Chapter 2 Literature Review

This chapter highlights previous studies carried out in the lubrication domain with specific attention to nanomaterials. The literature review on hybrid nanolubricants signifies their important as a subclass of advanced lubricants to furnish superior tribological performance. These lubricants offer distinct advantages over conventional lubricants and standalone nanolubricants, including improved thermal conductivity, enhanced anti-wear performance, and reduced friction. Hybrid nanolubricants have emerged as a promising solution for addressing the limitations of traditional lubrication technologies. The possible lubrication mechanisms suggested by various researchers have been discussed. The chapter identifies key challenges and limitations, such as nanoparticles agglomeration, high production cost, and environmental concerns associated with nanoparticle disposal. These challenges underscore the need for further research to optimize the formulation and application of hybrid nanolubricants. It also highlights technical gaps in the current research domain. This chapter also includes the final objective of the thesis work.

2.1. Background

The growing emphasis on sustainability and environmental regulation has prompted researchers to explore eco-friendly alternatives to conventional petroleum-based lubricants. Conventional lubricants, derived from non-renewable fossil fuels, pose significant environmental challenges due to their toxicity, non-biodegradability, and adverse effects on the ecosystem from their production, use, and disposal [18,19]. The climate change conference (COP29) held in Baku, Azerbaijan November 2024, brought together 200 countries along with scientists, policy makers, business leaders, and environmentalists to think on the issues of growing concerns on the climate and decided to phase-out of fossil fuels to achieve net zero by 2050 or sooner. Due to such reasons most of the industries would like to explore the green lubricants. The synthetic lubricants can be an excellent alternative unless the process for lubricant formulation doesn't produce high carbon footprint [20]. The global bio-lubricants market was valued at USD 2.13 billion in 2021 and is expected to grow at a CAGR of 4.1% during the forecast period[21]. Bio-lubricants are made from vegetable oils or animal fats and offer biodegradability along with non-toxicity.

Vegetable-based lubricants emerged as a promising sustainable substitute due to various advantages, including biodegradability, renewability, low toxicity, and superior lubricity [22,23]. Derived from natural plant oils such as soybean, sunflower, and castor oil, these lubricants exhibit excellent friction-reducing and anti-wear properties while being environmentally benign.

Hybrid nanolubricants, offer a potential solution to address the shortcomings of vegetable-based lubricants. By dispersing nanoparticles, such as graphene, carbon nanotubes [24], metal oxides [25], or hybrid nanocomposites [26], into vegetable oil-based lubricants, it is possible to enhance their anti-wear performance and load-carrying capacity. Nanoparticles act as friction modifiers, wear-resistant additives, and heat dissipation agents, improv the overall tribological performance of the lubricant. Moreover, hybrid nanostructures combining multiple nanoparticles can further synergize properties, enabling tailored solutions for specific applications. Thus, the development and deployment of hybrid nanolubricants with vegetable-based oils represent a significant step toward achieving a balance between industrial performance and environmental sustainability. Research in this field has the potential to revolutionize lubrication technologies while advancing global efforts to mitigate climate change and reduce ecological harm.

2.2. Base Oils

2.2.1. Mineral base oil

These are refined products of petroleum crude oil which is made by decomposition of plant and animal inside the earth crust over the time. Crude petroleum base stock primarily comprises covalently bonded hydrocarbon molecules such as paraffins and aromatics [27], along with small amounts of impurities like sulphur, nitrogen, and trace metals. Various refining processes are employed to eliminate these minor components. One of the key benefits is their abundant availability and low cost, as they are derived directly from crude petroleum through relatively simple refining processes. They also exhibit good lubricating properties under normal operating conditions, providing effective protection against friction and wear. Mineral oils have moderate oxidation stability, making them suitable for many standard temperature applications without rapid degradation. One major concern is their limited biodegradability, which poses environmental risks in the event of leaks or spills. They also have higher volatility, meaning they tend to evaporate more readily at elevated temperatures, leading to increased oil consumption and deposit formation.

2.2.2. Synthetic base oils

Synthetic oils are man-made oils designed with specific lubricating properties. These oils are prepared by chemical modification of petroleum products. Compared to mineral oils, synthetic oils offer superior thermal and oxidation stability [28], better viscosity index, and enhanced biodegradability. As a result, their use has grown steadily in for many lubricants where mineral oils fall short. In terms of chemical composition, synthetic oils are mainly categorized into synthetic hydrocarbons (like polyalphaolefins, esters, and polyalkylene glycols [29]) and silicon-based oils. Their properties are excellent but with the high production cost.

2.2.3. Animal fats-based bio lubricants

These lubricants are derived from animal fats such as tallow, lard, or other lipid by-products of animals. They possess high lubricity than mineral based oil [30], biodegradability, and moderate thermal stability. However, their utilization is less common due to ethical concerns and limited availability.

2.2.4. Vegetable-based lubricants

The family of oils derived from vegetable sources comes under this category. The oils can be extracted from various parts of the plant and the process can be optimized following the proper methodology [31]. The different vegetable oils are classified in Table 2.1. These oils can also be classified as edible and non-edible. Edible oils, while technically suitable for industrial lubricant production, cannot be widely utilized for this purpose due to their growing demand for human consumption. The use of edible oils in industrial applications imposes a significant ethical and economic constraint, as it directly competes with their primary role in addressing global food security. Additionally, diverting edible oils toward industrial purposes could exacerbate supply shortages, drive up food prices, and negatively impact vulnerable populations reliant on these oils as affordable dietary staples.

Karanja, scientifically known as Pongamia Pinnata, is a medium-sized tree that grows easily and reaches maturity within four to five years. It can withstand harsh conditions such as heat, drought, salinity, and frost. It belongs to a monotypic genus, is commonly found along coastlines, riverbanks, and marginal lands, but it requires ample sunlight during its early growth stages. In India, it is widely distributed from the Himalayan foothills to Kanyakumari. Despite ample availability, its seeds often go unused.

Table 2.1: Vegetable-based oil sources and their examples

Category	Source	Examples of Oils	Key Uses
Seed-Based Oils	Seeds of plants	Soybean, Sunflower, Canola, Cottonseed, Sesame, Flaxseed (Linseed), Castor, Safflower	Cooking, biofuels, cosmetics, paints, industrial applications
Fruit-Based Oils	Flesh or pulp of fruits	Olive, Palm, Avocado, Coconut	Cooking, skincare, biodiesel, lubricants
Nut-Based Oils	Nuts of plants	Almond, Peanut (Groundnut), Walnut, Macadamia	Cooking, gourmet dishes, cosmetics
Cereals and Grains	Grains or germ of cereals	Corn, Rice Bran, Wheat Germ	Cooking, margarine, skincare, industrial uses
Kernel	Specialty plants/seeds	Jatropha, Neem, Moringa, Pongamia (Karanja)	Biofuels, pesticides, cosmetics, lubricants

Karanja fruits remain viable for one year, with seed production varying between 9 and 90 kilograms per tree. The pods are elliptical, 2 to 3 cm wide, 3 to 6 cm long, and have thick walls, each containing a single seed. These seeds are brown, 10–20 mm in length, and contain 27–39% oil. However, due to the presence of toxic substances such as di-ketone pongamol and karanjin, Karanja oil is not suitable for consumption.

Another important oil is *Ricinus communis*, widely known as castor, is an annual oilseed crop. Although it is sometimes called castor bean, it is not a true bean. Belonging to the spurge family (Euphorbiaceae), the castor plant can grow in various geographic regions. It thrives in temperatures ranging from 20 to 25 °C, while temperatures below 12 °C or above 38 °C can adversely affect its germination and yield. The castor plant displays significant variability in its growth characteristics, including seed size and colour, growth pattern, stem and foliage colour, and oil content. Its seeds are typically elongated, ovoid, oval, or square in shape, with lengths ranging from 0.5 to 1.5 cm. The base colour of the seeds varies, appearing as shades of brown, red, black, or brownish-yellow, with surface patterns ranging from fine veining to bold splotches or dots. The leaves change colour from pale green to deep red, depending on the anthocyanin pigment levels. The fruit of the castor plant is globe-shaped and resembles a spiny capsule. The capsule splits open, when fully ripe, releasing the seeds. The composition and properties of these two oils are listed Table 2.2.

Table 2.2 Fatty acid composition and properties of Karanja and castor oils

Fatty acid	**Lauric (C12/0)**	**Myristic (C14/0)**	**Palmitic (C16/0)**	**Palmitoleic (C16/1)**	**Stearic (C18/0)**	**Oleic (C18/1)**	**Linoleic (C18/2)**	**Linolenic (C18/3)**	**Ricinoleic (C18:1-OH)**
Karanja oil	–	–	9.8	–	6.2	72.2	11.8	–	–
Castor oil	–	–	–	1.016	1.241	4.69	4.92	0.63	87.3
Properties	**Kinematic viscosity (mm^2/s)**	**Heating value (MJ/kg)**	**Cloud point (°C)**	**Pour point (°C)**	**Flash point (°C)**	**Density (kg/l)**	**Specific gravity**	**Acid value (mg of KOH/g)**	
Karanja	46	39.12	1	−2	230	0.93	0.90	0.74	
Castor oil	673	39.12	-13.4	−2	250	0.93	0.96	1.101	

2.3. Hybrid nanolubricants

The “hybrid” means the species formed by two genetically different parents. In the case of lubricant additives, the term hybrid has a similar meaning. So, we can say that a hybrid additive is the synergistic blend of two or more different types of materials. The hybrids have properties superior to their progenitors. A “nanolubricant” is a class of lubricant that contains nanoparticles dispersed within a base lubricant, typically oil or grease. The nanoparticles are added to enhance the tribological properties of the lubricant, such as reduction of friction, wear, and improvement in load-carrying capacity. A hybrid nanolubricant has superior characteristics to constituent material, and it provides multifunctional properties. The synergism between the two materials can also increases some properties by many folds [32].

Cheng et al. used Bi and Bi/Cu hybrid and found improved antifriction and anti-wear properties of Bi/Cu hybrid [33]. Similar results reported for Al_2O_3, SiO_2, and Al_2O_3/SiO_2 hybrid by Jiao et al [34]. Ye et al. synthesized environmentally friendly N-doped CQDs an inorganic-organic hybrid which improved antifriction as well as oxidation stability of base oil, and furnished better antiwear properties to constituent materials [35].

Hybrid nano lubricants can be broadly classified into two categories [36]

1. Two or more nano particles in the base fluid or “mixing hybrid”
2. Compound nano particles in base fluid “compound hybrid”

The 1st kind of hybrid lubricants is simply prepared by mixing two or more nano lubricants into the same base oil. The simple and easy way to process but difficult to find a suitable combination and optimization takes time. The other hybrid involves compounding of the nanolubricants using physicochemical methods. The 2nd type of hybrid lubricants synthesis is difficult in nature, but once prepared their properties are far better than any other hybrid [37].

2.3.1. Simple mixed hybrid

2.3.1.1. ***Binary hybrid***

Spherical ZnO and MWCNT were mixed by Bhaumik et al, [38] in castor oil and reported as multiple friction modifiers to reduce friction and wear but at an optimum ratio, and concentration. Kamal et al. prepared Al_2O_3/TiO_2 hybrid with aid of oleic acid to be used in the 5W30 lubricant [39]. Their finding illustrates a 47% reduction in friction and a 17% reduction in wear. Moreover, this hybrid is suitable for reducing scuffing wear. They also used bis(2-ethylhexyl) phosphate to enhance the stability of the Al_2O_3/TiO_2 hybrid [40]. Haldar et al. mixed multi walled carbon nanotube (MWCNT) and SiO_2 in a 1:4 ratio in standard SAE 68 oil [41]. They used four ball testing machines following ASTM D4172 standards. The viscosity of the oil increased with the addition of nanoparticles from 0.3 to 1.8% by volume. The oxide nano lubricants such as SiO_2, TiO_2, ZnO, Al_2O_3 improved the rolling action and tribo sintering effect on the tribosurface [42].

2.3.1.2. ***Ternary hybrid***

Sepehrnia et. al., used MoO_3-GO-MWCNT in 5W30 lubricant to make a ternary hybrid lubricant and analysed tribological and rheological properties [43]. Adun et al. used Al_2O_3-ZnO-Fe_3O_4 to prepare hybrid nano fluid and characterized its dynamic viscosity[44]. The GO-silica aerogel-MWCNT was mixed in 5W30 lubricant by Sepernia and colleagues. They analysed its dynamic viscous properties, friction, and wear behaviour [45].They revealed an increase of wear rate by 68% and a reduction in friction coefficient by a nominal 4.5%. These studies suggest the compatibility of nanoparticles is a major issue in such kinds of hybrids.

2.3.2. Compound hybrid

Compound hybrids are made by performing some chemical processing. This includes functionalization, modification, combining the nanolubricants of different size, shape, or material. Ceria dot functionalized GO/MWCNT hybrid is prepared by Min et al. [46] to be used in paraffin oil and found the hybrid outperform the primitives in terms of tribo-performance. Chen et al. [47] fabricated carbon dots on GO/MoS_2 hybrid and used these additives for preparing self-lubricating polymer composites. Jaisawal et al. combined TiO_2 and reduced graphene oxide by doping nitrogen and co-doping boron. The finally formed hybrid outperformed its primitives and its binary forms [48]. Tribological investigation as per the ASTM G099 using the pin on disk tribometer conducted by Zeinali et al and found that a 1:1 ratio of TiO_2 and MnO_2 doped GO perform best to reduce wear [49]. Researchers had worked on improving following properties

1. Friction and wear reduction

Hybrid nanoparticles demonstrate a remarkable ability to reduce friction and wear, contributing to extend machinery lifespan and enhanced energy efficiency. For example, Graphene/SiO_2 Hybrids [50] improved the load-bearing capacity and reduced the coefficient of friction. The addition of graphene provided self-lubricating properties, while SiO_2 enhanced stability and wear resistance. The graphene/SiO_2 nanolubricants showed a 48.5% reduction in COF and a 79% decrease in wear volume compared to single-component nanolubricants. The CNT/TiO_2 hybrid in calcium grease demonstrated reductions of 72.3% in wear scar width and 60% in COF, making them suitable for industrial applications. [51]MWCNT/ZnO [52] The synergistic interaction between multi-walled carbon nanotubes (MWCNTs) and ZnO in the MWCNT/ZnO hybrid extended superior tribological performance as additive to castor oil and decreased the COF and wear volume by 26.21 and 89.09 %, respectively. The GO/Al_2O_3 hybrids comprising the GO and Al_2O_3 nanoparticles enhanced the stress distribution and surface polishing. These hybrids reduced COF by 66% and improved surface finish by 64%, demonstrating superior tribological performance compared to base lubricants [53]

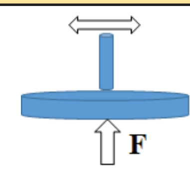
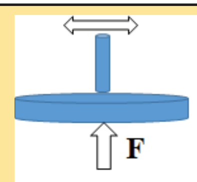
2. Enhancement in thermal conductivity

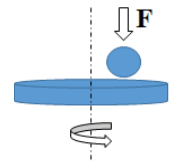
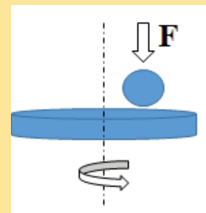
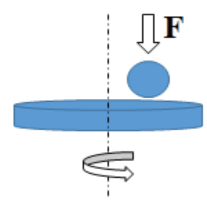
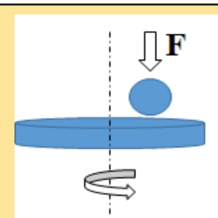
(0.1% to 2%). The MWCNT / g-Al_2O_3 in gum Arabic (GA)-based nano-fluid achieved a 20.68% enhancement in thermal conductivity at 0.1% volume fraction [54] The addition of TiO_2 with 0.1 wt% SDS improved the suspension stability and thermal conductivity over a month [55]. The TiO_2-ZnO in water-EG [56] The SiC-TiO_2 in diathermic oil increased the thermal conductivity with a maximum enhancement ratio of 8.39% at 1% volume fraction. Suspending SiC/TiO2 nanoparticles can enhance thermal capacity of the system [57] The 0.75% concentration of the MWCNTs-SiC in water-EG increased the thermal conductivity by 33% [58].

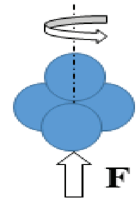
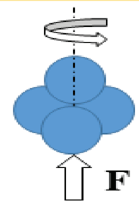
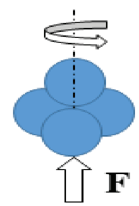
3. Stability:

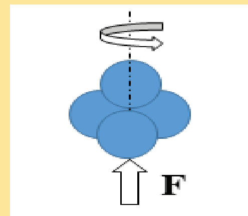
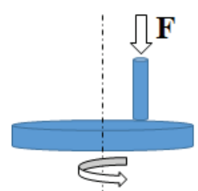
The Al_2O_3-MWCNT hybrids in thermal oil increased dynamic viscosity as the nanoparticle concentration rises [59], providing improved lubrication for thermoelectric modules. The TiO_2-ZrP hybrids exhibit enhanced suspension stability due to the unique surface properties of nanoplatelets [60]. The use of functionalized hybrids improved the dispersion stability by steric stabilization and with aid of electrostatically polar non-polar additive electroactive stabilization can be effectively induced in hybrid materials.

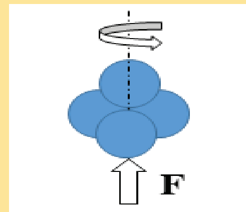
Table 2.3 Literatures available on tribological performance of nano lubricants

Base Oil	Nano additives	Parameters/ concentration	Test Setup	Results	Reference	Remarks
VHV18	3-glycidoxypropyl-trimethoxysilane grafted AlOOH/GO hybrid (0.5g/0.1g)	0.015, 0.030, 0.045, 0.060, 0.075 mg/mL	Ball on Disk; Four Ball Tester	Opt. 0.030 mg/mL 14%↓ COF 28%↓ WSD 73%↓ Wear rate	[61]	100Cr6 Balls
Engine Oil 5W30	Al_2O_3 (8-10nm); TiO_2 (10nm); Al_2O_3/TiO_2 hybrid	0.25 wt% NPs 1.75 wt% Oleic acid		Upto 50%↓ COF Upto 30%↓ WSD Stable more than 35 days	[62]	Thermal conductivity Pa=0.5 to 5.7 MPa
Engine Oil 5W30	Al_2O_3/TiO_2 hybrid 1:1 ratio	0.05, 0.1, 0.25, and 0.5 wt.% Oleic acid 1.95, 1.9, 1.75 and 1.5 wt%		47.61% ↓ COF At 0.1wt% 17%↓ wear by delamination	[63]	Tests for Scuffing Pa=1.95 MPa

Commercial Ca NLGI2 Li NLGI3	oleylamine @ CNT (dia 10-20 nm)-MoS_2 (1:10)	0.1 wt%		18% ↓ COF	[64]	Roughness of ball 0.5 µm.
PEG	GO@SiO_2 APTES Sheet GO & sphere SiO_2 14 nm	0.1; 0.5; 1.0; 3.0; 5.0 wt%		Upto 70%↓ wear volume with hybrid	[65]	Electrostatic assembly route Pa= 1.02 GPa
PEG	2-Mercaptobenzo-thiazolate IL With Mo nanoparticle (20 nm to 100 nm)	1% Mo 0.5% EM+0.5%Mo 0.5%N12+0.5%Mo		10%↓ COF @1wt% Mo 40%↓ COF N12 IL hybrid More than 70%↓ WV	[66]	Steel AISI 52100 Disk roughness Ra=0.025 µm
Polyol Ester	h-BN, exfoliated h-BNNPs, ODTES-h-BNNPs	0.01 to 0.06 mg/mL Steel/Steel disk (100Cr6 and 316LN)		0.04 mg/mL as optimum dose	[67]	(micro tribometer) Size plays imp role in NPs dispersion

PEG	CQDs, CQDsn (Diphenylamine coated)	0.5 to 2 wt%		1% CQD COF↓9% CQDsn COF↓ 75% Oxidation stability ↑ with CQDsn↑	[68]	AISI52100, CQD Not work for PEG as antioxidant
Castor Oil, PAO	CQDsn, oleylamine capped O-CQDsn	0.1 to 0.4 wt% in CO 0.1 to 2 wt% in PAO		0.2 wt% in CO opt. Scar Dia↓ 44.7% Whereas 0.5 wt% in PAO ↓ 22.3%	[69]	High dispersion stability, Oxidation stability improve PAO>CO
RBD Palm olein, Soybean oil	ZDDP (fixed 1%) Copper oxide	0.75, 1% Copper Oxide		57.6%↓ WSD For hybrid	[70]	Ra=0.029 µm

Esterified Bio Oil (EBO)	Graphene/MoS_2 Synergism (0:1, 1:4, 2:3, 1:1, 3:2, 4:1, and 1:0)	0.5 wt%; Load: 100 to 500 N Speed: 400 to 1400 rpm		Best synergy@3:2; Tribo Chemical this film formation of Fe_2O_3, MoO_3, Graphene; based on XPS and Raman results	[71]	EBO – adhesive wear; EBO 0.3 wt% graphene and 0.2 wt% MoS_2 – ploughing, EBO with 0.5 wt%, MoS_2, – ploughing and spalling. EBO with 0.5 wt% graphene, – ploughing
Canola Oil	Hybrid of h-BN 5 µm, 1.5 µm, 0.5 µm, and 0.07 µm size At 5wt%	Ra = 0.09, 0.11, 0.20, 0.49, 1.25 µm		Small particle: Ra↑ COF↑ Large Particle: Ra↑ COF↓	[72]	COF and Wear strongly depends on surface roughness. Size 3 to 4 times lesser than Ra going to reduce COF as well as

						Wear.
Castor Oil, Gear mineral Oil	Graphite, MWCNT, Graphene 0, 0.1, 0.5, 1.0, and 2 wt. %	ANN for input output correlation		Anti-wear property CO > mineral oil	[73]	Agglomeration Increased viscosity due to hindrance

Note : ↑ increase; ↓ decrease;

2.4. Influence of nanoparticles parameters on tribological performance

2.4.1. Influence of nanoparticle size

The size, shape, chemical nature, and mechanical properties of nanoparticles play a pivotal role in determining the tribological properties. This influence can be categorized into three key mechanisms:

1. **Size-dependent mechanical and physicochemical properties**: Nanoparticles exhibit size-dependent variations in their intrinsic mechanical and physicochemical characteristics, which directly affect their tribological behaviour. For instance, smaller nanoparticles tend to exhibit higher hardness due to the increased number of dislocation pileups in crystals with dimensions exceeding 100 nm [74]. This phenomenon, often referred to as the "size effect," is critical in tribological systems. Harder nanoparticles interacting with softer counter-surfaces can lead to indentation and scratching, which may result in wear and surface damage. Hence, while designing nanoparticles-based lubrication systems, careful consideration of the relationship between nanoparticles size and hardness is essential to mitigate potential adverse effects on the mating surfaces.
2. **Retention in the contact zone**: The ability of nanoparticles to remain within the contact zone during operation is another critical aspect influenced by their size [75]. If the characteristic surface roughness of the rubbing surfaces is smaller than the nanoparticle radius, the particles may escape from the contact zone, leading to inadequate lubrication and increased friction. On the other hand, when the surface roughness is significantly larger than the nanoparticles diameter, the particles can occupy the grooves and asperities of the surfaces, effectively smoothing the contact interface. This results in a more uniform surface profile and enhances the tribological

properties by reducing friction and wear. Consequently, selecting an appropriate size of nanoparticles relative to the surface roughness of the tribological system is crucial for optimizing lubrication performance.

3. **Colloidal stability and dispersion**: The colloidal stability of nanoparticles in lubricant formulations is strongly influenced by their size. Nanoparticles with larger specific surface areas and higher surface energy are more prone to agglomeration due to high cohesive interactions with each another [76]. This aggregation reduces dispersion stability, compromising the homogeneity of the lubricant. A stable colloidal suspension is vital for ensuring consistent tribological performance, as uneven dispersion can lead to localized wear or ineffective lubrication. Strategies to enhance colloidal stability, such as surface functionalization of nanomaterials or the use of stabilizing agents, are often employed to counteract these effects.

2.4.2. Influence of nanoparticles concentration

The concentration of nanoparticles within the lubricant is another critical parameter that governs tribological performance. Optimal concentration levels typically exist for a given system, beyond which performance can be either deteriorate or won't change:

1. **Low concentration effects**: At suboptimal concentrations, the formation of a continuous protective film on the contact surfaces is compromised. This results in inadequate surface protection along with higher friction and wear, as the nanoparticles are insufficient to sustain a robust tribological interface.
2. **High concentration effects**: Conversely, at concentrations exceeding the optimal level, the nanoparticles congestion occurs, leading to increased abrasiveness. This abrasiveness can intensify surface wear due to excessive particle-particle and particle-surface interactions. The dual challenge of insufficient lubrication at low

concentrations and excessive wear at high concentrations underscores the importance of determining the system-specific optimal concentration.

3. **System-dependent optimization**: The optimal concentration of nanoparticles is highly dependent on the specific operating conditions, such as load, temperature, and surface material properties. Therefore, lubricant formulations must be tailored to the unique requirements of each tribological system to achieve maximum efficiency and durability [77].

2.4.3. Influence of nanoparticles morphology

The morphology of nanoparticles is a crucial factor influencing their behaviour and effectiveness as lubricant additives. Different morphologies, such as granular, onion-like, sheet-like, spherical, and tubular structures, exhibit distinct tribological properties:

1. **Rolling action of spherical nanoparticles**: Spherical nanoparticles are particularly advantageous in lubrication applications due to their rolling mechanism, which facilitates a ball-bearing-like effect. This rolling action reduces friction and wear by minimizing direct contact between the mating surfaces, thereby enhancing tribological performance [78].
2. **Pressure distribution based on morphology**: The morphology of nanoparticles determines the type of contact they establish with counter-surfaces, which directly influences pressure distribution during operation. Spherical nanoparticles, due to their point contact, experience higher localized pressures under load. In contrast, planar-contact morphologies, such as nanosheets, distribute the applied load more evenly, resulting in lower contact pressures. This difference in pressure distribution can significantly affect wear patterns and overall lubrication performance [79].

3. **Other morphological considerations**: Nanoparticles with onion-like or tubular morphologies may exhibit additional mechanisms, such as exfoliation or sliding, which contribute to their tribological properties. Granular and sheet-like structures may also provide unique benefits, such as enhanced load-carrying capacity or better adherence to surface asperities. The selection of nanoparticles morphology should align with the specific demands of the application, such as load conditions, surface roughness, and desired lubrication effects.

The tribological performance of nanoparticles-based lubricants is intricately linked to the size, concentration, and morphology of the nanoparticles. A comprehensive understanding of these parameters is essential for designing effective lubrication systems that maximize performance and minimize wear under diverse operating conditions.

2.5. Mechanisms of tribological enhancement

The nanolubricants exhibit multiple tribological mechanisms that enhance lubrication performance:

1. Rolling/Ball-bearing effect

Spherical nanoparticles, such as silicon dioxide (SiO_2), copper oxide (CuO), and titanium dioxide (TiO_2), mimic the function of microscopic ball bearings when present between two engineering surfaces in relative motion. These particles reduce the shear forces between the contact surfaces by rolling rather than sliding, thereby minimizing friction. This effect is especially beneficial under boundary lubrication conditions, where the contact surfaces bear high pressure and insignificant oil film. By creating a rolling interface, these nanoparticles improve energy efficiency, reduce heat generation, and extend the lifespan of mechanical components.

2. Tribofilm formation

One of the most significant contributions of nanoparticles is the formation of a protective tribofilm on the contact surfaces. This occurs when nanoparticles are deposited under high pressure and temperature conditions, creating a solid or semi-solid film over surface asperities. Hybrid nanoparticles, such as graphene or silver combined with molybdenum disulfide (MoS_2), are particularly effective in this regard. The tribofilm reduces direct metal-to-metal contact, lowers wear rates, and improves overall lubrication. Furthermore, the chemical stability and low shear strength of such tribo films make them highly effective under extreme conditions, such as high loads and elevated temperatures.

3. Mending effect

Nanoparticles with smaller sizes can fill the micro pits, micro-valleys, cracks, scratches, etc. over time. This "mending effect" not only restores the smoothness of the surface but also reinforces its structural integrity, reducing wear to prolong the life of interacting components. This mechanism is particularly beneficial in systems experiencing high levels of abrasion or fatigue, as it helps to maintain surface quality even under prolonged use.

4. Polishing effect

The abrasive action of nanoparticles can smoothen rough surfaces, leading to reduced surface roughness and improved contact conditions. This "polishing effect" enhances the efficiency of lubrication by reducing frictional resistance. However, excessive polishing caused by an overabundance of abrasive particles can lead to undesirable wear, highlighting the importance of optimizing the nanoparticles concentration in lubricants. This balance ensures maximum benefits without compromising component durability.

5. Synergistic effect

The combination of different nanoparticles, known as hybrid nanoparticles, amplifies their tribological performance through a synergistic effect. For example, multi-walled carbon nanotubes (*MWCNTs*) combined with silver (*Ag*) or titanium dioxide (TiO_2) exhibit superior thermal conductivity and lubrication properties. These hybrid additives leverage the strengths of each material: MWCNTs provide high mechanical strength and wear resistance, while metallic nanoparticles like silver improve heat dissipation and anti-wear properties. This combination leads to enhanced load-carrying capacity, reduced friction, and improved stability of the lubricant under harsh operating conditions.

2.6. Limitations

While hybrid nanolubricants demonstrate immense potential to improve tribological properties, the dispersion stability of the nanomaterials has been a major challenge. Nanoparticles tend to agglomerate due to their high surface energy, reducing the effectiveness of the lubricant. Achieving long-term stability in diverse operational conditions remains a critical challenge. 2D materials have features and qualities that may improve the tribological performance of lubricants. However, their use is restricted due to their poor dispersion and stability in lubricants [80]. The use of advanced surfactants and stabilization techniques are gaining increasing attention to extend the dispersibility of nanomaterials. **Cost and scalability**: The high cost of nanoparticles and sophisticated synthesis methods make hybrid nanolubricants expensive. The large-scale production while maintaining quality and performance poses significant economic challenges. **Environmental and health concerns**: The environmental impact and biodegradability of hybrid nanolubricants are not well-documented. Some nanoparticles may pose risks to ecosystems and human health, necessitating comprehensive life-cycle analyses. **Optimal**

formulation: Determining the optimal combination and concentration of nanoparticles for specific applications is complex. Overloading nanoparticles can lead to increased viscosity, higher energy consumption, and reduced lubrication efficiency. **Performance under extreme conditions**: Hybrid nanolubricants often show promising results under controlled laboratory conditions, but their performance under extreme pressures, temperatures, and varying environments requires further investigation. **Compatibility with conventional systems**: The interaction of hybrid nanolubricants with existing materials, seals, and components in machinery may cause unexpected wear, corrosion, or degradation. Testing compatibility with conventional systems is crucial. **Recycling and reusability**: Developing methods to recover and reuse nanoparticles from used lubricants is essential for sustainable practices. This remains an unexplored area, requiring innovation.

2.7. Literature gap

The literature highlights several research gaps in the use of hybrid nano-additives in vegetable-based non-edible oils for lubrication:

1. Limited studies on tribological performance of hybrid nano-additives in vegetable-based non-edible oils under boundary lubrication conditions.

Boundary lubrication conditions, characterized by contact between asperities of rubbing surfaces, pose a critical challenge for lubrication systems. While vegetable-based non-edible oils have gained attention due to their environmental benefits and biodegradability, limited research has been focused on enhancing their tribological performance using hybrid nano-additives under such extreme conditions. The lack of comprehensive studies on hybrid nano-additives combinations of different nanoparticles hampers the understanding of their potential to improve wear resistance, reduce friction, and enhance load-carrying capacity in non-edible oils, particularly under boundary lubrication. Addressing this gap could pave the way for more effective and sustainable lubricant formulations.

2. Synergistic effects of combining different nanoparticles in non-edible oils.

Hybrid nano-additives combine various types of nanoparticles, such as metal oxides (e.g., TiO_2, ZnO), carbides (e.g., SiC), and carbon-based materials (e.g., graphene, carbon nanotubes). Each type of nanoparticle offers unique properties, such as high thermal conductivity, load-bearing capacity, or self-lubricating effects. However, the synergistic interactions between these nanoparticles, when used together in non-edible oils, remain largely unexplored. Investigating these interactions could reveal how the combined effects of different nanoparticles outperform their individual contributions, leading to enhanced tribological properties such as reduced friction, lower wear rates, and improved thermal stability.

3. Interaction between fatty acids of base oil and hybrid nano-additives.

Vegetable-based oils are rich in fatty acids, which influence their viscosity, thermal stability, and tribological behaviour. However, the interplay between the fatty acid's composition of base oils and the performance of hybrid nano-additives has not been adequately studied. The chemical structure and polarity of fatty acids may interact with nanoparticles, affecting their dispersion, stability, and lubrication properties. For instance, unsaturated fatty acids might interact differently with nanoparticles compared to saturated ones, potentially altering the protective film formation on contact surfaces. Understanding these interactions is crucial for optimizing lubricant formulations tailored to specific fatty acid profiles.

4. Comparative studies on chemically modified vs. unmodified vegetable oils with hybrid nano-additives.

Chemical modification of vegetable oils, such as epoxidation, transesterification, or hydroxylation, can enhance their thermal stability, oxidative resistance, and viscosity properties. However, comparative studies examining the performance of hybrid nano-additives in modified versus unmodified vegetable oils are sparse. The chemical modifications may influence the dispersion stability and interaction of nanoparticles with the base oil and surface asperities. Evaluating the tribological performance in both scenarios would provide insights into whether chemical modification synergizes with hybrid nano-additives to achieve superior lubrication performance or if unmodified oils can deliver comparable results.

5. Influence of hybrid nano-additives on surface and sub-surface properties

While many studies focus on the friction-reducing and anti-wear capabilities of hybrid nano-additives, their impact on surface and sub-surface properties remains underreported. Key aspects such as wear mechanisms, plastic deformation, and the ability of nanoparticles to dissipate heat during operation require deeper investigations. The interactions between hybrid nano-additives and the surface layers under high loads and extreme temperatures can lead to structural changes in the subsurface region, such as strain hardening or thermal softening. Understanding these effects would not only clarify the mechanisms of friction and wear reduction but also aid in designing additives that offer enhanced durability and thermal performance.

2.8. Motivation

The present work is motivated by the need to develop efficient, eco-friendly lubricants using hybrid nano-additives in vegetable-based non-edible oils. These oils, which are renewable and widely available, have great potential to replace harmful petroleum-based lubricants. Hybrid nano-additives can enhance their performance, making them suitable for industrial and automotive applications, particularly in boundary lubrication zone like those found in gearboxes, piston-cylinder systems, and bearings. The study also focuses on achieving superior lubrication with minimal concentrations of hybrid nano-additives to ensure cost-effectiveness and sustainability.

2.9. Problem identification

The growing global demand for lubricants, coupled with the finite availability of petroleum resources, necessitates a shift toward renewable and sustainable alternatives. Vegetable-based non-edible oils, which are biodegradable and non-toxic, offer a promising solution. However, their inherent limitations, such as poor oxidative stability and limited wear resistance, require enhancement through advanced additives. Hybrid nano-additives, which combine the benefits of multiple nanoparticles, hold significant potential to address these issues. Therefore, this research aims to formulate high-performance, environmentally benign biolubricants using 2D nanomaterial hybrid nano-additives, offering an effective alternative to conventional lubricants for industrial and commercial applications.

2.10. Objectives

Based on the limitations and gaps available in literatures the following objectives are finalized for the work.

- ❖ Vegetable based oils have least impact on the environment; hence two different viscosity oils have been selected as base oils; Castor oil (high viscosity) and Karanja oil (low viscosity). Both oils are non-edible and they can be utilized for industrial purpose.
- ❖ Different 2D nanomaterials-based hybrid lubricants are prepared, as they offer superior properties and benefits compared to standalone 2D materials even at the lower dosage.
    - ➢ Hybrid molybdenum disulphide-silica (MoS_2-SiO_2) has been prepared by hydrothermal and sol-gel method.
    - ➢ Zinc oxide (ZnO) sphere attached graphene oxide hybrid (AZnOGO) is prepared using graphene oxide (GO) and ZnO particles by combining them using a silane coupling agent.
    - ➢ Organosilicon-Inorganic hybrid of trichloro(octadecyl)silane-MXene (fMXene) is to be prepared to utilize Al etched MXene nano material as an efficient lubricant additive for castor oil.
    - ➢ Hybrid polymerized SiO_2 -functionalized hexagonal boron nitride (fh-BN) prepared by oxidizing hexagonal boron nitride (*h*-BN) using modified Hummer's method and reflux method.
- ❖ The characterization of these nano additives is to be done to investigate and justify the formation of finalized additive. The structural phase change can be collected by using XRD, change in bonding needs to be analysed using FTIR.

- Conduct the tribological investigation of additives and the worn surface analysis to comment about the effectiveness of the lubricant additive and the failure mechanism of lubricants.
- Carry out an in-depth investigation of the extreme performance characteristics of hybrid lubricants under severe operating conditions such as high load, and extended duration.
- Identify key parameters essential for optimizing hybrid lubricants, such as nanoparticle concentration, base oil viscosity, and additive compatibility. Conduct controlled experiments and apply statistical tools to determine their impact on friction, wear, and stability. Develop a parameter matrix to guide the formulation of future high-performance lubricants.