CHAPTER 1

INTRODUCTION

1.1. Tribology

The term tribology was first introduced by the renowned Jost report in 1966, combining two Greek words, "tribos" and "logos," which means rubbing and logic. It can also be referred to as studying interacting surfaces in relative motion [Bhushan et al. (2001)]. Tribology is a crucial component of mechanical engineering as it relates to the principles of friction, lubrication, and wear. Because of the complexity of surface interactions in tribology, it is essential to have a broad understanding of various disciplines, including chemistry, physics, mathematics, biology, material science, and machine design, in addition to mechanical engineering. Applications for tribology include everything from automobiles to home appliances to spacecraft [Bhushan et al. (1999)]. Besides the world of machines and materials, tribology is vital for many activities in the human body [Zhou et al. (2015)].

1.1.1. Friction

The force that prevents motion when the surfaces of two objects come into contact is known as friction. Owing to the friction, energy loss in the system takes place. More energy loss is observed when there is more friction. Some common examples of friction in our daily life are; playing any instrument, driving a car, shaving, walking, lighting a matchstick, writing, skating, drilling a nail into the wall, brushing teeth to remove particles, mopping surfaces, and ironing a shirt, etc. There are four types of friction: static, sliding, rolling, and fluid. According to the law of friction provided by Guillaume Amontons in 1699, for typical materials, except extremely hard and soft materials, the frictional force (F) is directly proportional to the load, N, and formulated **as**

$$\mathbf{F = \mu . N} \qquad \mathbf{1.1}$$

Where μ = coefficient of friction, depending on working conditions and material properties, etc., as long as surfaces are not remarkably smooth, frictional force (F) is independent of the contact area. According to Coulomb's law, kinetic friction does not depend on sliding velocity when speed is not very high.

1.1.2. Wear

Wear is defined as the removal of material from two interacting surfaces under the applied load. However, friction is a system response rather than material property. In general, it is supposed that if the materials have high friction, they will show a high wear rate, but this is not true in every case. The interfaces with polymer and solid lubricants have high wear but low friction, whereas ceramic materials have extremely low wear but moderate friction. The magnitude of wear is determined by material properties such as surface roughness, mechanical strength, operating conditions, environment, proximal surfaces geometry, and hardness. Adhesive, abrasive, surface fatigue, fretting, erosive, and chemical interactions can all lead to wear.

1.1.2.1. Adhesive wear

Adhesive wear occurs when surfaces that come into contact with asperities deform irreversibly and adhere to each other, resulting in significant seizure, wear, scuffing, or galling. It depends on chemical and physical factors like a corrosive atmosphere, material properties, applied load, and dynamics like velocity. Cold welding, pits, scoring, seizing, scuffing, built-up edges, and tool breakage are all problems caused by adhesive wear. Lowered load, contaminated rubbing materials, harder rubbing materials, presence of lubrication oil, solid lubricants, and antiwear additives in oil are all factors that reduce adhesive wear.

1.1.2.2. Abrasive wear

When the hardness of the adjacent surfaces varies greatly, abrasive wear occurs. The softer material is abraded by the harder surface, resulting in furrows and scratches. It is the most common wear mechanism encountered in industry.

1.1.2.3. Surface fatigue wear

Pitting or cyclic crack development that arises abruptly after a significant number of revolutions characterizes surface fatigue wear. The material deteriorates due to structural changes, which cause subsurface cracks to spread and give rise to palling, flaking, and peeling**.**

1.1.2.4. Fretting wear

Fretting wear is a type of surface abrasion that happens when two contacting surfaces are subjected to small-amplitude cyclic motion. In shafts and other highly strained parts, it starts fatigue cracks, frequently leading to fretting fatigue failure. It is a kind of surface-to-surface wear. The issue is brought on by fretting wear, such as normal loading, displacement amplitude, properties of the material, count of cycles, lubrication, and humidity.

1.1.2.5. Erosive wear

In erosive wear, material degradation is caused by the impact of external particles, either solids or liquids, on the material surface. It can also be defined as the destructionof material surfaces caused by an object impinging at a high velocity.

1.1.2.6. Chemical wear

Chemical agents that are generated in the oil induce chemical wear. One example of controlled chemical wear is extreme pressure lubrication.

1.1.3. Lubrication

Friction is associated with heat and wear. These are overwhelmed if the coefficient of friction is somehow decreased. Lubrication decreases these by avoiding direct metal-metal contact and promoting heat dissipation between contact surfaces by introducing a low-viscosity material between the moving surfaces. In addition to reducing frictional heat and wear, the other roles of lubrication include oxidation control, corrosion prevention, removal of wear particles from the contact zone, etc. [Jones et al. (1983), Dorinson et al. (1985)]. Losses in both energy and materials can be attributed to poor lubrication. In manufacturing processes and machine parts, lubrication is thus essential. The technological revolution has modified machine designs, encouraged using lightweight metal tools rather than heavy-weight ones, and imposed tight regulations to protect the environment by lowering emissions, etc. According to Kuratomi et al. (2009), proper design and development of energy-efficient lubrication face problems.

Stribeck first gave the variation of the friction coefficient (COF), μ for a sliding bearing in 1902. He discussed a hypothetical fluid-lubricated bearing and provided a curve where μ was shown as a function of the product of absolute viscosity, η, and rotational speed in revolutions per unit second, V divided by load, N (**Fig.1.1**). Based on the lambda ratio, λ that is equal to the minimum film thickness, h divided by composite roughness, σ^*.

$$\text{Lambda ratio, } \lambda = \frac{h}{\sigma^*} \qquad \textbf{1.2}$$

Where h = Minimum film thickness, and σ^*= Composite roughness

The regimes of the Stribeck curve could be identified as for the boundary ($\lambda < 0.5$), mixed lubrication ($\lambda = 0.5 – 3.0$), and hydrodynamic lubrication ($\lambda > 3$), depicted in **Fig.1.1**.

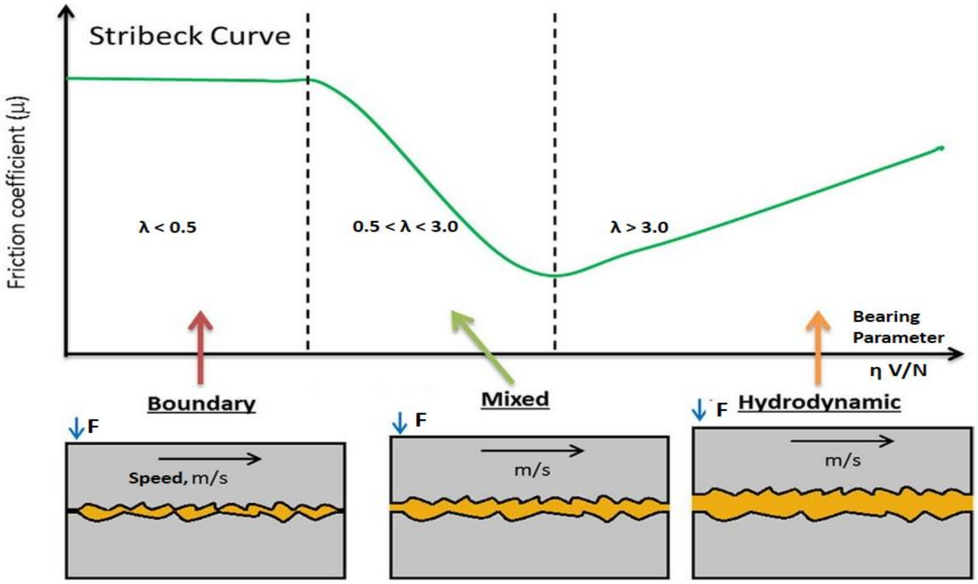

Fig. 1.1. The Stribeck curve for a lubricated sliding system shows the dependence of friction coefficients on speed, load, and viscosity

1.1.3.1. Boundary lubrication

Boundary lubrication is also known as thin film lubrication. It occurs when the lubricant film becomes too thin to enable complete separation of the proximal surfaces. Graphite and molybdenum disulfide are usually recommended either alone or as a stable suspension in oil. This lubrication operates at a relatively low speed and heavy load (pressure), and a thin film of lubricant is adsorbed on the surface by weak van der Waals forces. For the thin film lubrication regime, $\lambda < 0.5$; therefore, μ is very high, and there is a massive loss of energy and material; as a result, the regime is the most damaging [Myshkn et al. (1997)].

1.1.3.2. Mixed lubrication

More than one lubrication mechanism is active simultaneously in mixed lubrication. The load is supported partly by the fluid film and surface asperities. As a result, friction is much lower than in boundary lubrication but much higher than in hydrodynamic lubrication [Myshinn *et al.* (1997)]. The asperity contacts and hydrodynamic lubrication are both present in this lubricant film. The lambda value (λ) for mixed lubrication ranges from 0.5-3.0.

1.1.3.3. Hydrodynamic lubrication

Hydrodynamic lubrication (hydro meaning liquid and dynamic meaning relative motion) is also known as fluid film or thick film lubrication. Here moving or sliding surfaces are separated by a thick film of liquid lubricant fluid of about 1000 A^o preventing direct surface-to-surface contact and consequently reducing the wearing and tearing of the surfaces. The thick film of lubricant covers entirely moving surfaces and fills irregularities. The friction coefficient in such cases is as low as 0.001 to 0.03. In thick film lubrication, the film thickness is directly proportional to the sliding speed (V) of the surfaces in motion and viscosity (η) of the fluid, and it is inversely proportional to the load (N) as given by the relationship: $\eta V/N$. Hydrodynamic lubrication is beneficial in delicate and light machines such as guns, watches, clocks, sewing machines, scientific instruments, etc. The lambda value (λ) for hydrodynamic lubrication is greater than three.

1.2. Lubricants

The material known as a lubricant reduces wear and friction when added between moving surfaces. The primary function of a lubricant is to absorb heat, which improves mechanical performance. In addition, it serves as a sealing agent, keeping dirt and moisture out of the space between the moving parts. The life expectancy of a mechanical system can be increased, energy loss can be decreased, and emissions can be managed by reducing friction and wear. A lubricant should generally have the following properties: excellent thermal as well as oxidative stability, high viscosity index, moderate volatility, non-corrosiveness, and good fluidity at low temperatures [Kuratomi et al. (2009)]. Lubricants can be classified based on their physical and chemical properties, which are listed below.

1.2.1. Liquid lubricants

Liquid lubricants are also known as lubricating oils; these oils reduce wear and friction between the two sliding surfaces by making a thin layer of fluid**,** reduce heat generation, act as cooling and sealing agents, and prevent corrosion. The oils with a high boiling point, low freezing point, low viscosity, high viscosity index, and high resistance to oxidation and corrosion are considered to be excellent liquid lubricants. These can be classified into five groups: animal oil, vegetable oil, mineral oil, blended oil, and synthetic oil.

1.2.1.1. Vegetable oils

Vegetable oils are triglycerides obtained from plants and are used to lubricate Scientific equipment, watches, etc.; examples of vegetable oil are olive oil, castor oil, palm oil, cotton seed oil, rapeseed oil, etc.

1.2.1.2. Animal oils and fats

Animal oils are extracted from the crude fat by the rendering process in which the enclosing tissue is broken by treatment with steam or the combined action of steam and water. Animal and vegetable oils possess good oiliness. As a result, these are tenaciously adsorbed on metallic surfaces and have a lower friction coefficient and higher load-bearing ability. These oils have minimal uses as a lubricant because they are costly, have less resistance to oxidation, form gummy and acidic products after oxidation, and get thickened on coming in contact with air. Examples of animal oils include tallow oil, neat foot oil, whale oil, sperm oil, lard oil, and seal oil.

1.2.1.3. Mineral or petroleum oils

Mineral oils, such as naphthenic and paraffin, have replaced mainly animal and vegetable oils. These are lower molecular weight hydrocarbons, ranging from 12 to 50 carbon atoms. Their viscosity rises as the hydrocarbon chain gets longer. They are prepared using the petroleum distillation process. These are inexpensive, stable under service conditions, widely available, and reusable. They are, therefore, frequently employed. Compared to vegetable and animal oils, mineral oils have less oiliness. The oiliness of mineral oil is consequently increased by adding substances with greater molecular weights, such as stearic acid and oleic acid.

1.2.1.4. Synthetic oils

Synthetic oils are chemically prepared compounds and are very effective under various conditions. They have low volatility, high viscosity index values ranging from 120 to170, and excellent oxidation stability. Because of their uniform structure, these oils have a negligible variation in viscosity with temperature. Synthetic oils are preferred owing to better reliability, reduced maintenance, improved energy efficiency, applicability in the broader temperature range, and safer operation. Examples of synthetic oils are; polyalphaolefins, polybutenes, polyethers, diesters, silicones, polyols, polyalkylene glycols, fluorocarbons, etc.

1.2.1.5. Blended oil

No single oil can serve as the ideal lubricant for all modern types of machinery. The properties of petroleum oils can be improved by mixing specific additives. These blended oils give desired quality of lubrication. Oil blending is done to increase oiliness, reduce pour point, resist oxidation, reduce corrosion, and improve viscosity, color, and lubrication.

1.2.2. Semi-solid lubricants

Semi-solid Lubricants are comprised of a soap dispersed throughout liquid lubricating oil. Examples of Semi-solid lubricants are greases, waxes, and vaseline. Generally, greases are utilized in areas where a regular oil supply cannot be sustained. The major limitation of greases is their poor heat dissipation. Impurities like dust, dirt, and wear debris are always present in greases.

1.2.3. Solid/dry lubricants

A solid lubricant is a powder or thin film that reduces friction and wear on contacting surfaces in relative motion and protects them from damage. Solid lubricants are used in water/ oil or dry conditions [Krishna et al.(2011)]. Under vacuum and at high temperatures, greases or liquid lubricants cannot be used on bearings; solid lubricants are applied. Solid lubricants are characterized by high thermal and chemical stability, high mechanical strength, low shear strength, and usually, a lamellar structure. These lubricants are widely used for automotive, marine, and industrial applications (turbines, industrial gears, hydraulics, and compressor). Examples of solid or dry lubricants are; hexagonal boron nitride, graphite, tungsten disulfide, molybdenum disulfide, zinc oxide, PTFE(Polytera Fluoro Ethylene), talc, ceramic coatings, and silicon. The main disadvantages of solid lubricants are their poor self-healing ability and a high coefficient of friction value when compared to liquid lubrication [Vamsi et al. (2011), Scharf et al.(2013), Reeves et al.(2013)].

1.2.4. Gaseous lubricants

Gaseous lubricants, such as nitrogen, air, helium, oxygen, etc., are used in aerostatic and aerodynamic lubrication. Gaseous lubricants are suitable for wide temperature ranges. The viscosity of gaseous lubricants increases with temperature; this is the primary advantage of gaseous lubricants over liquid lubricants. The major challenge, however, is the storage of gaseous lubricants.

1.3. Lubricant additives

These are inorganic and organic chemical compounds or nanomaterials when added to a base oil (lubricant) in small quantities, improve its specific properties [Ludema et al. (1996)]. Today's market offers a variety of lubricant additives, such as pour point depressants, detergents, anti-foam agents, dispersants, demulsifying agents, corrosion inhibitors, antioxidants, viscosity and viscosity index improvers, extreme pressure, antiwear and friction modifiers, etc. Depending on the use, only a small number of them are present in properly formulated lubricants. Various kinds of lubricants and additives have developed during the past few decades to extend the service life of machinery. Lubricant additives are classified into the following types based on their chemical compositions; conventional organic/inorganic compounds, nanomaterials, and ionic liquids. Detailed information about these substances is given below.

1.3.1. Organic/inorganic compounds as conventional additives

Organic/inorganic compounds are usually added to base oils as lubricant additives like foam inhibitors, viscosity modifiers, pour point depressants, etc., to change the respective physical characteristics of base oil. On the other hand, the tribological performance of the lubricants is improved by antiwear, antifriction, and extreme pressure additives, which contain tribologically active elements such as N, S, P, Cl, B, Zn, and Mo or mixtures of these elements. These may be categorized as nitrogen, oxygen, sulfur, phosphorus, boron, halogen compounds, and ionic liquids. Tribochemistry studies the chemical interactions between two or more interacting surfaces, usually under the boundary or mixed lubrication regimes [Hutchings et al. (1992), Waara et al. (2001), Hsu et al.(2002), Wong et al. (2007)]. Understanding the nature of tribochemical reactions and their mechanism is crucial to know how lubricants work to minimize wear and friction. The additives molecules are adsorbed on the interacting surfaces in boundary or mixed lubrication regimes reducing contact between moving surfaces. These additives decompose at high temperatures and loads, generating a protective tribochemical film. This tribofilm shields the interacting surfaces by preventing direct metal-to-metal interactions. The additive reactivity with surfaces is essential. A tribochemical film will not form if the nature of the additive is inert. Oppositely, the chemical attack is promoted by the hyperactivity of the lubricant additives with the metal surfaces, which will cause tribochemical wear. The reactivity of the antifriction, extreme pressure and antiwear additives in real applications will depend on the nature of interacting surfaces, other lubricant additives in the system, and the base oil type. The contact asperity temperature and nascent metal surface typically catalyze a tribochemical reaction of a lubricant additive with a surface. The contact temperature is about 400 ºC or higher, but it is only short-term. The contact temperature increases frictional heat between the sliding asperities [Hsu et al. (2005)]. The nascent surface has active sites and a lot of surface energy. Because of the effect of heat and the active surface, several different chemical reactions may occur. These reactions primarily involve lubricant degradation and oxidation, oxidation of surfaces, polymerization, surface catalysis, and the formation of organometallic or inorganic products on sliding surfaces [Hsu et al. (1996)]. The nature of tribochemical products is influenced by the structure, reactivity, and composition of the additive.

1.3.1.1. Nitrogen and Oxygen compounds

These compounds are used as prospective ashless additives because of their outstanding properties; antiwear, anticorrosion, extreme pressure, antioxidation, and high thermal stability [Rent et al. (1993)]. Lundgren and coworkers utilized lubricating oil with amine salt to minimize friction in the internal combustion engine [Lundgren et al. (2016)]. Rent et al. (1993) evaluated the antiwear behavior of nitrogen-containing compounds with one/two/three N atoms. Usually, as the number of N atoms increases, antiwear nature also increases, provided all of them access the surface. From the literature review, The tribological properties of several N, O containing compounds such as amine compounds (propylamine, ethylenediamine, triethylenetetramine) [Huang et al.(2006)], amide compounds (adipamide, caproamide, caprolactam, acrylamide) [Huang et al. (2005)], fatty acyl amino acids (lauroyl glutamine, lauroyl glycine, lauroyl alanine) [Chen et al. (2010)], etc. have been observed. Heterocyclic compounds containing N and O like pyridines, pyrazines, furans, pyrans, pyrimidines oxadiazoles pyridazines, tetrazoles dioxanes, pyrroles, imidazolines pyrazoles, imidazoles, triazines, oxazoles [Li et al. (2000), He et al. (2002), Kamano et al. (2014), He et al. (2004), Yang et al. (2013), Xiong et al. (2016)], and Schiff bases [Rastogi et al.(2013), Jaiswal et al.(2014), Kumar et al.(2019)], etc. have been reported for their excellent tribological properties. In addition, this category of compounds with fused benzene rings is also tribologically active such as coumarin, indazole, benzimidazoles, quinazolinones, indole, quinolines, benzotriazoles, benzoxazoles, etc. [Zhang et al. (1999), Xu et al. (2000), He et al. (2002), Elkholy et al. (2019),Verma et al. (2019), Tang et al. (2021)]. Besides, lanthanum complexes of Schiff bases have also been studied as extreme pressure additives[Maurya et al.(2016)]. Adsorption of heterocyclic compounds mainly occurs through π-electrons, negatively charged center, lone pair of electrons on heteroatom, and aromatic ring electrons. The adsorbed compounds have a high affinity to nascent steel surfaces, forming tribolifms, which impart tribological properties [Bentiss et al.(1999)].

1.3.1.2. Sulfur compounds

Numerous lubricants contain sulfur, either alone or its organic/inorganic compounds, with distinct chemical compositions [Stewart et al. (1993)]. In order to improve extreme pressure, antiwear and antifriction performances under severe conditions, sulfur-containing compounds play a vital role. The additive molecule decomposes and gets physically/chemically adsorbed on the steel surface, generating an iron sulfide coating that prevents direct metal-metal contact and lowers friction and wear [Davey et al. (1957]. Organic sulfur compounds like sulfurized olefins, fats, esters, terpenes, dithiocarbamates [Agarwal et al. (1980), Mammen et al. (1984)], xanthates[Agarwal et al.(1981)] thioamides [Kuliyev et al. (1989a)], isodithiobiurets [Agarwal et al. (1981)], thioacetamides [Kuliyev et al. (1989b)], phenylacetothioamides [Kuliyev et al. (1983], alkano-amidosulfides [Bhattacharya *et al*. (1995)], dialkanoylacetamides [Croudace et al. (1991)], thioglycolic acid ester, di-isobutyl polysulfide, aromatic sulfur compounds like aromatic disulfides, mercapto benzo-thiazole, molybdenum/tungsten complexes of dithiocarbamates, thiobiurets, dithiobiurets, thiosemicarbazides [Mitchel et al. (1984), Rastogi et al. (2001), Rastogi et al. (2003)] lanthanum complexes of dithiocarbamates, dithiohydrazodicarbona- mides etc. have been used as extreme pressure/antiwear additives [Rastogi et al. (2012), Rastogi et al. (2013)].

1.3.1.3. Phosphorus compounds

Numerous phosphates and dithiophosphates like dialkyl dithiophosphates [Najman et al. (2004)], dithiophosphatedisulfide [Bansal *et al*. (2002)], triarlyphosphorothionates [Heuberger *et al*. (2008)], etc. have been studied for possible tribological applications. The phosphate group is first adsorbed on the surface, breaking down at a higher temperature to produce alkyl-acid phosphates. The alkyl-acid phosphates then react with the metal surface to produce high-melting salts; these salts improve lubrication and protect the surface from friction and wear. Zinc dialkyl dithiophosphates are well-known antiwear additives. However, their excessive use is restricted because of the direct environmental harm caused by their high phosphorus, sulfur, and zinc contents and their indirect impact on the exhaust emission system by inhibiting the catalysts[Njiwa et al.(2011)].

1.3.1.4. Boron Compounds

The tribological advantages of boron-containing lubricants include high-temperature resistance, self-lubrication properties, and antiwear efficiency. Many forms of boron, such as boric acids, oxides, and esters, can be used as lubricants. The element boron has a high affinity for oxygen due to its electron deficiency. Boron compounds have vital characteristics such as low toxicity, antioxidant behavior, pleasant odor, good fire resistance, ready availability, and non-volatility [Choudhary et al. (2002)]. The lubricating properties of boric acid are directly affected by the lamellar structure and triclinic crystal lattice [Larsson et al. (2022)]. Several borates showing tribological behavior are; sodium metaborate, titanium borate, zinc borate, potassium borates, aluminum borate, strontium borate, magnesium borate, lanthanum borate, cerium borate, calcium borate and ferrous octoxyborates [Adams et al. (1978), Hu *et al*. (2000), Martin *et al*. (2000), Shah *et al*. (2013)]. Feng et al. (1963) reported that borate additives create a thin, amorphous glassy tribofilm under boundary lubrication conditions. One of the significant limitations of inorganic borates is the difficulty in preparing homogeneous solutions in base oils, resulting in inadequate access of the particles to the surface. Since organic borates are soluble in base oils, they make excellent candidates for lubricating gearboxes and engines. Reports claim that borate esters containing nitrogen are more stable [Yao et al. (1997), Choudhary et al. (2002)]. These additions create boron nitride-containing tribofilm. The lamellar structure of boron nitride, which is itself a very effective lubricant, enhances the antiwear performance under higher loads.

1.3.1.5. Halogen compounds

Chlorine compounds are the earliest extreme pressure and antiwear additives applied in the lubricant industry among halogen compounds. [Gong et al. (1990), Gao et al. (2004)]. These compounds react with the iron surface to produce iron chloride, as demonstrated by Kotvis et al. (1993). The main problem with chlorine-containing compounds is that they pose risks to the environment and human health. As a result, these are not recognized as feasible alternatives for present lubricants.

1.3.2. Ionic liquids

Ionic liquids (ILs) are liquid salts that melt at temperatures below 100°C. They are made up of a combination of large, asymmetric cations and anions. The viscosity and melting point of ionic liquids are directly related to their molecular structures, alkyl chain length, and nature of the anions and cations. Ionic liquids are suitable as potential lubricants due to their beneficial characteristics, which include high thermal stability, low volatility, miscibility with organic compounds, inherent polarity (ions) enabling strong adsorption on the surface, and nonflammability. Various cation-based ILs, including pyridinium, imidazolium, phosphonium, ammonium, etc.[Jimenez et al. (2008), Palacio et al. (2010), Hallett et al. (2011), Westerholt et al. (2015)], anion-based like hexafluoro phosphate $[PF6]^-$, tetrafluoro borate $[BF4]^-$, $[Sulfonate]^-$, $[sulfate]^-$, (trifluoromethylsulfonyl) imide $[Tf_2N]^-$, trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [DEHP], etc. and mixed ILs have been utilized in the field of lubrication[Zhou et el. (2017)].

1.3.3. Nanoadditives

The failure of conventional additives under extreme conditions restricts their use in tribology. Moreover, these additives are non-biodegradable, toxic by nature, inefficient at low temperatures, and highly reactive. Their tribological applications are strictly limited due to these characteristics. As a result, developing eco-friendly lubricants with high tribological performance is essential. With the arrival of nanotechnology, it is now possible to create such helpful engineering materials. Nano lubricants have been considered colloidal suspensions of nano-sized substances like nanoparticles, quantum dots, nanotubes, nanofibers, nanorods, nanosheets, and nanowires. Nano lubricants exhibit tremendous tribological efficiency when added in a small amount (<1 wt %) as their small size enabled immediate tribological activity at the surface. Concurrently, emissions are significantly reduced due to their chemical stability [Zhang et al. (2017), Zhai et al. (2019), Xie et al. (2019)]. Nano lubricants have high thermal conductivity, encouraging heat dissipation caused by friction. Consequently, such lubricants fulfill the needs of green tribology, a new area of study for tribologists.

Carbon-based substances possess high conductivity and mechanical, chemical, and thermal stability [Wang et al. (2016)]. Among these substances, mesoporous carbon, fullerenes [Turan et al. (2018)], activated carbon, carbon nanotubes [Moghadam et al. (2015)], carbon spheres[Kumar et al. (2019), Kumar et al. (2020)], graphene [Paul et al. (2019), Liu et al. (2019), Sun et al. (2019)] and carbon nano-onions [Joly-Pottuz et al.(2008)] have been considered to be extremely important for reducing wear and friction.

Carbon spheres have been recognized for their numerous activities in various fields, such as electrode materials, supercapacitors, fuel cells, catalysis, picolitre containers, hydrogen storage, tribology, and electromagnetic devices. These spheres are advised for high-pressure bearing [Dennis et al. (2011)]. The tribological properties of the carbon spheres in poly-alpha-olefin (base oil) were reported by Mistry et al. (2015). The friction/wear-reducing behavior of ultrasmooth submicrometer carbon spheres has been investigated by Alazemi et al. (2015). Ultrasmooth carbon spheres may cause rolling motion when operating in the boundary and mixed lubrication regimes, where they may act as nanometer-scale ball bearings [Alazemi et al. 2015]. Carbon spheres improved the tribological activity of polyether ether ketone [Wu et al. (2019)]. Outstanding tribological performance of nanocomposites of carbon spheres, ionic liquid stabilized Ag@C, and copper@C has been reported from our laboratory [Kumar et al. (2020a), Kumar et al. (2020b)].

1.3.3.1. Nanoparticles (NPs)

The inorganic nanoparticles contain metals such as palladium [Kumara et al. (2018)], nickel [Chou et al. 2010)], silver [Kumara et al. (2017)] and copper [Guo et al. (2020)], oxides of metal like TiO_2 [Zhang et al. (2018)], Fe_3O_4[Zhou et al. (2013)], ZrO_2 [Rylski et al. (2020)], Al_2O_3 [Luo et al. (2014)], CuO [Pena-Paras et al. (2015)], ZnO [Battez et al. (2008)], CeO_2 [Shen et al. (2016)], MgO [Singh et al.(2021)], V_2O_5 [Dai et al. (2017)], SnO_2 [Bonu et al. (2016)], Bi_2O_3 [Jaffar et al. (2023)], WO_3 [Karimi-Nazarabad et al. (2015)], metal sulfides such as ZnS [Liu et al. (2000)], CuS [Kang et al. (2008)], Ag_2S [Ma et al. (2019)], WS_2 [Ratoi et al. (2014)], MoS_2 [Xie et al. (2016)], and metal halide like lanthanum fluoride (LaF_3) [Zhou et al. (2001)]. According to Tang et al. (2014) and Uflyand et al. (2019), nanoparticles (NPs) are distinguished by their high surface-to-volume ratio, which makes them more chemically reactive. Consequently, they tend to agglomerate and do not disperse readily in the base oil. The functionalization of the surface of NPs inhibits their aggregation in the non-polar base oil and increases the stability of the dispersion in oil, thereby boosting the lubricating properties [Xu et al. (2018), Chen et al. (2019)]. Indeed, after functionalization, a significant number of surface atoms cause electrostatic or steric stabilization of the dispersion preventing their aggregation in a specific lubricant [Uflyand et al. (2019)]. A polymer or surfactant coating significantly lowers aggregation [Philip et al. (2019), Hong et al. (2020), Singh et al. (2020)]. Uflyand et al. (2019) state that functionalized NPs restrict material transfer and cold welding between the shearing surfaces. The exemplary tribological behavior of lead sulfide nanoparticles stabilized by oleic acid has been reported by Chen et al. (2006). As lubricant additives, silver NPs functionalized by organic compounds have been investigated by Kumara et al. (2017)]. The antiwear ability of phosphonium-based ionic liquids combined with stabilized oxide nanoparticles in synthetic motor oil (5w40) and polyalphaolefin (PAO) has been established by Valbe and colleagues [Valbe et al. (2017)]. The metal salt lattice doped with various metal ions created defects that resulted in slip systems, reduced the shear strength, and improved the tribological activity [Jaiswal et al. (2014), Kalyani et al. (2016), Li et al. (2017)]. The tribological performance of SDS-stabilized magnesium- and aluminum-doped zinc oxide nanoparticles improved significantly [Kalyani et al. (2016)]. Zinc-doped calcium copper titanate nanoparticles stabilized by stearic acid [Jaiswal et al. (2014)], and calcium-doped ceria nanoparticles stabilized by sodium dodecyl sulfate (SDS) and 1-decyl-3-

methylimidazolium bis(trifluoromethylsulfonyl) imide [Kumar et al. (2020)] studied by our research group have shown appreciable tribological behavior. The tribological properties of zirconia in a mechanically stable tetragonal phase could be improved by doping with elements like calcium, magnesium, yttrium, and aluminum [Jaiswal et al. (2014)]. The wear and friction-reducing properties of ZrO_2 and Y_2O_3 stabilized ZrO_2 have been investigated by Li et al. (2017).

Numerous mechanisms, including tribosinterization (mending, restoration, or self-repairing), rolling(ball bearing), polishing, and the formation of tribofilm or a combination of these mechanisms, have been proposed to explain the lubricating performance of nanoparticles. The polishing and mending mechanisms are indirect, but the tribofilm and ball-bearing mechanisms are direct. For the rolling mechanism, the typical spherical feature of nanoparticles is essential; they behave as tiny ball bearings that roll into the contact area and convert sliding friction to a combination of sliding and rolling friction. The protective tribofilm can be formed by the interaction of tribo-surfaces with additives. Tribo-film formation should take precedence over wearing for improved surface protection. For tribosinterization, nanoparticles are to be filled in the grooves and scars that result in mending or healing the surface. Nanoparticles being hard, tend to abrade rough surfaces, resulting in polished surfaces.

1.3.3.2. Nanosheets

Due to their unique properties, particularly their large specific surface area, inorganic two-dimensional layered nanomaterials such as graphene, molybdenum disulfide, tungsten disulfide graphitic carbon nitride, and hexagonal boron nitride have found great importance in various research fields. In a layered system, weak van der Waals forces between adjacent layers enhance lubricating behavior.

1.3.3.2.1. Graphene

Graphene comprises a monoatomic thick planar sheet of carbon atoms that have sp^2 hybridization and are placed into a honeycomb crystal lattice. Electrons easily and quickly pass through it and encounter less resistance, carrying electricity more effectively than in conductors like copper. Graphene is a very suitable material due to its unrivaled mechanical strength, optical properties, chemical stability, resistance to allow the entry of liquids or gases, and excellent electrical and thermal conductivity [Zhu et al. (2010), Geim et al. (2009), Ferrari et al. (2015)]. A single sheet of graphene theoretically has a vast surface area, approximately 2630 m^2g^{-1} [Demon et al. (2020)]. Numerous studies have examined the uses of graphene in various fields, such as sensors, gas adsorption and storage, solar cells, fuel cells, supercapacitors, Li-ion batteries, tribology, and catalysis [Eswaraiah et al. (2011), Paul et al. (2019, Liu et al. (2019), Sun et al. (2019)]. Graphene nano lubricant has enhanced the tribological properties of the engine [Eswaraiah et al. (2011), Yang et al. (2014), Paul et al. (2019), Ali et al. (2018), Sun et al. (2019)]. Dangling carbon bonds help graphene adhere to the surface of the steel. Its ability to stick to the surface serves as a barrier against metal-metal contact and can lower friction [Restuccia et al. (2016)]. Based on its structure, it is a chemically inert substance, therefore, undergoes weak adsorption and fast removal on the surface of the metal. With rotating, oscillating, and sliding contacts in micro- and nano-electro-mechanical systems, the importance of graphene in minimizing friction and wear is realized due to its ultrathin nature, even with multilayers [Kulia et al. (2012), Paul et al. (2019), Mungse et al. (2014)]. At the macroscale level, graphene and functionalized graphene don't possess excellent lubricating characteristics. At low concentrations, graphene can reduce friction and wear; at greater concentrations, it causes agglomeration due to its large surface area and surface energy.

Consequently, abrasive wear occurs. An essential intermediate material between graphite and grapheme is graphene oxide. It has often been produced by graphite oxide exfoliation. Typically, graphite oxide is mechanically or ultrasonically stirred in aqueous media or polar organic solvents to produce it [Kuila et al. (2012)]. The ultrasonication technique efficiently and swiftly exfoliates the graphite oxide. The degree of graphite oxidation, sonication period, ultrasonic frequency, and dispersion medium collectively affect how effectively graphite oxide exfoliates to produce graphene oxide (GO). It has been observed that as oxidation intensity, ultrasonic frequency, and sonication duration rise, so does the degree of exfoliation. In a moist environment, graphene oxide exhibits significantly greater friction and wear than graphene, whereas the converse occurs in a dry environment. The dispersions of reduced graphene oxide (rGO) with fewer functional groups(epoxy,-OH, and -COOH) show far better thermal and electrical conductivity than GO [Kuila et al. (2012), Paul et al. (2019)].

The literature review demonstrates that depending on the type of modifier used, covalent functionalization of graphene oxide can occur both on the surface and at the ends of the sheets [Georgakilas et al. (2012), Kuila et al. (2012), Mungse et al. (2014), Gusain et al. (2016), Zhang et al. (2017), Chouhan et al. (2018), Tang et al. (2018), Mungse et al. (2019, Paul et al. (2019)]. The attack of amines, ionic liquids, amino acids, silane compounds, and small molecular weight polymers results in nucleophilic substitution reaction at the epoxy groups. On the other hand, hydrogen atom displacement and edge selection are used in substitution by an electrophile, such as aryl diazonium salt. The compounds such as amines, isocyanates, and diisocyanates undergo a condensation reaction with functional groups -COOH and -OH forming amides and carbamates. Numerous reports show how eco-friendly ionic liquids can functionalize graphene to improve lubrication characteristics [Pu et al. (2011), Khare et al. (2013), Fan et al. (2015), Pamies et al.(2018), Gusain et al. (2016)]. Due to the synergistic effect of several nanomaterials, composites typically perform better than solo ones. Therefore, non-covalent functionalized graphene composites also produced good tribological performance. Molecules physically adhere to the surface of graphene through weaker interactions like van der Waals forces, π-π, or electrostatic interactions [Singh et al. (2011), Georgakilas et al. (2012), Kuila et al. (2012)]. There are a lot of aromatic compounds as well as conjugated polymers, including poly(3-hexylthiophene), poly (sodium 4-styrene sulfonate), conjugated polyelectrolyte, sulfonated polyaniline, pyrene,7,7,8,8- tetracyanoquinodimethane anion, macrocyclic ligands porphyrins, perylene diimide, and zinc phthalocyanine that are said to use π-π interactions to stabilize graphene structure in composite materials [Georgakilas et al. (2012), Kuila et al. (2012), Serra et al. (2019)].

Zhao et al. (2019) reported lubricating characteristics of Mn_3O_4/graphene nanomaterial with a sandwich-like nanostructure. A nanocomposite of reduced graphene oxide with zirconia was utilized as a lubricant additive by Zhou and his colleagues [Zhou et al. (2015)]. SiO_2/graphene nanofluids performed better for rolling magnesium alloys than pure nanofluids in lubrication [Xie et al. (2019)]. Copper/graphene nano lubricants increased the antiwear qualities of engine oil 5W-30 in automobile engines [Ali et al. (2019]. Wang et al. (2020) examined the tribological behavior of the mono-dispersed Ag/Graphene nanocomposite in pure paraffin liquid using a four-ball tribometer. The antifriction and high load-carrying abilities were observed using nanohybrid r-GO/multiply-alkylated cyclopentane [Mo.et al. (2013)]. Li and his associates studied the tribological properties of reduced graphene oxide (rGO)-3-aminopropyltriethoxysilane (APTES) thin film prepared on a Ti alloy substrate [Li et al. (2013)].

From our laboratory, the potential of nanomaterial TiO_2-reinforced boron and nitrogen co-doped reduced graphene oxide as effective antiwear additives has been investigated [Jaiswal et al. (2016)]. Our research team has improved the tribological efficiency of paraffin oil (PO) using some graphene-based nanocomposites, ZnO and Mg-doped ZnO/ rGO [Verma et al.(2018)], ZrO_2 /rGO /MoS_2 [Verma et al.(2020b)], and La-Y_2O_3-MoS_2-methionine functionalized GO [Shukla et al.(2020)] using a four-ball lubricant tester.

1.3.3.2.2. Molybdenum disulfide (MoS_2)

Molybdenum is arranged in a trigonal prismatic pattern with six S atoms to form the hexagonal close-packed arrangement. There are weak van der Waals forces between molecular S-Mo-S trilayers responsible for the lubricity. Tribological studies of highly dispersed thiol-functionalized nanosheets of MoS_2 in water have been carried out [Zhao et al. (2016), Rajendran et al. (2018)]. According to Xu et al. (2017), graphene and molybdenum disulfide dispersed in esterified bio-oil exhibit synergistic tribological activity. Song and coworkers reported the tribological behavior of hydrothermally synthesized graphene oxide/molybdenum disulfide nanocomposite [Song et al. (2017)]. The synergistic tribological activity of ternary nanocomposites of methionine-functionalized GO/ La-doped Y_2O_3 nanoparticles/ MoS_2 nanosheets and zirconia,cerium-doped zirconia NPs /r-GO / MoS_2) in paraffin oil on four-ball lubricant tester machine has been examined by our research group [Shukla et al. (2020), Verma et al. (2020b)]. Wu et al.(2018) conducted tribological studies of the chemically capped zinc borate/molybdenum disulfide nanohybrid in oil and grease. The tribological behavior of a Fe_3O_4/MoS_2 hybrid in oil or water was investigated by Zheng et al. (2016). According to Liu and his associates, Fe_3O_4/MoS_2 nanohybrid exhibits improved lubricating qualities in base oils and considerable photocatalytic degradation [Liu et al. (2018)]. Zabinski and his associates investigated the antiwear/antifriction efficiency of the MoS_2/Sb_2O_3/C composite films [Zabinski et al. (2006)].

1.3.3.2.3. Tungsten disulfide (WS_2)

Due to its layered structure, tungsten disulfide has been used as a conventional solid lubricant additive. Jiang et al.(2019) reported the outstanding tribo-activity of ultrathin tungsten disulfide nanosheets in poly alpha olefin base oil. The tribological Properties of carbon-coated tungsten disulfide nanosheets have been assessed by Li and coworkers [Li et al. (2019)]. A nanocomposite WS_2/TiO_2 was synthesized by Lu and collaborators (2019), and they discovered that it had a synergistic effect on the lubricity of di- iso octyl sebacate [Lu et al. (2019)]. Xu and his associates studied the tribological activity of WS_2 nanosheets decorated by uniformly dispersed copper nanoparticles [Xu et al. (2019)].

1.3.3.2.4. Hexagonal boron nitride (h-BN)

The two-dimensional boron nitride (h-BN) contains an equal number of B and N atoms alternately organized in a honeycomb pattern. With another name, white graphite, its lattice structure is most comparable to that of graphite. Due to the presence of unique B-N covalent connections, it exhibits greater thermal stability, mechanical stability, self-lubricating, and antioxidation abilities than graphite [Yuan et al. (2019), Zhang et al. (2019)]. As an additive in water- and oil-lubrication systems, BN nanosheets with tens of nanometers of thickness produced encouraging results [Wu et al. (2020a), (2020b)]. When exposed to high temperatures and organic vapors, h-BN exhibits exceptional antifriction performance that may be explained by the weakening of the interlayer interaction. Due to its chemical inertness, the hexagonal boron nitride surface must be modified to attain high dispersibility in lubricating fluids via physical adsorption or chemical functionalization [Yuan et al. (2019), Fan et al. (2022)]. Aromatic organic substances can be readily adsorbed on the hexagonal boron nitride surface using π-π interaction [Kumari et al. (2015), Kumari et al. (2016)]. Chemically functionalized hexagonal boron nitride (h-BN) and its nanohybrids with various nanomaterials, such as carbon nanotubes (CNTs), Fe_3O_4 NPs, MoS_2, and graphene, have been reported to be significantly tribologically active as a result of synergistic interactions between the constituents [Liu et al. (2018), Zhao et al. (2019), Yuan et al. (2019), Bondarev et al. (2020), Wu et al. (2020b)].

1.3.3.2.5. Graphitic carbon nitride (g-C_3N_4)

The most stable allotrope of carbon nitride is considered to be polymeric graphitic carbon nitride (g-C_3N_4), a metal-free semiconductor consisting of carbon (C), nitrogen (N), and traces of hydrogen (H). It exhibits high thermal and chemical stability owing to its two-dimensional structure stacked by weak van der Waals interactions [Gaddam et al. (2020), Wu et al. (2019 b), Liu et al. (2019), Wen et al. (2017]. The tribological behavior of octadecyl amine grafted g-C_3N_4 nanosheets was investigated by Kumar and his group [Kumar et al. (2017)]. Xu and his associates reported the Antiwear/antifriction properties of hybrid g-C_3N_4/MoS_2 [Xu et al. (2018)]. Yang et al. (2015) examined the friction and wear-reducing behavior of composite (copper nanoparticles/g-C_3N_4) in paraffin oil. The tribological properties of nanohybrid, copper nanoparticles/polydopamine functionalized oxygenated g-C_3N_4 nanosheets were evaluated by Min and coworkers [Min et al. (2020)]. Wu and associates improved the antiwear nature of polyimide using the composite CuO/g-C_3N_4 [Wu et al. (2019 a)]. They also studied the tribological properties of phenolic coating with varying percentages of g-C_3N_4 nanosheets [Wu et al. (2019 b)]. The antiwear bahavior of hybrid g-C_3N_4/TiO_2 was investigated by Zhang and coworkers [Zhang et al. (2019)]. The hybrid g-C_3N_4/Ag - poly phthalazinone ether sulfone ketone (PPESK) shows excellent tribological behavior [Chen et al. (2022)]. Our research team recently reported composite N−ZnO nanorods/g-C_3N_4 as a friction and wear modifier in paraffin oil using four ball lubricant tester machine [Singh et al. (2021)].

1.3.3.3. Carbon nanotubes (CNTs)

A layer of graphene rolls up to form a single-walled carbon nanotube (SWCNT), while the rolling of multi-layered graphene creates a multi-walled carbon nanotube (MWCNT). These nanotubes have a wide range of industrial uses. They make excellent lubricant nano additives or solid lubricants because of their shape, exceptional mechanical abilities, high length-to-diameter ratio, and considerable flexibility to improve tribological properties [Zhai et al. (2017), Sivanand et al.(2022)]. Chen et al. (2005) investigated the tribological performances of stearic acid-modified multi-walled carbon nanotubes (MWCNTs) with enhanced dispersibility using a pin-on plate wear tester. When carbon nanotubes were added, the tribological activity of paraffin oils and Mobil gear 627 improved, as reported by Khalil and his group [Khalil et al. (2016)]. In addition to enhancing the extreme pressure, antiwear, and antifriction capabilities of the water-based lubricants, the SDS functionalized multi-walled carbon nanotubes enhanced load-bearing capacity, too [Peng et al. (2007)]. Increased dispersibility may be associated with significant activity. For the same reason, the ionic liquid/MWCNTs hybrid displayed outstanding friction and wear-minimizing behavior [Zhang et al. (2015)]. Using UMT-2MT Tribo-tester, tribological efficiency of 1-methyl-3-hexylimidazolium hexafluorophosphates (Room Temperature Ionic Liquid, RTIL) composite of MWCNT (RTIL)/MWNTs) was reported by Yu and his associates [Yu et al. (2008)]. Dong et al. (2001) examined the antiwear/antifriction behavior of Cu-matrix composite reinforced by CNT. Zhang and his associates reported the tribological behavior of the composite CNT/MoS_2 [Zhang et al. (2009)]. Vardhaman and collaborators examined the tribological performance of ZnO/MWCNTs composite dispersed in 10w40 engine oil as a lubricant additive [Vardhaman et al. (2020)]. The influence of carbon nanotubes on developing a nanostructured double-deck tribofilm with superior self-lubrication performance was reported by Che, Qinglun, et al. (2020).

1.3.3.4. Nanorods

Nanorods are solid, rod-shaped nanoscale structures produced through chemical synthesis. In addition to other nanomaterials, the shape of nanorods has shown potential in tribology. The ZnO, N-doped ZnO, TiO_2, MnO_2, CuS, Fe_2O_3, Fe_3O_4, and Al_2O_3 nanorods are widely recognized for their features that facilitate friction reduction. [Song et al. (2012), Zhang et al. (2013), Liu et al. (2015), Kumar et al. (2017), Chen et al. (2017), Fei et al. (2018), Luo et al. (2018), Lin et al. (2020), Singh et al. (2021)]. Because of the sliding and rolling effects, Khatri et al. observed that copper oxide nanorods were more lubricious than nanoparticles [Gusain et al. (2013)]. Akbulut and his associates reported that the superior tribological properties of ZnS nanorods result from a synergistic interaction between their shape and surfactant (octadecylamine) coating, which makes it simpler for nanorods to roll and slide between the interacting surfaces [Akbulut et al. (2006)]. The tribological behavior of WS_2 nanorods was examined by Zhang and his associates [Zhang et al. (2007)]. The friction and wear-reducing properties of WSe_2 nanorods in base oil (HVI500) were investigated by Yang et al. (2008). A significant advancement in the tribological activity of N-doped ZnO nanorods functionalized g-C_3N_4 has been reported by us [Singh et al. (2021)].

1.4. Statement of Problem

Friction and wear together have been immanent adversaries to mechanical systems. Lubrication stands as the only remedial measure to safeguard such systems. Sundry lubricant systems with numerous additives have been fabricated to address the issue. Among them, heterocyclic organic compounds, metal complexes, and nanomaterials find paramount significance. Zinc dialkyl dithiophosphates (ZDDP) have often been employed as multifaceted antiwear additives. On the contrary, their continued use is prohibited because of their susceptibility to attenuate the efficacy of exhaust emission catalytic converters, thus enhancing air pollution. From an environmental perspective, various standards have been implemented to control sulfated ash, sulfur, and phosphorus (SAPS) contents in an additive. Therefore, different categories of tribological additives, including nano additives, are to be developed to surmount the above problems.

1.5. Aims and Objectives

The goal of the current research is to develop zero SAPS compounds with high tribological activity, which may have the potential to be recommended as an alternative to ZDDP in lubricating oils. Heterocyclic compounds containing heteroatoms nitrogen and oxygen are categorically advocated for their friction/wear-lowering disposition due to their high solubility in base oils and high adsorbability at the metal surface through lone pairs of electrons at hetero atoms. Fused heterocyclic rings are supposed to give better results because of the increased number of hetero atoms, provided all of them can approach the surface. Further, various nanomaterials like nanoparticles of metal/ metal compounds, nanosheets of graphene, molybdenum disulfide, boron nitride, etc., and several composites have been investigated as wear and friction modifiers due to their quick action at the surface under tribological conditions. There is a scope to explore some nanoparticles, nanosheets, and composites with high tribological efficiency.

The following are the main objectives of the investigation:

1. To synthesize, characterize and evaluate the tribological performance of fused heterocyclic organic compounds containing nitrogen and oxygen
   - ❖ Substituted tetrahydropyrazopyridines (THPP-H, THPP-Me, THPP-OMe) containing fused pyrazole and pyridine rings
   - ❖ Substituted Pyranopyrazoles (PPz-R, R = H, Me, OMe) having fused pyran and pyrazole rings
2. To correlate the above tribological data with computational calculations from Density Functional Theory (DFT) and Molecular Dynamics (MD) Simulations
3. To synthesize, characterize and examine the tribological efficiency of nano additives
   - ❖ Polyaniline (PANI), exfoliated V_2O_5 nanosheets, and the in situ synthesized composite PANI-$V_2O_5.nH_2O$ (PVO)
   - ❖ Graphitic carbon nitride; g-C_3N_4 nanosheets, lanthanum orthovanadate; m-$LaVO_4$ nanoparticles and their nanocomposite (g-C_3N_4/m-$LaVO_4$)
4. To analyze the surface morphology of worn surfaces using contact mode Atomic Force Microscopy (AFM) Scanning Electron Microscopy (SEM) techniques
5. To propose the tentative mechanism of lubrication using Energy Dispersive X-ray spectroscopy (EDX) and X-ray Photoelectron Spectroscopy (XPS) techniques