	L 5N and speed 300 rpm (constant) 0.5-3.0wt% for CS 0.1-1.0wt% for GO	Ball-on-disc	• 0.3wt% optimum for GO. • AF↑ • GO better than CS.	Song et al. (2016)
Palm-TMP ester	TiO_2/SiO_2 (nano-composite 50 nm)	Concentration 0.25 to 1wt% Speed 1770 rpm Step loading 10N/10sec	Four ball	Weld load performance optimum at 0.75wt%.	Gulzar et al. (2017)
Water	SiO_2 (60nm)	Concentration 0.1-0.5wt%	Pin-on-disc	0.3wt% concentration optimum. AF↑ and AW↓.	Bao et al. (2017)
Palm oil methyl ester	TiO_2/SiO_2 composite (50 nm)	Concentration 0.25-1.0wt%	piston ring–cylinder liner sliding	0.75wt% optimum. AW ↑ up to optimum concentration then worsen.	Gulzar et al. (2017)
Karanja oil	Cu nanoparticles modified with oleic acid	Concentration 0.5, 1.5, and 2.5wt %	Four ball	0.5wt% optimum. μ↓ by 61%. AW↑ by 30%.	Garg et al. (2017)
Palm oil based ester	Graphene platelets	L 40 – 80 kg Concentration 0.01-0.1wt%	Four ball	Optimum 0.05wt%, μ↓ by 7%, AW↑ by 16.2%.	Rashmi et al. (2017)
Jatropha oil	h-BN	Concentration 0.05 to 0.5wt%.	Four ball	0.5wt% optimum. AW↑ by 20% AF↑ by 75%	Talib et al. (2017)
AW: antiwear property, AF: antifriction property, μ: COF, L: load, RT: room temperature, T: temperature, ↑: increase/improve, ↓: decrease/impair, s: sliding distance					

2.5. Effect of nanoparticle parameters on tribological behavior

2.5.1. Effect of nanoparticles size in the contact zone

The two main characteristics associated with the size of the nanoparticle based lubricants. First, the size of the nanoparticles exhibits their physicochemical and mechanical potential that directly influences the tribological properties. The decrease in particle size increases hardness due to increment in dislocation pileup for a crystal (generally in the size range 100nm or higher) (Weertman 1993; Yamakov et al., 2004). The harder nanoparticle, when coming in contact with comparatively softer mating surfaces, creates indents and scratches. Thus, nanoparticle size induced variation in performance (based on hardness) must keep in mind during nanolubricant formulation. Second, lubricants containing nanoparticles should stay at contact interface during loading and shearing to protect against wear (Narayanunni et al., 2011). For example, if the roughness of the friction surface is less than the nanoparticle size (Figure 2.1), the nanoparticles tend to escape from contact zone, which leads poor lubrication. On the contrary, if the roughness of the friction surface is higher than nanoparticle size, then these nanoparticles fills the surface dimple and valleys to smoothen them. It improves the tribo-performance of nanolubricants (Akbulut 2012).

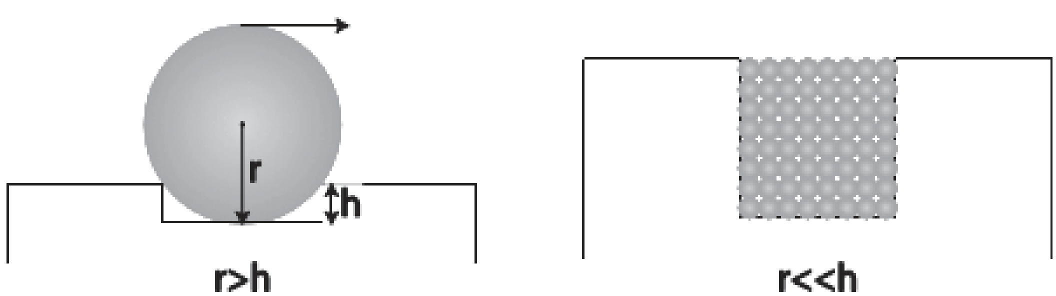

Figure 2.1. Effect of nanoparticle size and surface roughness (Akbulut 2012).

2.5.2. Effect of nanoparticles shape in contact zone

Another parameter of consideration for nanolubricants is its shape. The spherical shape of the nanoparticles is more pronounced as compared to sheets, tubes, and irregular shapes. This is because of rolling action of the spherical particles. In another word, nano-sphere act as nano-bearing by carrying fraction load at interface and keep the rubbing surfaces away, thus improved tribological properties. However, due to point contact geometry of nano-spheres, it experiences more contact pressure as compared to nano-sheets and irregular shapes (Akbulut 2012).

2.5.3. Effect of nanoparticles concentration in the contact zone

The concentration of nanoparticles plays a vital role to influence the tribological properties of nanolubricant (Akbulut 2012). For a particular range of concentration, there may be an optimum concentration at which lowest friction or wear may be achieved. Probably with low concentration, insufficient number of particles causes asperity-asperity collision under higher contact stress. On the contrary, at high concentration particle agglomeration and abrasion takes place (Ma et al., 2010; Akbulut 2012; Gupta and Harsha 2017). Past studies exhibit that the optimum concentration of the nanoparticle in the lubricating oil is strongly system dependent, and it needs to be investigated for each operating condition differently.

2.6. Hypothesis of nanolubrication mechanism

The nanoparticles behavior in lubricating oil varies in different ways under different contact situations. Especially in boundary lubrication, when mating surfaces are too close, the role of these ultrafine particles in lubricants becomes crucial. Some of the possible mechanisms are as follows and depicted in Figure 2.2.

2.6.1. Reduction in real area of contact

At the atomic level, it was evident that no surface is perfectly smooth. It contains numerous asperities and valleys. For the close contact and dynamic situations, the chance of asperity-asperity locking, asperity collision, and material loss is more prone. In the situation when nanoparticle in the oil comes in the contact zone, it reduces the real area of contact thus reduce the wear (Figure 2.2(a)) (Lee et al., 2009; Ghaednia and Jackson 2013; Gupta and Harsha 2017).

2.6.2. Nano-bearing

If the nano-particles have spherical or almost spherical (i.e. metal or metal oxide), tube (i.e. single- or multi-wall carbon nanotube) or capsules (i.e. carbon nanocapsules) like morphology, during surface sliding it rolls over the friction surfaces by keeping it separate. It acts as nano-bearing and carries a fraction of the applied load as in Figure 2.2(b) (Lee et al., 2009; Viesca et al., 2011; Arsul et al., 2013; Gupta and Harsha, 2017)

2.6.3. Surface mending and formation of the protective film

The nanoparticles can form a thin film that reduces the interfacial shear stress between tribo-pairs and prevent micro damage and scratches on the surfaces. Also, the nanoparticles fill the surface valleys and dimples to make them smooth as in Figure 2.2(c). These protective layers form by the nanoparticles is also called as deposition film (Liu et al., 2004; Xiaodong et al., 2007; Viesca et al., 2011; Ali and Xianjun. 2015)

2.6.4. Surface polishing

If the nanoparticles have irregular morphology as presented in Figure 2.2(d), it breaks the micro asperities and material is transferred away from the contact zone by the lubricants. This phenomenon helps the friction surfaces smoothening (Tao et al., 1996; Ingole et al. 2013; Feng et al. 2015).

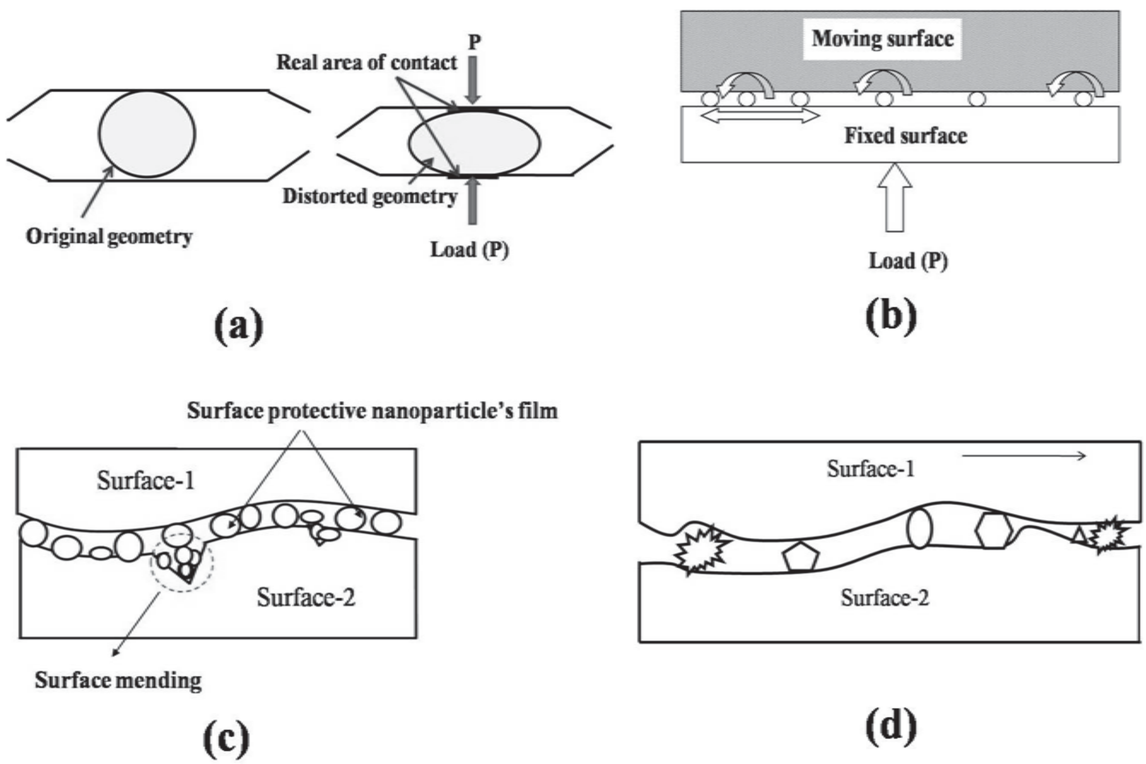

Figure 2.2. Hypothetical mechanism of nanolubrication showing; (a) behavior of single particle under load; (b) rolling-sliding phenomena; (c) Surface mending with formation of nanoparticles film; and (d) polishing action (Lee et al., 2009; Ghaednia and Jackson 2013; Gupta and Harsha 2017).

2.6.5. Exfoliation

This mechanism associated for layered like nanoparticle in the oil as depicted in Figure 2.3. When the tribo-pairs are in sliding condition, the layered particles start to peel out and propagate from top layer to core under high contact stress (Tevet et al., 2011). These peeled out parts come in contact with friction surfaces and form a protective layer to reduce friction and wear. Joly-Pottuz et al. (2005) reported similar phenomena for IF-MoS_2 particles to improve tribo-performance.

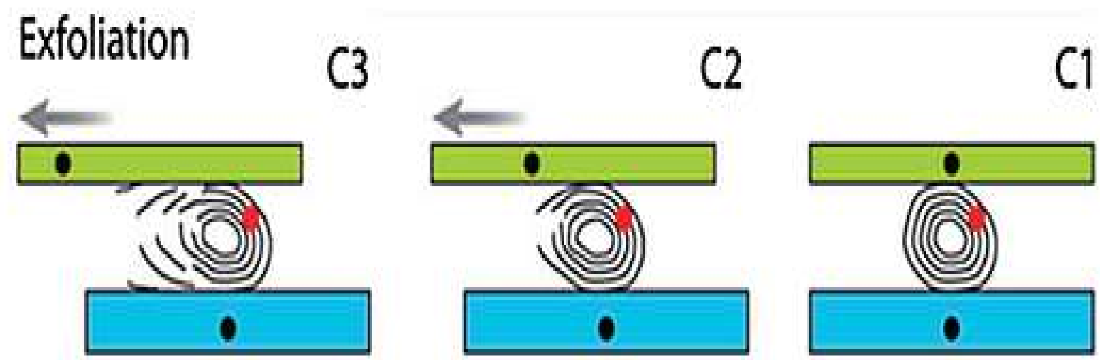

Figure 2.3. Exfoliation mechanism of multilayer nanoparticles (Tevet et al., 2011).

2.6.6. Hardening the contacting surfaces

Continuous rolling and sliding of the nanoparticles in the contact zone make the friction surface work hardened up to a certain extent. This also may be responsible for the improvement in the tribological properties for the nanolubricants (Chou and Lee, 2010).

2.7. Problem formulation

2.7.1. *Unprecedented work, motivation, and problem identification*

Literature study shows that the following experimental research works are required in the area of lubrication:

i. Very few studies were done with the biolubricants in the tribological contact situations especially in the boundary lubrication conditions.

ii. The role of fatty acid compositions of biolubricants with the tribological performances have not reported extensively.
iii. Metal oxides, chemical reagent, and polymeric additives are rarely compared in terms of tribo-performance for different biolubricants with mineral oil.
iv. The comparative study of unmodified and chemically modified biolubricants not explored with various nano-additives.
v. The role of surface and sub-surface lubricated with different nanolubricants was not explained earlier which may be responsible for improving/impairing the tribo-properties.

- ***Motivation***

This work is motivated towards the development of environmentally benign and potential lubricants to replace the hazardous mineral and synthetic oils. Notably, in the automobile industries where many parts work under boundary lubrication like piston-cylinder, submerged gear-box, which need the potential lubricant to work efficiently. In this study, a minimal range of nanoparticle concentration was opted to formulate the nanolubricants, and it may be efficient and cost effective.

- ***Problem identification***

Considering continuous increasing demand for lubricant and availability of limited petroleum stock, it is necessary to move towards the lubricants that can be achieved from the renewable sources so that upcoming generation can survive without interruption. Also, it is apparent that the role of lubricant is essential for all the industrial and commercial applications. Therefore, the present work focused on formulating potential eco-friendly additive based biolubricant.

2.7.2. Problem definition

Nanotechnology has been spread all over the engineering and science domain. The various researchers reported the improvement in tribo-performance of different mineral and synthetic oils with the use of micro- to nano- size particles, but very few with the vegetable based biolubricants. In view of the past research in the field of nanolubricants, the following questions arise:

(i) Whether all nanoparticles show good compatibility with each base oils to enhance tribological properties?

(ii) Is there any effect of nanoparticles concentration and shape on tribo-performance with biolubricants?

(iii) Are biolubricants and mineral oils have same affinity with different nano-additives?

(iv) Can shortcomings of the vegetable oils be removed by oil modifications and show similar or better effect with the nanoparticles?

All these queries are aimed to solve in this study by experimental examinations. Therefore, the objectives of the work were defined accordingly.

2.7.3. The objective of the work: Considering lubricant availability, tribological prospect, and environmental health

The objectives of the present research work were as follows:

- To explore vegetable oils as a base lubricant for the tribological test.
- To understand the role of the fatty acid composition of castor, rapeseed, sunflower, cottonseed, olive, sesame and neemseed oil on the tribological behavior.
- To investigate the different additive based lubricants to verify for enhancement in the tribo-performance (i.e., antiwear, antifriction and extreme-pressure) by using four-ball test rig. The details of the additives investigated are as follows:

- ✓ ZDDP, a commercially available chemical reagent as an additive.
- ✓ Different nanoparticle additives (i.e., CCTO, CuO, CeO_2, and PTFE)
- ✓ Different additive concentrations (i.e., 0.1, 0.25, 0.5 and 1.0 %w/v)

- To analyze the tribological performance of castor, rapeseed and sunflower oil after the chemical modification (i.e., epoxidation) with different nano-additives.
- To optimize the additives concentration and propose the tribo-mechanism to get the best tribo-performance.

Justification for selection of additives

ZDDP has an excellent antiwear and extreme pressure properties and it is documented well in the literature, therefore ZDDP was considered for the comparison of the performance with the different nano-additives. The CCTO nanoparticles were chosen to study the combined effect of CuO, CaO, TiO_2 as one oxide particle in the biolubricants; The CuO nanoparticles were used in various mineral and synthetic based oils and they have demonstrated good tribo-performance but less explored with biolubricants; The CeO_2 nanoparticles were selected because it is available abundant in nature; PTFE nanoparticles were selected because it is well known as antifriction material and less explored with biolubricants for tribological study.

2.8. Summary of the chapter

This chapter provides a deep insight about the base oils, additives, nanolubricants and their tribological behavior based on the past work. The gap in the field of nanolubricant's tribology identified and objective of the work defined accordingly.