九州大学学術情報リポジトリ Kyushu University Institutional Repository

Nano Bio-Lubricant as a Sustainable Trend in Tribology towards Environmental Stability: Opportunities and Challenges

Koleola Ebenezer Ojaomo

Faculty of Mechanical Engineering, Universiti Teknologi Malaysia

Samion, Syahrullail Faculty of Mechanical Engineering, Universiti Teknologi Malaysia

Mohd Zamri Mohd Yusop

Faculty of Mechanical Engineering, Universiti Teknologi Malaysia

https://doi.org/10.5109/7172279

出版情報: Evergreen. 11 (1), pp.253-274, 2024-03. 九州大学グリーンテクノロジー研究教育センター

バージョン:

権利関係: Creative Commons Attribution 4.0 International



Nano Bio-Lubricant as a Sustainable Trend in Tribology towards Environmental Stability: Opportunities and Challenges

Koleola Ebenezer Ojaomo^{1, 2*}, Syahrullail Samion¹, Mohd Zamri Mohd Yusop¹
¹Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, Johor Bahru 81310. Skudai, Malaysia.

²Department of Mechanical Engineering, Federal Polytechnic Ado-Ekiti, Nigeria.

*Corresponding E-mail: ebenezer@graduate.utm.my

(Received May 16, 2023: Revised December 18, 2023: Accepted January 6, 2024)

Abstract: Bio lubricants derived from biomass can lessen the carbon footprint of production, lubrication, and energy production. When nanoparticles (NPs) additives are used, the performance improvement from the usage of bio-lubricant is more pronounced. This brief review highlights the key characteristics of current bio lubricants and the argument for utilizing sustainable bio lubricants that may be produced from agricultural feed stock with the potential to replace conventional mineral oil products. There is a need to shift to waste-derived oils and conduct research on alternative sources of bio-products to address the challenges of the lubricant/food competition, even though existing studies on bio lubricants have primarily focused on the use of vegetable oils and some non-edible oils. Most NPs additives combined with bio-lubricant, according to the literature, have the potential to reduce wear and friction. Furthermore, it was discovered that the NPs mechanisms during operations were responsible for the friction and wear reduction from nanofluids application. As a result, sliding contact was converted to rolling, and tribo-film was formed, separating the sliding bodies from direct contact. However, there are several complex problems related to bio-lubricant that should be handled before fulfilling the lubricating need. More thorough research was required to analyze crucial characteristics such viscosity, flash point, thermo-oxidative and storage stability of the oils, techno economics, and sustainability, which will be the focus of future work to resolve these problems.

Keywords: bio lubricant; nano-additives; base stock; biodegradability; vegetable oil; nanofluid stability

1. Introduction

In tribology, lubrication is regarded as technique that involves using a lubricant between two moving surfaces in close proximity to reduce wear on either one or both of them¹⁻³⁾. The pressure (or load) created between the opposing surfaces is relieved by the lubricant. In addition to serving as an anti-friction medium, lubricant also promotes fluid motion, upholds dependable machine operations, and minimizes frequent failure^{4,5)}. Lubricant can be liquids, semi-solids like grease and solids, including coatings and particles. The key roles of lubrication in sliding contact are to: (a) reduce wear and minimize overheating the surfaces; (b) preserve the surface from corrosion by lowering oxidation and (c) act as a sealant against dust, debris and water. Although employing lubricants is not foolproof for total removal of wear and heat in contacts, it has however shown acceptable capability in bringing it to its barest minimum^{3,4,5)}. Primarily, purposes of lubricants, according to Minami⁶⁻⁷⁾

are to reduce friction, clean and cool the contacting surfaces.

In the industrial and transportation sectors, the world relies entirely on materials made from fossil fuels, such as petroleum and petrochemicals. These products have the potential to adversely affect the environment due to some inherent toxic constituent and their non-degradability coupled with disposal challenges. As a result, researchers have suggested the replacement of petroleum-based mineral lubricants with bio-lubricants for lubrication⁸⁾ to mitigate the associated environmental consequences. Some functional bio solid and liquid fuels, methanol, bio-oil, bio chemicals, and biomass are just a few examples of the fuels that may be produced from solid and liquid wastes and biomass. Bio-lubricants are renewable and biodegradable in addition to having promising lubricating qualities over conventional lubricants. Bio-lubricants usually have their origin from vegetable oils, plant polymeric carbohydrates, and wax esters.

The process of making bio lubricants requires a

transesterification reaction, in which an ester and an alcohol are combined to create another ester by exchanging their alkyl groups. Vegetable oils are trans-esterified to produce fatty acid alkyl esters with various alcohol chain lengths⁹⁾. Mineral acids and bases are typically used to catalyze the process, and the resulting fatty acid alkyl esters can be used as fuel, biodiesel, and lubricants. Based oil and additives that improve the oil's characteristics make up the basic components of a lubricant. The base oil to additives ratio in lubricant is typically 9:16. Conventional lubricants employ synthetic base oils including hydrogenated polyolefins, esters, silicones, and fluorocarbons, while bio lubricants use vegetable oils, as illustrated in Table 1. The use of vegetable oils has also drawn interest as base oils due to their renewability and environmental concerns. Triacylglycerols (98%), sterols (0.3 %), diglycerols (0.5%), free fatty acids (0.1 %) and tocopherols (0.1 %) are the main components of vegetable oils [14]. Three hydroxyl groups that have been esterified with fatty acid carboxyl groups make up the triglyceride structure. The triglycerides' high molecular weight contributes to their high viscosity and viscosity index.

2. Why Bio-lubricant

The concept "bio lubricant" refers to all lubricants that are quickly biodegradable and safe for people and the environment¹³⁾. Even though their use is still quite limited compared to mineral oil-based lubricants²⁾, they represent attractive possibilities because they are renewable and produce no greenhouse gases at all. The phrases mineral oil, base stock, and base oil are just a few of the crucial ones to comprehend¹⁴⁾. The liquid by-product of crude oil distillation known as mineral oil is hydrocarbon. No matter the source of the feedstock or the location of the producer, base stock is typically developed through a single process with the same specifications (API 1509 2005)¹⁵⁾. A pure oil is a single type of base stock or a mixture of several base stocks that is used to formulate lubricants.

In comparison to other lubricants, bio lubricants have been said to have superior lubricity and to reduce friction coefficient, frictional forces, and wear¹⁶⁾. Vegetable oils are thought to be particularly efficient lubricants because they naturally possess great tribological characteristics. Vegetable oils' hydrolytic and thermal stability, however, has been reported to be worse than that of conventional mineral oils and must be improved¹⁷). Shah et al. ¹⁴). emphasized the importance of base oils and sustainable lubricants in terms of both the economy and the environment. Fuel efficiency must be improved because roughly 66% of fuel energy is wasted on the environment through thermal, frictional, transmission, and other components. Therefore, sustainable bio lubricants must be developed for tribological advancement. According to estimates, using superior lubricants in the production, transportation, energy production, and residential sectors might result in yearly GDP savings of more than 1%¹⁴).

The chemical alteration of vegetable oils to create a

Table 1. Various base stock lubricants and their sources

| S/N | Base | Source | Ref. |
|-----|---|--|--------|
| | Stock | | |
| 1 | Base stock of Mineral oil | Crude oil after solvent refining, catalytic dewaxing, hydrotreatment and hydrocracking: likely naphthenic, aromatic, paraffin in nature, categorized in API Group I, II and III oils | 10,11) |
| 2 | Base stock of Re- refined oil | Refined petroleum after removal of volatile and insoluble constituents and contaminants via acid/clay treatment. Belonging to API Group I, II and III oils | 10,11) |
| 3 | Base stocks of Syntheti c oil | Obtained from petroleum crude oil after chemical modification via hydrotreating and hydro-processing. Belong to API group IV and V oil | 10,11) |
| 4 | Base stock of Biomass | Obtained from plant and animal-based oil like vegetable oil, lipids and oils derived from agro-residues and waste via thermochemical and catalytic processing | 10,11) |

substitute for petroleum-based components is another intriguing study area^{18,19}). Through a four-step catalytic process, bio lubricants can also be made from used cooking oil and cyclic oxygenates. Some experts have noted that viscosity is the most significant characteristic of lubricants since it controls the degree of friction between two surfaces^{13,20)}. Higher viscosity lubricants have lower wear rates and a higher viscosity ratio, which reduces wear²⁰. Vegetable residual oils used to make eco-friendly multipurpose lubricating greases have been examined, and it has been found that their tribological performance is superior to that of commercial grease²¹⁾. It has been demonstrated that while choosing a stern tube lubricant, the operating shear rate of the ship should be considered²²⁾ by examining the rheological and wetting behavior of Environmentally Acceptable Lubricants (EALs) for use in stern tube seals²³⁾. By using a heterogeneous base catalyst of CaO and ethylene glycol (EG) and trans-esterifying fatty acid methyl esters (FAMEs), researchers created ecofriendly ethylene glycol di-esters (EGDEs) as bio lubricants from a variety of bio-oils^{24,25)}.

Additionally, bio lubricants can be made by trans esterifying 2-ethyl-1-hexanol, 1-heptanol, and 4-methyl-2-

pentanol with methyl esters from castor and rapeseed oils using titanium isopropoxide as a catalyst¹⁸⁾. Thus, the goal of the current study is to fill a gap in the body of knowledge about bio lubricants. This mini review has four main goals. First is overview of the importance of lubricants on sliding contact. Second is necessity of replacing fossil lubricant source with bio-lubricant due to their environmental friendliness when compared to conventional mineral lubricants. Thirdly, nanoparticles preparations, stability mechanism, nano-particles behaviors in bio-lubricants and lastly, challenges and opportunities of bio-lubricant in tribology were clarified.

The development of bio lubricants from non-vegetable oil and non-edible are demonstrated in Fig. 1. Although the base bio-lubricant had certain desirable qualities, it lacked some qualities leading to its subpar performances; as a result, needful improvements are implemented by adding appropriate nanoparticles as additive. The advantages and disadvantages of the use of bio-lubricants are listed in Table 2.

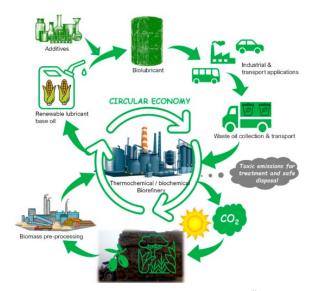


Fig. 1: Life cycle of bio base lubricants¹⁾

Contrasting the physiochemical characteristics of different oil lubricants. The kinematic viscosity values of mineral oils with hydrocarbon bases are high (40–150 cSt) ¹⁾, and those obtained from the decomposition of polyethylene or polypropylene are considerably higher (200–700 cSt), as can be shown in Table 3. When high molecular weight polymers break down at low temperatures or for insufficient amounts of time, waxy compounds with carbon chains longer than 30 are more likely to develop, which tends to make the mixture more viscous.

The viscosity can be reduced to levels comparable to those of conventional oils obtained from both edible and inedible seeds, though, after catalytic upgrading. The viscosity of the oil tends to be reduced due to the creation of aromatic hydrocarbons such as ethylbenzene, benzene, toluene, xylene and other alkyl benzenes during catalytic treatment employing acidic catalysts such as zeolites.

Although biomass-derived pyrolysis bio-oil has a low viscosity and is oxygen-rich, it cannot be used as a bio lubricant²⁷⁾. It has also been demonstrated that the poor viscosity of some oil samples, which is normally in the range of vegetable oil bio lubricants, may be produced by co-pyrolyzing polymers/plastics with biomass and then subjecting the mixture to catalytic treatment.

The techniques used in the creation of vegetable lubricants have significant impact on their properties, particularly on their bonds²⁷⁾. Hence, it is imperative to deploy the right strategy to avoid weakening the internal molecular structure. The viscosity, flash points, thermo-oxidative stability and other anticipated lubricant qualities are impacted when the bonds are too weak to endure the effects of operational stress on their properties. Further enhancement in the performance of bio lubricants requires sustained research and development to upgrade their frictional load bearing capacities from their physiochemical properties point of view. Modifications in their molecular structures by esterification, hydroxylation, epoxidation and additives inclusions are quite apt until better formulations of nano bio lubricants are established.

Table 2. Pros and cons of bio-lubricants^{1,12,26)}

| S/N | Pros | Cons |
|-----|---------------------------|-------------------------------------|
| 1 | Biodegradability is high | Poor oxidation stability of |
| | (as they are free of | pyrolysis bio-oils. |
| | aromatics) | |
| 2 | High boiling point (lower | Vegetable oils have higher |
| | emissions) | melting points. |
| 3 | High viscosity index | Higher extent of upgradation |
| | | required for thermochemically |
| | | derived base stocks. |
| 4 | Lesser number of | High acidity of pyrolysis bio-oils. |
| | contaminants | |
| 5 | Longer tool life | High cost. |
| 6 | High lubricity | Several vegetable oils are edible |

3. Nano-particles additives

Nanoparticles are made up of metal, metal oxide, supplied, nanocomposites, carbon nanoparticles, and group of rare earth elements, based on their chemical makeup²⁸⁻³²⁾. The common elements used in nano-additives formulations are presented in Fig. 2. Metal-containing NPs are the focus of most studies and make up 72% of reviews, according to Ijaz et al³³⁾.

Studies on carbon NPs, nanocomposites, and rare earth group, on the other hand, only made up 7%, 6%, and 7% of the total.

NP additives are formulated based on the foundation for lubricant modification, thus mostly applied extreme pressure reduction, anti-friction, antioxidant and anti-wear^{33,34}).

Three categories such as operational, economic, an

Table 3. Physio-chemical properties of edible, non-edible, Synth etic/mineral and Pyrolysis-derived oil

| Ref. | Oil | Oxidation Stability | Density at 298 | Cloud | Kinematic Viscosity at | Flash Point |
|--------|---------------|---------------------|--------------------|-----------|------------------------|-------------|
| | | 383 K, h | K (kg/m3) | Point (K) | 313 K (cSt) | (K) |
| | | | | | | |
| | | | Edible oils | | | • |
| 43) | Sunflower | 0.9 | 878 | 276.42 | 4.45 | 525 |
| 44) | Palm | 4.0 | 875 | 286 | 5.72 | 438 |
| 45) | Peanut | 2.1 | 890 | 278 | 4.92 | 450 |
| 46) | Rice bran | 0.5 | 880 | 278 | 4.95 | 591 |
| 47) | Soybean | 2.1 | 885 | 274 | 4.05 | 598 |
| 48) | Linseed | 0.2 | 890 | 269.2 | 3.74 | 451 |
| | Coconut | 35.4 | 805 | 273 | 2.75 | 598 |
| | Rape seed | 7.5 | 880 | 269.7 | 4.45 | 525 |
| | Olive | 3.4 | 892 | NR | 4.52 | 591 |
| | | | Non-Edible oil | S | | |
| 43) | Jatropha | 2.3 | 878 | NR | 4.82 | 4.9 |
| 44) | Rubber seed | NR | 870.9 | NR | 31.4 | NR |
| 45) | oil | | | | | |
| 46) | Castor | 1.2 | 15.25 | 259.5 | 15.25 | 533 |
| 47) | Mahua | NR | 850 | NR | 3.40 | 483 |
| 48) | Karanja | 6.0 | 918 | 282 | 4.80 | 423 |
| | Neem | 7.2 | 885 | 287.5 | 5.20 | 317 |
| | 1 | | Synthetic and mine | ral oil | | • |
| 49) | Neat mineral | NR | 880 | NR | 62.9 | 497 |
| | oil | | | | | |
| 44) | ISOVG100 | NR | NR | NR | 90 | 519 |
| 44) | ISOVG32 | NR | NR | NR | 28.8 | 477 |
| 44) | ISOVG46 | NR | NR | NR | 41.4 | 493 |
| 44)50) | SAE20W40 | NR | NR | NR | 105 | 473 |
| | 1 | • | Pyrolysis-derived | oils | • | JI. |
| 51) | PI-biomass | NR | 880-892 | NR | 4.1-7.5 | NR |
| | mixtures | | | | | |
| 51) | PS-biomass | NR | 1096-1192 | NR | 2.0-2.75 | NR |
| | mixtures | | | | | |
| 52) | Biomass | NR | 1100-1300 | NR | 13-80 | 323-373 |
| 53) | 70 | ND. | 777.045 |) ID | 247206 | 207.200 |
| 33) | Rice straw | NR | 777-847 | NR | 34.7-39.6 | 387-390 |
| 54) | PS | NR | 1100 | NR | 1.4 | 375 |
| 54) | Catalytically | NR | 979 | NR | 1.63 | 350 |
| | upgraded oil | | | | | |
| | from PS | | | | | |
| 51) | LDPE | NR | 856 | NR | 476.6 | NR |
| 51) | PI | NR | 841 | NR | 6.4 | NR |
| 53) | Bagasse | NR | 813-893 | NR | 28.8-31.2 | 382-385 |

environmental impact, can be used to highlight the advantages of nano-based lubricants additives^{35,36}).

Friction reduction will enhance machine and equipment performance while also reducing wear, which can lower the frequency of maintenance^{37,38)}. Good lubricity has economic advantages in that it reduces fuel consumption and lengthens the life of the machinery. Less often occurring downtime reduces production losses. It has been demonstrated experimentally that adding nanoparticles to different oils or lubricants has good tribological properties, with environmental benefits such as increased fuel efficiency and a decrease in emissions and particulate matter^{39,40)}. Additionally, nanolubes are frequently created using non-toxic, eco-friendly ingredients^{1,41,42)}. Figure 2 clearly presents the

pronounced key nano-additives in the market and their producers. Different techniques for nano particle (NP) additives to work are possible. The protective layer effect⁵⁶⁾, colloidal effect, small-size effect, rolling effect³⁹⁾ and third body effect are the methods through which oils with nano-additives minimize friction and wear under sliding lubrication⁵⁷⁾. Soft nanomaterials, which radically flex underload and to adapt surface velocity differences primarily by sticking to surfaces and shearing in the bulk media, operate as a cohesive third body which develops between two surfaces to minimize wear and friction⁵⁸⁾. Granular NPs are hard, cohesion-free particles with adequate spherical shape maintenance under stress and the ability to handle surface velocity changes by sliding and roll at low shear rates

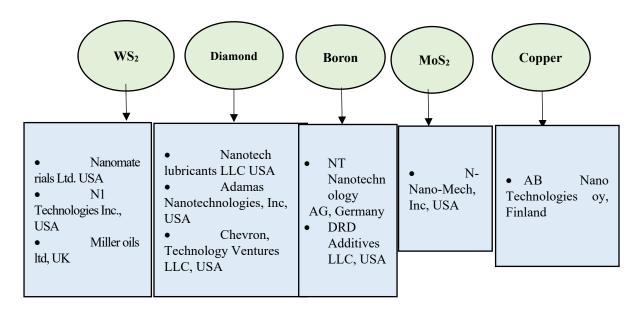


Fig. 2: Key Nano-lubricant additives and their producers³⁴⁾

4. Nanofluids preparations

The most typical approach for producing nanofluids is a two-step process. In this procedure, nanoparticles (NPs) like; nanotubes, nanofibers and other nanomaterials are first created as dry powders using physiochemical Processes^{7,60)}. Again, a way of reducing agglomeration of nanosized particles into fluid is through application of high-intensity magnetic mixing machine, ultrasonic agitation or homogenizer machine. Fig.3 shows the link between the particles and the mixing enhancements to minimize particle agglomeration within the base lubricant. Another way to stop nanoparticles from aggregating is to add a dispersion because it establishes continuity between

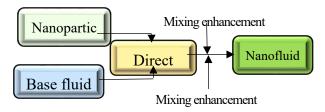


Fig. 3: Two-step Technique of formulating nanofluids⁵⁵⁾

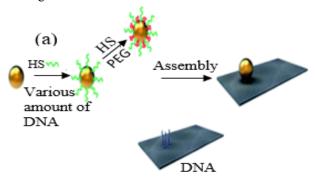
the particles and base fluids by acting as a bridge. Enhancing the immersion of nanoparticles, dispersants reduce the surface tension of base fluids. Since nano powder synthesis procedures had been scaled up to levels of commercial formulation, the two-step technique is considered as the most cost-effective method to developing nanofluids in a large scale⁶¹.

NPs have a propensity to assemble into larger particles due to their large surface area and surface activity. The use of surfactants is a crucial strategy to improve the stability of nanoparticles in fluids as demonstrated in Fig. 3. However, a major worry is the surfactants' ability to function at high temperatures, particularly in highapplications. Numerous cutting-edge temperature methods, like the one-step technique⁶²⁾, have been created by the nanofluids manufactures due to the challenges in formulating stable nanofluids under the two-step method, thus making researchers extend into more depth on another approach called one-step method which seems more standardized with better results.

Eastman et al.⁶³⁾ created a one-step physical vapour condensation approach to create nanofluids of Cu/ethylene glycol to minimize the aggregation of NPs. The creation and dispersion of the fluid's particles take place concurrently in the one-step process. This approach avoids the drying, storing, transportation, and dispersion of nanoparticles, which minimizes the agglomeration of nanoparticles and increases fluid stability⁶⁴⁻⁶⁶⁾. The onestep procedures can produce nanoparticles that are uniformly dispersed and can be maintained in a stable suspension in the base fluid. Creating nanofluids with various dielectric liquids in the vacuum-submerged arc nanoparticle synthesis system (SANSS) is another effective technique for achieving homogeneous nanofluids⁶⁷⁻⁶⁹⁾. The variable thermal conductivity characteristics of the dielectric liquids have a significant impact on and dictate the distinct morphologies. The produced nanoparticles have morphological shapes that resemble needles and are polygonal, square, round, and square-like. The technique does a good job of preventing unwanted particle aggregation. Apart from application of surfactant in reducing the nanofluid agglomeration, surface modification has an excellent response in improving the homogeneity of nanofluid for tribological enhancement⁷⁰⁻⁷²⁾.

Functionalization can change the surface of nanoparticles^{73,74)}. Long-term stability is simply obtained by mixing functionalized nanoparticles with the basic fluid. Wang et al⁷⁵⁾ created a practical approach for surface functionalization of gold nanoparticles, replacing the original pure DNA with mixed DNA/PEG polymers with functionalization illustration presented in Fig. 4(a). It is polymeric in nature and has the ability to raise the base lubricant's viscosity. Only a small amount of DNA was needed in comparison to pure DNA alteration to get the same result. Using an ultra-sonicator to disperse the surface-modified ceria (CeO₂) nanoparticles in methanol, created a stable methanol-based CeO₂ nanofluid⁷⁶). Similar investigation was conducted on methanol synthesis from CO/CO₂ on Cu/CeS₂, yielded good results in terms of active sites for the direct hydrogenation with improved outcome⁷⁷⁾. By using amide functionalization, Alzatecarvajal et al78), modified graphene oxide and nanodiamond, with recommended results. The process

involved solvent-free gas-phase treatment and made use of aromatic and aliphatic amines. There is some molecular breakage caused by van der Waals forces during the nanolubricant treatment, which results in the creation of homogeneous solutions. In the absence of a dispersant, Pati et al⁷⁹⁾ described a straightforward procedure to create stable Fe₃O nanofluid. In the study, Fe₃O NPs were prepared first through separation and purified with acetone and water, then soaked in NaOH solution and dried at 150 °C for 30 minutes. Then dried powder was sonicated for 30 minutes after dispersing in water. The images of the solutions stabilities at different time interval as illustrated in Fig. 4(b) (a–e), with sample A and D placed under 0, 1, 4, 24 and 48hrs during formulation mixing method.



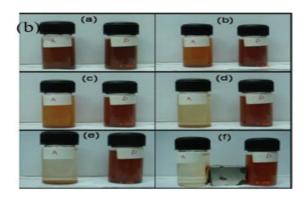


Fig. 4 (a and b): Illustration of gold nanoparticles Surface modification (4a)⁷⁵); and nanofluid stability without and with mixing technique⁷⁹) (4b), nanofluids prepared with sample A (0 ppm) and D (500 ppm) after different time intervals; (a) 0hr (b) 1 hr (c) 24hrs (d) 48hrs and (f) samples A and D under mixing technique.

5. Stability of Nanofluids

Due to the tendency of nanoparticles to attract one another due to their high surface energies, stability is the most important issue for nanofluids⁶⁰⁾. The electrical double layer repulsive force and the van der Waals attractive force are the two forces that interact with nanoparticles, respectively, according to the DLVO hypothesis. Hamaker's formula, which is represented by the equation (1) provides attractive potential energy.

$$V_A = \frac{A^r}{12H} \tag{1}$$

Where VA is the attractive potential energy; A is the Hamaker constant. Repulsive potential energy is provided by equation (2) in the absence of direct electrical double layer contact between two particles.

$$V_R = \frac{64\pi r n_o k T \gamma^2}{K^2} \exp(-KH)$$
 (2)

The upshot of the two conflicting forces is the stability of nanofluids. The nanofluid is in a relatively stable condition when the repulsive force outweighs the attractive force and can do so during the collision process due to Brownian movement^{80,81)}. Several surfactants, including SDBS, SDS, and CTAB, can prevent the aggregation of dispersed nanoparticles in nanofluids based on steric repulsion. The surfactants possess hydrophilic heads and hydrophobic tails which make them perform. The hydrophobic head stretches out into the nanofluids, while the hydrophilic tail forms a lengthy loop that adheres to the surface of nanoparticles^{82,83}). Sterically stabilized nanofluids maintain their dispersion and viability for a long time as a result. Because of the adsorption of ions, the nanoparticles in nanofluids carry charge during electrostatic stabilization. Nanoparticles are surrounded by an electrical double layer, which produces a repulsive force that balances the attraction force between the particles.

6. Mechanism of Nanoparticles

It was shown that adding different nanoparticles improved the tribological properties of the lubricants. Alves et al., 8,84) described four particle mechanisms as follows: (a) roll between friction surfaces and change sliding friction to rolling friction (rolling effect); (b) polish the contact surface and reduce surface roughness (polish effect); (c) form physical films and account for mass loss (healing/repairing effect); and (d) form a protective film between the friction pairs (protective effect). Figure 5 shows various nano-mechanisms for friction and wear reduction such as protective layer, as well as the effects of repairing, polishing, and rolling.

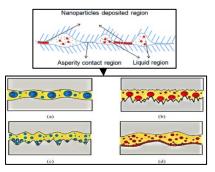


Fig. 5: The four NPs Mechanism in tribology for lubricant enhancement; (a) rolling effect; (b) polishing effect; (c) protective or tribo-film formation; (d) mending effect^{60,85,86}).

Researchers have posited various mechanisms processes for various types of nanoparticles^{60,85}. Zhou et al.⁸⁷), created LaF₃ nanoparticles and coated them with an organic material that contains phosphate and Sulphur (LaF₃-DDP). The LF3-DDP particles have the structure of hexagonal possession by LaF3 capable of rolling between the sliding contact, thus reducing body-body contact leading to friction reduction. During the surface examination, it was found that the chemical reaction between sulphur and phosphate and the deposition of LaF₃ nanoparticles produced the efficient tribo-film⁸⁸⁾. Ye et al., 89) on their analysis, they used the sol-gel method to produce modified TiO2 nanoparticles with tetrafluoro benzoic acid surfaces. The TiO₂ nanoparticle with liquid paraffin at the rubbing surface was found to increase the tribological properties of the nanofluid because of a coating of nano-TiO₂ content on the rubbed surface. The lowest worn scar diameter (WSD) was found to be 0.25 wt.%89).

Rapoport et al.⁹⁰⁾ claim that inorganic fullerene (IF), such as WS₂ and MoS₂ nanoparticles, reduce friction when added to paraffin oil through the third body method. Under difficult contact conditions, IF nanosheets delaminate and form a third body with the oil and wear debris. The outcome demonstrated wear reduction in the owing to the frictional asperities, enhancement⁹⁰⁾. Peng et al.⁹¹⁾ evaluated the tribological properties of diamond and SiO₂ nanoparticles in liquid paraffin. The change in WSD with respect to surface roughness was discovered to be least noticeable for nanofluids. This is primarily due to the presence of these nanoparticles, which will polish the rubbed surface⁹²⁾. Owing to the nature of the used lubricant, the sliding contact observed smoother while the wear scar appears the same during the operation^{3,30,93}).

Quihong and Xifeng⁵⁹⁾ found that the synthesized copper nanoparticle in SF15W/40 lubricating oil produced a protective layer or self-repairing layer that decreased shear stresses and partially repaired worn surfaces, boosting tribological properties. Jiao et al.94) claim that when an aluminum oxide/silicon dioxide (Al2O₃/SiO₂) composite nanoparticle with lubricant reaches the friction surface, sliding friction transforms into rolling friction. After modification, the additive possesses an elliptical form with particles that are 70 nm in size. It can easily penetrate between contacts and dissolve more quickly in base lubricant. This is due to the rolling impact that the absorbed nanoparticle has on the rubbing surface. Al2O₃/SiO₂ composite nanoparticles at 0.5 weight percent were shown to have a 50% reduction in friction coefficient⁹⁴⁾. According to Yu et al.,⁹⁵⁾ research on surface-modified Yttrium oxide nanoparticles may have entered the micro-cracks existing on the worn surface under the lubrication of liquid paraffin, where the organic and inorganic groups in the nano-fluid had generated a protective covering. The differences in the performance of these nanoparticles

7. Nanoparticles as Additives in Vegetable Oil

As stated in section 2, vegetable lubricants are obtained from different animals, fish and agricultural feed stocks. Based on their physiochemical characteristics, they are considered biodegradable, renewable environmentally friendly, thus proposed by researchers as alternative products to mineral/petroleum lubricants which are associated with some toxic constituents⁹⁶). Researchers presented that vegetable lubricants have a compatible affinity with nano-additives, resulting in improved tribological properties^{2,8,96,97)}. In addition, it has little effect on the environment in terms of pollution compared to petroleum counterpart. Another area of tribological investigation presented that application of base vegetable lubricant and bio-additive yielded excellent compatibility, tribological performance with good environmentally friendly response^{26,49}).

Opia et al.,4) investigated on the tribological performance and behavior of organic formulated Eichhornia Cracipess carbon nanotubes (EC-CNTs) in vegetable rapeseed oil using high frequency reciprocating rig (HFRR) and uni-directional tribo-meter. The EC-CNTs is an organic formulated additive with amphipathic properties capable of forming tribo-film during lubrication. The performance of the operation yielded enhanced results under 1wt% EC-CNTs than other concentration, compared the base repassed oil. The investigation further revealed that EC-CNTs blended rapeseed oil was performed better on HFRR mode than unidirectional operation due to high agglomeration of nanoparticles and starvation⁴⁾ of lubricants at the contact point. The particles accumulations on the various testing orientations leading to different levels of film formation for the low COF under HFRR and high COF generation under unidirectional mode due to low film formation are presented in Fig. 6 and Fig. 7, respectively. Another investigation was conducted using organic formulated Eichhornia crassipes carboxymethyl (EC-CMC) polymer, application of surfactant on EC-CMC polymer together rapeseed oil⁹⁸⁾. Surfactant increases the solubility of the nano lubricant. The outcome of the result was recommendable, suggesting the good compatibility of the formulations, similar functional groups possessed by the vegetable oil and the bio-additive^{99,100)}.

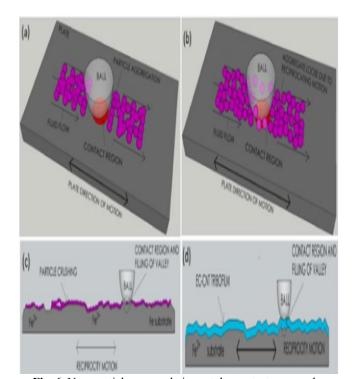


Fig. 6: Nanoparticle accumulations at the contact zone under reciprocating orientation⁴⁾

Tribological analysis was conducted by Thottackkad et al., ¹⁰¹⁾ using CuO NPs mixed with coconut oil. The results showed that a concentration of 0.34 % by weight of CuO nanoparticles was the best for achieving the lowest wear rate and friction coefficient. While the surface roughness decreased when the nano-additive was added, the viscosity and fire point increased ¹⁰¹⁾.

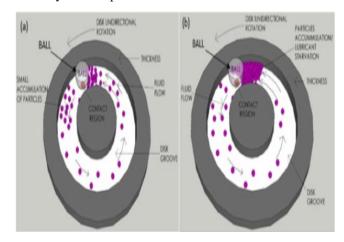


Fig. 7: Nanoparticle accumulations and lubricant starvation at the contact zone during unidirectional orientation ⁴⁾.

Alves et al,⁸⁾, demonstrated the rise in friction coefficient and the presence of abrasive wear on the worn surface rendered both the nanoparticles of zinc oxide and copper oxide ineffective as an anti-wear additive for soybean and sunflower oil. Chemically altered rapeseed was given a TiO₂ nanoparticle and microparticle addition was argued by Arumugam and Sriram¹⁰²). When compared

to TiO_2 microparticles, TiO_2 nanoparticles were shown to have improved lubricating properties $^{102,103)}$. With nanoscale TiO_2 and 6.9 % with micro TiO_2 , the friction coefficient of chemically treated rapeseed oil was lowered by 15.2% and 6.9%, respectively $^{102)}$.

Rapeseed oil with hollow spherical MoS₂ precipitated in nano TiO₂ has better tribological properties than the sample with MoS₂ alone, according to Xu et al. ¹⁰⁴). The well-distributed hollow spherical nanoparticles in the nanofluids affect the friction mode because they have the ability to change from sliding to rolling friction. Friction is reduced by the hollow sphere additive's fractional exfoliation, which permits sufficient deformation and the creation of a third body for contact separation. On the work carried out by Boshui et al. 105), when compared to the unmodified nanoparticle and base oil, it reported that acid-modified Cerium Borate nanoparticle improved the anti-wear and anti-friction capacity of rapeseed oil. Reporting to other conducted analysis, CuO and MoS2 nanoparticles' impact on enhancing the anti-wear and extreme pressure properties of chemically altered palm oil was studied by Gulzar et al 106). These nano-additives had increased the tested qualities by 1.5 times, according to the data. In comparison to CuO, MoS₂ nanoparticles showed superior characteristics and dispersion stability¹⁰⁶⁾.

In the analysis conducted by Rani et al. 107) using TiO₂, CeO₂, and ZrO₂ nanoparticles, blended to rice bran oil. The findings indicated that 0.5wt.% CeO2 and 0.3wt.% TiO₂ respectively showed the highest reduction in friction coefficient and wear. Suthar et al. 108) conducted investigations on Al₂O₃ nanoparticles blended with jojoba oil at a concentration of 0.1 wt.%, the least amount of friction and wear was achieved. Rajubhai et al., 109) conducted tribological analysis on copper nanoparticles blended with Pongamia oil, discovered that 0.075wt.% of copper nanoparticles was the ideal concentration based on the least amount of wear and friction. Again, copper and h-BN nanoparticles were added to epoxidized olive oil during tribological investigatory work by Kerni et al⁴²). The outcome observed that certain lubricant properties like wear volume and COF improved after adding 0.5 wt.% nano-additives.

Kumar et al¹¹⁰⁾, investigated tribological performance of CuO nanoparticles in canola oil using 0.1 wt.%, which yielded the lowest friction coefficient and lowest specific wear rate. Brassica and palm oils were combined with CuO and TiO2 nanoparticles with idea of knowing their tribological behaviors and was conducted Rajaganapathy et al¹¹¹). When compared to other nanolubricants created, palm oil containing 0.5 wt.% CuO nanoparticles had the lowest COF and specific wear rate. Similarly, Singh¹¹²⁾, observed that minimum friction coefficient and wear rate for castor oil mixed with TiO2 nanoparticles occurs at 0.2 wt.%. In the study carried out by Zaid et al. 113) using TiO2 nanoparticles, it improved the lubricating properties of jojoba oil. The outcome revealed that the COF and wear scar were lowered under 0.3 wt% TiO₂ nanoparticles were added to jojoba oil.

Rastogi et al¹¹⁴) conducted a tribological test and Jatropha oil was incorporated with SiO₂ nanoparticles. After the addition of 0.6wt.% nanoparticles, it was found that the COF and wear loss was lowest. The tribological properties of modified desert date oil containing copper nanoparticles were studied by Singh et al¹¹⁵). The tribological results of the bio-lubricant formulation improved when copper nanoparticles were added up to a maximum of 0.9 wt.% introduced SiC nanoparticles in various amounts after chemically altering moringa Oleifera oil through two-step transesterification. At 0.5 wt.% SiC nanoparticle, the COF and wear was found to be the lowest.

When lubricant additives of silicon dioxide (SiO₂) and titanium dioxide (TiO2) nanoparticles were studied by Cortes et al¹¹⁶), for their effects on the tribological and rheological properties of sunflower oil. The outcomes showed that the type and concentration of the nanoparticles utilized affect the rheological properties. The friction coefficient and wear volume loss were respectively reduced by 93.7 and 70.1 %, and 77.7 and 74.1 % by TiO₂ and SiO₂ nanoparticles¹¹⁶). Halloysite nano-clay was tested by Sneha et al117) as anti-wear additive in base rice bran oil and turmeric oil. When compared to other nano-clay concentrations, the tribological results of rice bran oil with 0.1 wt.% halloysite nano-clay revealed the lowest friction coefficient and wear scar diameter (WSD) (0.072, 0.531 mm). The WSD decreased to 0.491 mm by the addition of 1.5 wt.% turmeric oil as an antioxidant ingredient in rice bran oil with halloysite nano clay¹¹⁷). Supporting the mechanism of NPs in reducing friction and wear, Zhou et al.,118) revealed that COF substantially reduced through application of FeS NPs with excellent wear protection when used under dry sliding conditions. The behavior of the FeS NPs on the sliding material surfaces, illustrating the sulfur (S) atom diffusion resulting in friction reduction, thus illustrated in Fig. 8.

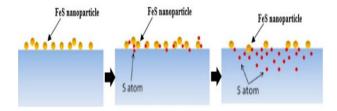


Fig. 8: Behavior of FeS NPs through diffusion Mechanism into the sliding substrate¹¹⁸)

In boundary lubrication conditions, Alves et al., ⁸⁾ studied the tribological behavior of vegetable oil-based lubricants (sunflower (SFO), soybean (SBO) with Soybean nanoparticles of oxides (CuO, ZnO). The findings demonstrated that the tribological properties of traditional lubricants can be greatly enhanced by nanoparticles. The worn surface has developed a smoother, more compact tribo-film, which is what has caused the wear and friction to be further reduced. When coupled

with mineral oil, ZnO exhibits outstanding efficacy in reducing friction and wear, even though the base oils, soyabean and sunflower, show lesser COF reductions when compared to synthetic oil (SO) and mineral lubricants, as shown in Fig. 9. Formation of good tribofilm was observed under mineral base oil with ZnO than other base lubricants used.

Refined, Bleached and Deodorized Palm Stearin, a refined form of palm oil, was tested for viability¹¹⁹⁾ when employed as a lubricant in a forward strain extrusion process. The solid fraction is produced by fractionating palm oil during crystallization at a regulated temperature, known as RBD palm stearin. Reduced extrusion load and superior surface finishing are two benefits of using RBD palm stearin. Again, Tiong et a¹²⁰, conducted tribological performance on refined, bleached, and deodorized (RBD) palm stearin (PS). Fatty acids efficiently increased the presence of lubricant film in additive-free refined, bleached, and deodorized (RBD) palm stearin (PS), resulting in a lower coefficient of friction (COF) than additive-free paraffinic mineral oil (PMO). Similarly, refined, bleached, and deodorized (RBD) palm olein's friction and wear performance was studied by Ing et al¹²¹⁾ and Zulhanafi & Syahrullail¹²²⁾. In comparison to paraffinic mineral oil, RBD Palm Olein has demonstrated a lower COF.

The performance of stamping oil, hydraulic oil, jatropha oil, RBD palm olein, and palm fatty acid distillate under high pressure circumstances was studied by Syahrullail et al¹²³). In the analysis, jatropha oil showed the lowest and best results, followed by RBD palm olein and palm fatty acid distillate in terms of WSD and COF. Due to the inclusion of anti-wear additives, stamping oil demonstrated the lowest COF and wear scar diameter. Supporting the presentation, according to Golshokouh et al⁹⁾, jatropha oil and palm fatty acid distillate (PFAD) performed better than mineral oils. Jatropha and PFAD oils demonstrated lower and best friction torque against mineral oil and hydraulic oils, thus revealed that Jatropha oil exhibited optimal shear stability in protecting substrate against wear. Based on the recommended performance of nano-lubricants in operation. Table 4, summaries some of the results from the use of nano-bio lubricants.

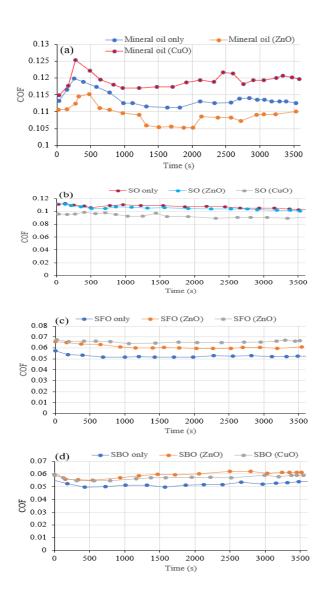


Fig. 9: COF against time for the various lubricants incorporated with additives: (a) mineral oil, (b) synthetic oil, (c) sunflower oil and (d) soybean oil 8)

8. Challenges and Future of Vegetable Lubricants

Though bio lubricants exhibit food tribology features including lubricity at moderate temperature with other properties justifying their popular recommendation for the replacement of fossil sourced lubricants. However, there are associated property drawbacks which limit the wider applications of the group in all areas of lubrication. The performance limitations of biobased lubricants were observed to be to be inherent properties from the base source, thus necessitating further modifications by inclusion of suitable additives to upgrade their tribological properties. Challenges associated with the use of biolubricants are quite mane, but the important ones are listed as follows.

8.1. Weak Oxidation and Thermal Stability

The poor oxidation nature of vegetable lubricants is a big concern in lubricant formulation. Since base stocks constitute 90% of the entire lubricant, they are employed in analyzing features like high biodegradability, low volatility, low acid content, high solvency etc., for optimal response to additives and working systems. Thermal stability is the resistance to molecular breakdown at high temperatures in the absence of oxygen, whereas oxidation stability, in the application working conditions of lubricants, is the resistance of a lubricant to chemical breakdown at high temperatures in the presence of oxygen. According to this justification, lubricants that oxidize quickly have inadequate oxidation stability and must be upgraded to endure usage-related situations. Again, low oxidation stability is a problem for vegetable lubricants, which are primarily made of polyunsaturated oils. The oxidation and thermal stability of vegetable oil are reduced because of problems with double bonds from fatty acids and alcoholic components, as well as strong linoleic contents. When creating bio-lubricants, the proper additives are required to address these issues.

8.2. Competition and high cost among lubricants and food

Food and energy (for biofuel and lubricant products) are in competition with one another, particularly in the field of edible vegetable oil. Currently, some nations are fully reliant on foreign nations for their ability to have edible and non-edible vegetable oils, thus making the product scarce and expensive in the market.

Industrial sector in India consumed 16.6 million tonnes of vegetable lubricants each year, the majority of which were imported, raising the price of the commodity on the market¹²⁵⁾. Vegetable lubricants are in great demand as the globe transitions to a sustainable economy. According to research, the cost of bio lubricants is 30–40% higher than the cost of traditional lubricants¹²⁶⁾. The government should participate in extensive farming practices to produce a significant amount of vegetable oil in a variety of kinds as a means of resolving the issue.

Research into various vegetable products, including edible and non-edible vegetable lubricants, is necessary to prevent these competitions and the high cost of vegetable lubricants. To combat scarcity, governments' support is crucial in cultivation and manufacturing of vegetable lubricants to supplement efforts of individual operators. Adequate funding would encourage farmers to increase cultivation and manufacturers support for improved machinery to produce in surplus quantity. Having a sustainable cycle of production would prevent the food component from being endangered. In addition, advances have been made toward treatment of used lubricants by enhancing the degraded properties, as well as blending petroleum and vegetable counterparts in order to reduce

the amount of each product in use. Promoting increased cultivation of edible and non-edible vegetable oil crops towards preventing the challenges associated with lubricant/food competition.

Further research and development on the potential methods of developing bio-lubricants from both edible and non-edible vegetable oil crops should be funded. The approach will further strengthen their adaptation for bio lubricants without adversely affecting their usage as source of food.

8.3. Poor low temperature and hydrolytic properties

Low temperature is what causes cloudiness, poor flowability, and precipitation¹⁷⁾. Many vegetable lubricants exhibit the features as described. Because these oils include ester functionality groups, they are vulnerable to hydrolytic breakdown and can become contaminated with water in the form of emulsion. Many vegetable oils have precipitation at low temperatures, which might impact lubrication during use, according to studies.

For instance, according to research on their low temperature features. However, a high ester group content makes vegetable lubricants vulnerable to hydrolytic degradation¹²⁴⁾. As a result, during preparations, it was necessary to avoid contaminants such water in the form of an emulsion. Once more, vegetable lubricants do a poor job of protecting against corrosion, especially in a humid environment. In the presence of oxygen and moisture, hydrogen atom is easily removed from the molecular structure, which causes the esters to break down into acid and olefin.

Table 4: Summary of some results from the use of nano-bio lubricant

| N/S | Base lubricant and nano- additive | Tribological test | Results | Ref. |
|-----|--|--|--|------|
| 1 | Palm oil + TiO2 NPs additives | Four ball testers ASTM D4172 | Results show that for both 40°C and 100°C of lubricant with 0.1wt. % of the TiO2 nano additives produced the lowest COF and wear scar diameter, the viscosities of samples increased as the weight percentage of the TiO2 nanoadditives increased. | 127) |
| 2 | Modified bio-lubricants + MoS2 NPs and CuO NPs | Four ball testers ASTM D4172 | Compared to CuO nanoparticles, MoS2 nanoparticles displayed improved AW/EP characteristics. Agglomerates might be reduced more easily with the addition of a surfactant containing 1 wt.% of oleic acid. | 106) |
| 3 | Bio-lubricants + Ti2 and SIO2 NPs | Four-ball tests and piston ring— cylinder liner sliding tests | The results revealed that the nano-lubricants improved load-carrying capacity, anti-wear behavior, and friction reduction capabilities as well as noticeable dispersion performance without a surfactant. | 128) |
| 4 | Soyabean oil, mineral oil, and additives suitable for use in sliding bearing is describe | Viscosity test ASTM D 445, Flash test ASTM D92-12b., Pour point test ASTM D97-12, | Observations on pour point, flash point, and viscosity index show promising properties for use in a wider temperature range. | 129) |
| 5 | Lubrication of refined, bleached and deodorized (RBD) palm stearin + Zinc dialkyldithiophosphate (ZDDP) additive | Pin on disk tribo- tester ASTM G99 | The results reveal that when RBD palm stearin stands alone, it has higher COF and WSD than that of SAE 40. | 130) |
| 6 | Palm oil blended a phenolic antioxidant yielded better lubrication at higher temperatures | Four ball testers ASTM D4172 | Results discovered that a uniform mixture of tertiary-butyl hydroquinone and palm oil had good antioxidant qualities by reducing lubricants degradation leading to decrease on wear and friction. | 131) |
| 7 | Vegetable oil (GN, CNT, GO) + graphene nanosheets (GN), carbon nanotubes (CNT), and graphene oxide (GO) | Four ball testers ASTM D4172 | In terms of enhancing the tribological properties of vegetable oil, the results showed that the addition of 50 ppm GN has the most beneficial effects. | 132) |
| 8 | TMP ester + TiO2 NPs friction and wear reduction characteristics | Four ball testers ASTM D4172 | Comparing the TMP ester with and without the addition of TiO2 nanoparticles at 160 kg, the COF was lowered by 15% and the wear scar diameter was reduced by 11%, respectively. | 133) |
| 9 | Modified Jatropha-based (MJO+AIL10% and MJO+PIL1%) in metalworking fluid | Four ball testers ASTM D4172 | Enhanced corrosion inhibition, outstanding friction reduction, reduced worn surface area, good surface polish, and better tapping torque efficiency were all displayed by MJO+AIL10% and MJO+PIL1%. | 134) |

9. Bibliometric Review

9.1 Method

The data used in bibliometric analysis were collected from Scopus database¹³⁵⁾. Material search was conducted from start of review till 15th April 2023. Theme of Boolean strings considered were "biolubricant", "nanobio lubricant", bio lubricants OR bio-lubricant, "Biolubricant AND Biolubricants and prospects", "bio lubricants and challenges". Characteristics of relevant publications were analyzed using Microsoft excel and frequency was analyzed using Bib-excel¹³⁶⁾. Cooperational network diagram was developed with VOS viewer application software¹³⁷⁾. Publications related to the Boolean strings theme were 467 documents with year filter range from 2015-2023. Further filtering and exclusion unrelated disciplines like arts and commerce left the document in the year range at 306.

9.2 Total number of publications

A total of 467 published documents related to the Boolean strings filtering set between 2015-2023 consisting of articles, conferences proceedings and letters on bio lubricants and related strings as mentioned in the above section. Numbers of publications found in the eightyear search period was low. This may be due to the fact the research into bio lubricants and nano bio lubricant is still a fledging adventure in Tribology and environmental concerns. Figure 10 showed the list of ten (10) affiliations with highest publications. The number document as shown by Fig. 10 indicated increasing affiliations' interests from Universiti Teknologi Malaysia leading with 25 documents to APJ Abdul Kalam Technology University India which is the 10th affiliation with 7 documents shown in Fig. 10 portrays that the trend is promising. Figure 11 also presented the number of related documents published yearly within the search period. The chart revealed an upward trend for research interest. This trend suggests great potential in nano bio lubricants.

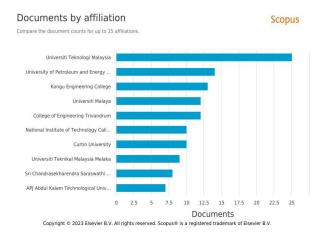


Fig.10. Documents per affiliation for 10 most published

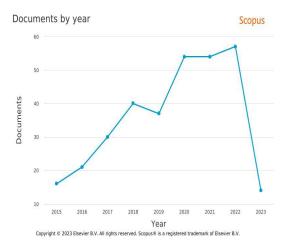


Fig.11. Documents by year

9.3 Documents per subject area

Figure 12 shows the number of documents by subject area. Researchers' contributions in different subject areas revealed that studies were highest in the field of Engineering with 24% of the relevant documents from the field of Engineering. This development is probably due to the increased desire for greener technology and quest for biodegradable lubricants. Material Science was closely next to engineering with 23.2% suggesting that research in engineering has significant influence on materials hence, research for improved technology would attract research in materials knowledge, methods, design and selection for improved performance. Physics/astronaut was 3rd with 11.3% while energy was 4th with 10.3%. The implication of this was that more researchers in different subject areas are exploring the opportunities and potentials of nano bio lubricant while Chemical engineering was 5th with 8.4%; Chemistry 6th with 8% followed by Environmental Science was 7th with 5.6%, Biochemistry 8th with 2.3%; earth and planets was 9th with 1.5% and others subject areas are left with mere 1.6%. The development also underscores the significance of the chemistry behind formulation and application of bio lubricant. The various interests shown by these subject areas point to the increasing concerns for environment which can be enhanced with improved technology as very vital to sustainable growth in which lubricant and lubrication tech improvement is a crucial component.

9.4 Documents per year by source

Figure 13 showed document count per source per year and cite score view for the 10 sources with highest count. The figure showed Proceedings of the Institution of Mechanical Engineers Part J Journal of Engineering Tribology having the highest count of 6 documents in 2021; Biomass conversion and biorefinery has 5 counts in both 2020 and 2021; Lecture notes in Mechanical engineering recorded 5 counts in 2022. Generally, research contribution from the remaining sources showed

consistent interests that suggest there are gaps and opportunities from engineering aspect to materials and methods as well as environmental concerns. Meanwhile, more interest is necessary in the environmental field to throw more light on the opportunities of bio lubricant towards preserving the ecosystem.

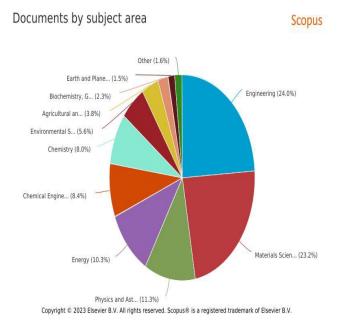


Fig. 12: Documents by subject area

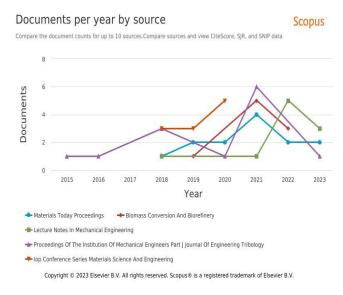


Fig. 13: Documents per year by source

Figure 14 showed the analysis of contributions of different types of documents in which research articles were the largest portion of 75.2%, conference papers covered 16.1% while review papers got 6.8%. Others are data paper and short surveys which amounted to 0.3% each. The implication is that research interests are high

and that researchers are making efforts to intensify studies on bio lubricant. On contribution by countries, India has the highest number of documents which was 140 as shown in Fig. 15. This number was followed by Malaysia with 58 documents while China is third on the list with 22 documents. This indicated that Asia is taking the lead in their research contributions because these three leading contributors are from Asia continent. Perhaps because Malysia is predominantly one of the largest producers of palm oil. Figure 15 further showed contributions of Australia, Italy, Spain, Indonesia, Mexico, Canada and United Kingdom with contributions respectively between 8 and 16 documents published within this study. India, Malaysia and China have shown significant contribution as shown, Australia and Europe also made significant impart. Unfortunately, African countries contribution did not appear within he first 15 countries to make the documents appear. Perhaps, studies in region may reveal more knowledge about nano bio lubricants and the concomitant merits and demerits.

9.5 Contribution of authors

Figure 16 showed the contributions of prominent researchers in the field of lubrication. Documents by authors were compared and the authors with highest document were Rani S. and Singh Y with 13 documents each while Samion S. and Shankar S. were both having 12 documents each on the topic. This was followed by Kalam M.A, Pramanic A. and Singlar A with 10 documents each while Arumugam S., Masjuki H.H. and Nithyaprakash R. were shown to contribute 8 documents each.

Figure 17 presents the keywords co-occurrence using Vos viewer bibliometric mapping¹³⁸⁾. It indicated the trend and knowledge structure of the research field. The links strength was mapped through co-occurrence of the keywords. The keywords are presented by nodes linked together by array of lines. The minimum threshold frequency of 5. If two keywords in a sentence are related by co-occurrence, the literature predominantly includes bio lubricant, bio-lubricant, nano additive, friction, wear, lubricant, coefficient of friction, epoxidation, chemical modification, biodegradable, mineral oil, nano particles, biodiesel, boundary lubrication, viscosity, rheology. This co-occurrence of keywords indicates the causes, effects, methods, opportunities, challenges and possible research interest available around the bigger nodes in the keywords. It is a pointer to the crosslink in the future research areas around the bio lubricant which could be further explored. Table 5 further explained the highest occurrence and total strength of the keywords "bio lubricant" as 49 and 37 respectively, indicating vast research interest and publications. It also showed least occurrence in the keyword "boundary lubrication" total strength and occurrence of 10 and 5 respectively, indicating minimum research interest suggesting researchable gaps. Number of authors that made the threshold of being cited at least twice was equal to 10.

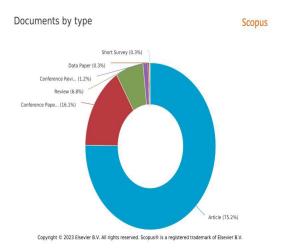


Fig. 14. Documents by type

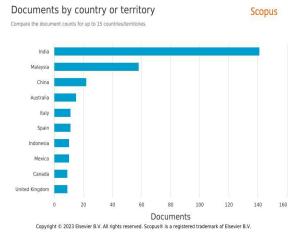


Fig. 15: Documents by country.

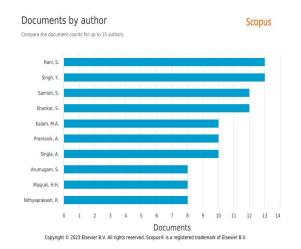


Fig. 16. Documents by author

| Table 5. Keyword co-occurrence | | | | | |
|--------------------------------|----------|------|-------------------|------------|--|
| Keywords | Clusters | Link | Total strength | occurrence | |
| lubrication | 6 | 9 | 18 | 12 | |
| Boundary lubrication | 4 | 7 | 10 | 15 | |
| Bio lubricant | 4 | 20 | 49 | 37 | |
| Bio lubricant | 5 | 7 | 7 | 6 | |
| Palm oil | 1 | 10 | 25 | 18 | |
| COF | 2 | 12 | 18 | 12 | |
| Nanoparticle | 3 | 14 | 28 | 15 | |
| Biodegradable | 1 | 7 | 14 | 7 | |

biodes adable mode of viscosity tube cant pain oil viscosity transeste ification additives rheology transeste ification biolubricant waste cooking oil epoxidation escentication friction friction friction biolubricants biolubri

Fig. 17: Keywords co-occurrence

10. Conclusion

As replacements for petroleum-based lubricants, bio lubricants have become more popular because of the need to prevent climate change. The lubricant industry is moving toward the use of biodegradable, environmentally friendly lubricants derived from renewable sources because of growing awareness of environmental issues. Bio lubricants made from sustainable resources have a negligible effect on the environment. The government's restrictions on the use of mineral lubricants as well as the availability, renewability, and ecologically favorable characteristics of bio lubricants all have an impact on their use. Vegetable oil-based bio lubricants with comparable performance can take the place of petroleum-based lubricants in industrial applications, reducing the need for nonrenewable resources and expanding opportunities.

Base bio lubricants provide excellent lubricity, low volatility, high viscosity index, high flash point, and minimal evaporative loss^{52, 139)}. Base bio lubricants are readily available, non-toxic, renewable, biodegradable, and sustainable^{19, 26, 129)}. Additionally, bio lubricants have better lubricating properties and stick to metal surfaces. due to the presence of their polar ester group⁹⁸⁾. Mineral oils can be mixed or substituted with base bio lubricants to lessen reliance on nonrenewable oil supplies. The focus is on the study and creation of base bio lubricant additives to lessen wear and friction in tribological systems. Since bio lubricants have poor cold flow characteristics and minimal oxidation stability, these drawbacks can be improved by adding additives or chemical modifying the bio lubricants.

It could be necessary to moderately upgrade oils made from agricultural waste to lower the fuel's oxygen concentration. Usually, catalysts are used in a hydrogen environment to accomplish this. Although this is a wellknown technique, it is required to carefully hydrogenate and hydro-deoxygenate materials to modify characteristics of bio lubricants. There are few studies on the stability of current bio lubricants made from waste and from vegetable oil. According to literature, a fundamental analysis of nanofluids stability, oxidative stability, hydrolytic stability, and thermal stability is not sufficient thus needs more research as to ascertain the appropriate application of bio-lubricants. The formulations of bio lubricants need to have their biodegradability and ecotoxicity thoroughly evaluated, established by the specialist. Better emphasis is required for comprehensive comparative research examining the benefits and drawbacks of various bio lubricants for a range of applications.

Research into various vegetable products, including edible and non-edible vegetable lubricants, is necessary to prevent competition and the high cost of vegetable lubricants. Similarly, governments should enhance funding for research and development, making cultivation of edible and non-edible vegetable oil crops attractive to

farmers and ease the production procedures. This will contribute meaningfully towards preventing the challenges associated with lubricant/food competition.

Acknowledgement

The authors hereby express our thanks to the Ministry of Higher Education of Malaysia for the Research Consortium Grant (Geran Konsortium Kecemerlangan Penyelidikan) 4L961 (JPT/(BKPI)1000/016/018/25/4(7)), UTMFR Grant (22H46), FRGS Grant (FRGS/1/2018/TK03/UTM/02/14), University Research Grant (21H50), TDR Grant (05G23), Automotive Development Centre (ADC) and Tertiary Education Trust Fund (TETFund) Nigeria for the support provided.

Reference

- 1) R. N. Sarma and R. Vinu, "Current status and future prospects of biolubricants: properties and applications," *Lubricants*, 10 (4) 5–55 (2022).
- J.M.L. Del Río, E.R. López, M.G. Gómez, S.Y. Vilar, Y. Piñeiro, J. Rivas, D.E.P. Gonçalves, J.H.O. Seabra, and J. Fernández, "Tribological behavior of nanolubricants based on coated magnetic nanoparticles and trimethylolpropane trioleate base oil," *Nanomaterials*, 10 (4) (2020). doi:10.3390/nano10040683.
- 3) X. Zhang, M. Xue, X. Yang, G. Luo, and F. Yang, "Hydrothermal synthesis and tribological properties of mose2 nanoflowers," *Micro Nano Lett*, 10 (7) 339–342 (2015). doi:10.1049/mnl.2015.0014.
- 4) A.C. Opia, A.H.M. Kameil, S. Syahrullail, C.A.N. Johnson, M.I. Izmi, S.C. Mamah, A.I. Ali, A.B.A. Rahim, and I. Veza, "Tribological behavior of organic formulated anti-wear additive under high frequency reciprocating rig and unidirectional orientations: particles transport behavior and film formation mechanism," *Tribol Int*, 167 1–34 (2022). doi:10.1016/j.triboint.2021.107415.
- J. Kałużny, A. Merkisz-Guranowska, M. Giersig, and K. Kempa, "Lubricating performance of carbon nanotubes in internal combustion engines – engine test results for cnt enriched oil," *International Journal of Automotive Technology*, 18 (6) 1047–1059 (2017). doi:10.1007/s12239-017-0102-9.
- 6) I. Minami, "Molecular science of lubricant additives," *Applied Sciences (Switzerland)*, 7 (5) (2017). doi:10.3390/app7050445.
- 7) Wei Yu and Huaqing Xie, "A review on nanofluids: preparation, stability mechanisms, and applications," *J Nanomater*, 2012 (28) 1–33 (2012).
- 8) S.M. Alves, B.S. Barros, M.F. Trajano, K.S.B. Ribeiro, and E. Moura, "Tribological behavior of vegetable oil-based lubricants with nanoparticles of oxides in boundary lubrication conditions," *Tribol Int*, 65 28–36 (2013). doi:10.1016/j.triboint.2013.03.027.
- 9) I. Golshokouh, S. Syahrullail, F.N. Ani, and H.H.

- Masjuki, "Investigation of palm fatty acid distillate oil as an alternative to petrochemical-based lubricants," *J Oil Palm Res*, 26 (MAR) 25–36 (2014).
- 10) L.R. Rudnick, "Synthetics, Mineral Oils, and Bio-Based Lubricants," 2020.
- 11) Noria Corporation, "Base Oil Groups Explained: Machinery Lubrication," 2015.
- 12) A. Ruggiero, R. D'Amato, M. Merola, P. Valášek, and M. Müller, "On the tribological performance of vegetal lubricants: experimental investigation on jatropha curcas l. oil," *Procedia Eng*, 149 (*June*) 431–437 (2016). doi:10.1016/j.proeng.2016.06.689.
- 13) O.M. Timothy Yakubu, Sunday Albert, Asipita Salawu, Olutoye M., "Vegitable oil based lubricants: challenges and prospects," *Tribol Lett*, 14 (2) 60–70 (2019).
- lubricants: challenges and prospects," *Tribol Lett*, 14 (2) 60–70 (2019).
- 14) R. Shah, M. Woydt, and S. Zhang, "The economic and environmental significance of sustainable lubricants," *Lubricants*, 9 (2) 1–11 (2021). doi:10.3390/lubricants9020021.
- 15) Nees Jan Van Eck and Ludo Waltman, "Software survey: vosviewer, a computer program for bibliometric mapping," *IOP Conf Ser Mater Sci Eng*, 7 (*I*) 1–6 (2022). doi:10.1088/1757-899X/496/1/012060.
- 16) N.W.M. Zulkifli, M.A. Kalam, H.H. Masjuki, M. Shahabuddin, and R. Yunus, "Wear prevention characteristics of a palm oil-based tmp (trimethylolpropane) ester as an engine lubricant," *Energy*, 54 167–173 (2013). doi:10.1016/j.energy.2013.01.038.
- 17) S. Arumugam, and G. Sriram, "Synthesis and characterization of rapeseed oil bio-lubricant dispersed with nano copper oxide: its effect on wear and frictional behavior of piston ring-cylinder liner combination," *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 228 (*11*) 1308–1318 (2014). doi:10.1177/1350650114535384.
- 18) J. Encinar, S. Nogales-Delgado, N. Sanchez and J Gonzallez, "Biolubricants from rapeseed and castor oil transesterification by using titanium isopropoxide as a catalyst: production and characterization," *Catalysts*, 4 (29) (2020).
- 19) N. Talib, N.A. Jamaluddin, T.K. Sheng, L.W. Kiow, H. Abdullah, S. Ahmad, and A. Saleh, "Tribological study of activated carbon nanoparticle in nonedible nanofluid for machining application," *Evergreen*, 8 (2) 454–460 (2021). doi:10.5109/4480728.
- 20) I.S. Aisyah, W. Caesarendra, D. Kurniawati, M. Maftuchah, D. Agung, A. Glowacz, K. Oprzędkiewicz, and H. Liu, "Study of jatropha curcas linn and olea europaea as bio-oil lubricant to physical properties and wear rate," *Lubricants*, 9 (4) (2021). doi:10.3390/lubricants9040039.
- 21) H. Noureddini, B.C. Teoh, and L. Davis Clements,

- "Densities of vegetable oils and fatty acids," *J Am Oil Chem Soc*, 69 (12) 1184–1188 (1992). doi:10.1007/BF02637677.
- 22) M.A. Damasceno, J.K. de M. Penha, N.F. da Silva Junior, R.N.B. Felipe, R.C.T. dos S. Felipe, and G.G. de Medeiros, "Influence of the temperature, pressure and viscosity on the oil measurement with turbine type measurers," *Brazilian Archives of Biology and Technology*, 49 (spe) 65–72 (2006). doi:10.1590/s1516-89132006000200011.
- 23) W.B. Wan Nik, M.A. Maleque, F.N. Ani, and H.H. Masjuki, "Experimental investigation on system performance using palm oil as hydraulic fluid," *Industrial Lubrication and Tribology*, 59 (5) 200–208 (2007). doi:10.1108/00368790710776784.
- 24) N.K. Attia, S.A. El-Mekkawi, O.A. Elardy, and E.A. Abdelkader, "Chemical and rheological assessment of produced biolubricants from different vegetable oils," *Fuel*, 271 (2020). doi:10.1016/j.fuel.2020.117578.
- 25) R. Thaoklua, J. Janjaroen, and K. Tedsree, "The study of activity and selectivity of calcium oxide nanocatalyst for transesterification of high free fatty acid crude palm oil," *Chiang Mai Journal of Science*, 45 (2) 973–983 (2018).
- 26) A.C. Opia, M.K.B.A. Hamid, S. Syahrullail, A.B.A. Rahim, and C.A.N. Johnson, "Biomass as a potential source of sustainable fuel, chemical and tribological materials overview," *Mater Today Proc*, (2020). doi:10.1016/j.matpr.2020.04.045.
- 27) H. Venkatesan, S. Sivamani, S. Sampath, V. Gopi, and M. Dinesh Kumar, "A comprehensive review on the effect of nano metallic additives on fuel properties, engine performance and emission characteristics," *International Journal of Renewable Energy Research*, 7 (2) 825–843 (2017). doi:10.20508/ijrer.v7i2.5678.g7064.
- 28) S.S. Teske, and C.S. Detweiler, "The biomechanisms of metal and metal-oxide nanoparticles' interactions with cells," *Int J Environ Res Public Health*, 12 (2) 1112–1134 (2015). doi:10.3390/ijerph120201112.
- 29) W. Dai, B. Kheireddin, H. Gao, and H. Liang, "Roles of nanoparticles in oil lubrication," *Tribol Int*, 102 88–98 (2016). doi:10.1016/j.triboint.2016.05.020.
- 30) A.C. Opia, M.K.A. Hamid, S. Samion, C.A.N. Johnson, A.B. Rahim, and M.B. Abdulrahman, "Nano-particles additives as a promising trend in tribology: a review on their fundamentals and mechanisms on friction and wear reduction," *Evergreen*, 8 (4) 777–798 (2021). doi:10.5109/4742121.
- 31) C. Runnisa, K. Thu, T. Miyazaki, A. Wij Ayanta, "Highly microporous activated carbon from acorn nutshells and its performance in water vapor adsorption," *Evergreen*, 8 (1) 249–254 (2021) doi.org/10.5109/4372285.
- 32) W.B. Wannik, A.F. Ayob, S. Syahrullail, H.H. Masjuki, and M.F. Ahmad, "The effect of boron

- friction modifier on the performance of brake pads," *International Journal of Mechanical and Materials Engineering*, 7 (1) 31–35 (2012).
- 33) I. Ijaz, E. Gilani, A. Nazir, and A. Bukhari, "Detail review on chemical, physical and green synthesis, classification, characterizations and applications of nanoparticles," *Green Chem Lett Rev*, 13 (3) 59–81 (2020). doi:10.1080/17518253.2020.1802517.
- 34) Deepika, "Nanotechnology implications for high performance lubricants," *SN Appl Sci*, 2 (6) (2020). doi:10.1007/s42452-020-2916-8.
- 35) S.N.A. Yusof, N.A.C. Sidik, Y. Asako, W.M.A.A. Japar, S.B. Mohamed, and N.M. az Muhammad, "A comprehensive review of the influences of nanoparticles as a fuel additive in an internal combustion engine (ice)," *Nanotechnol Rev*, 9 (*I*) 1326–1349 (2021). doi:10.1515/ntrev-2020-0104.
- 36) M. Hassan, F.N. Ani, and S. Syahrullail, "Tribological performance of refined, bleached and deodorised palm olein blends bio-lubricants," *J Oil Palm Res*, 28 (4) 510–519 (2016). doi:10.21894/jopr.2016.2804.12.
- 37) A. Hernández Battez, R. González, J.L. Viesca, J.E. Fernández, J.M. Díaz Fernández, A. Machado, R. Chou, and J. Riba, "CuO, zro2 and zno nanoparticles as antiwear additive in oil lubricants," *Wear*, 265 (3–4) 422–428 (2008). doi:10.1016/j.wear.2007.11.013.
- 38) Y. Aiman, S. Syahrullail, H. Hafishah, and M.N. Musa, "Friction characteristic study on flat surface embedded with micro pit," *Evergreen*, 8 (2) 304–309 (2021). doi:10.5109/4480707.
- 39) Y.Y. Wu, W.C. Tsui, and T.C. Liu, "Experimental analysis of tribological properties of lubricating oils with nanoparticle additives," *Wear*, 262 (7–8) 819–825 (2007). doi:10.1016/j.wear.2006.08.021.
- 40) I. Uflyand, V. Zhinzhilo, V. Burlakova, "Metal-containing nanomaterials as lubricant additives: state-of-the-art and future development," *Friction*, 7 (*1*) 93–116 (2019).
- 41) E.H. Okechukwu, D. Connolly, Y.S.H. Najjar, A.M. Abubaker, I. Minami, A. Almutairi, P. Pilidis, N. Al-Mutawa, L. Farfan, E. Gallardo, M. Cruz, M. Vite, I.P. Nacional, G. De Tribología, Mobil, A. Vasishth, P. Kuchhal, G. Anand, B. Zhmud, B. Pasalskiy, R. Nguele, H.S. Al-Salim, K. Mohammad, A.S. Mohammed, A. Gangopadhyay, J. Cuthbert, S. Taj, M.A. Munawar, S. Khan, S. Zzeyani, M. Mikou, J. Naja, J.Y. Xu, J.L. Mo, B. Huang, X.C. Wang, X. Zhang, Z.R. Zhou, W. Paper, W. Kończewicz, O. Grabowska, D. Lachowicz, Z. Otremba, and R. Dwivedi, "Physicochemical characterization of the synthetic lubricating oils degradation under the effect of vehicle engine operation," *Lubricants*, 20 (4) 135–138 (2013). doi:10.29333/ejac/90761.
- 42) L. Kerni, A. Raina, and M.I.U. Haq, "Friction and wear performance of olive oil containing nanoparticles in boundary and mixed lubrication regimes," *Wear*, 426–427 819–827 (2019).

- doi:10.1016/j.wear.2019.01.022.
- 43) H.M. Mobarak, E. Niza Mohamad, H.H. Masjuki, M.A. Kalam, K.A.H. Al Mahmud, M. Habibullah, and A.M. Ashraful, "The prospects of biolubricants as alternatives in automotive applications," *Renewable* and Sustainable Energy Reviews, 33 34–43 (2014). doi:10.1016/j.rser.2014.01.062.
- 44) C. J. Antonio, D. Plata, R. Saboya, F. de Luna, C. Cavalcante and E. Rodriguez-Castellon, "An overview of the biolubricant production process: challenges and future perspectives," *Processes*, 8 (3) 257 (2020).
- 45) Kamalakar et al., "Rubber seed oil-based biolubricant base stocks: a potential source for hydraulic oils," *Ind Crops Prod*, 51 249–257 (2013).
- 46) Rozina, S. Asif, M. Ahmad, M. Zafar, and N. Ali, "Prospects and potential of fatty acid methyl esters of some non-edible seed oils for use as biodiesel in pakistan," *Renewable and Sustainable Energy Reviews*, 74 687–702 (2017). doi:10.1016/j.rser.2017.02.036.
- 47) Erhan Sevim and Asadauskas Svajus, "Lubricant basestocks from vegetable oils," *Ind Crops Prod*, 11 (2) 277–282 (2000).
- 48) M.M. Gui, K.T. Lee, and S. Bhatia, "Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock," *Energy*, 33 (*11*) 1646–1653 (2008). doi:10.1016/j.energy.2008.06.002.
- 49) S. Bekal, and N.R. Bhat, "Bio-lubricant as an alternative to mineral oil for a ci engine-an experimental investigation with pongamia oil as a lubricant," *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, 34 (11) 1016–1026 (2012). doi:10.1080/15567031003735303.
- 50) S. Rani, M. Jay, and K. Nair, "EValuation of physiochemical and tribological properties of rice bran oil biodegradable and potential base stoke for industrial lubrication," (n.d.).
- 51) D. V. Suriapparao, and R. Vinu, "Biomass waste conversion into value-added products via microwave-assisted co-pyrolysis platform," *Renew Energy*, 170 400–409 (2021). doi:10.1016/j.renene.2021.02.010.
- 52) Q. Zhang, J. Chang, T. Wang, and Y. Xu, "Review of biomass pyrolysis oil properties and upgrading research," *Energy Convers Manag*, 48 (*I*) 87–92 (2007). doi:10.1016/j.enconman.2006.05.010.
- 53) D. V. Suriapparao, R. Vinu, A. Shukla, and S. Haldar, "Effective deoxygenation for the production of liquid biofuels via microwave assisted co-pyrolysis of agro residues and waste plastics combined with catalytic upgradation," *Bioresour Technol*, 302 (2020). doi:10.1016/j.biortech.2020.122775.
- 54) R. Miandad, M.A. Barakat, M. Rehan, A.S. Aburiazaiza, J. Gardy, and A.S. Nizami, "Effect of advanced catalysts on tire waste pyrolysis oil," *Process Safety and Environmental Protection*, 116 542–552 (2018). doi:10.1016/j.psep.2018.03.024.

- 55) J.P. S A Angayarkanni, "Review on thermal properties of nanofluids: recent developments," *Adv Colloid Sci*, 225 146–76 (2015).
- 56) A.C. Opia, A.H.M. Kameil, S. Syahrullail, S.C. Mamah, M.I. Izmi, C.D.Z. Hilmi, A.A. Saleh, A.B.A. Rahim, and C.A.N. Johnson, "Effect of concentration on the tribological behavior of cyclic heated formulated organic carbon nanotubes in base lubricant under boundary conditions," *Tribology Online*, 16 (4) 199–209 (2021). doi:10.2474/trol.16.199.
- 57) B. Li, "Tribochemistry and antiwear mechanism of organic inorganic nanoparticles as lubricant additives experimental details preparation and characterization of the composite nanoparticles," 1–14 (2020).
- 58) X. Zheng, Y. Xu, J. Geng, Y. Peng, D. Olson, and X. Hu, "Tribological behavior of fe3o4/mos2 nanocomposites additives in aqueous and oil phase media," *Tribol Int*, 102 79–87 (2016). doi:10.1016/j.triboint.2016.05.024.
- 59) Q. Pan, and X. Zhang, "Synthesis and tribological behavior of oil-soluble cu nanoparticles as additive in sf15w/40 lubricating oil," *Xiyou Jinshu Cailiao Yu Gongcheng/Rare Metal Materials and Engineering*, 39 (10) 1711–1714 (2010). doi:10.1016/s1875-5372(10)60129-4.
- 60) L. Kong, J. Sun, and Y. Bao, "Preparation, characterization and tribological mechanism of nanofluids," *RSC Adv*, 7 (21) 12599–12609 (2017). doi:10.1039/c6ra28243a.
- 61) A. Adhvaryu, Z. Liu, and S.Z. Erhan, "Synthesis of novel alkoxylated triacylglycerols and their lubricant base oil properties," *Ind Crops Prod*, 21 (*1*) 113–119 (2005). doi:10.1016/j.indcrop.2004.02.001.
- 62) T.S. and D.J. Blazej Podlesny, "One-step sorting of single-walled carbon nanotubes using aqueous two-phase extraction in the presence of basic salts," *Sci Rep*, 8 (10) (2020).
- 63) J.A. Eastman, S.U.S. Choi, S. Li, W. Yu, and L.J. Thompson, "Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles," *Appl Phys Lett*, 78 (6) 718–720 (2001). doi:10.1063/1.1341218.
- 64) R. Ruliandini, Nasruddin, and T. Tokumasu, "Assessing hbn nanoparticles stability in trimethylolpropane triester based biolubricants using molecular dynamic simulation," *Evergreen*, 7 (2) 234–239 (2020). doi:10.5109/4055225.
- 65) F. Li, L. Li, G. Zhong, Y. Zhai, and Z. Li, "Effects of ultrasonic time, size of aggregates and temperature on the stability and viscosity of cu-ethylene glycol (eg) nanofluids," *Int J Heat Mass Transf*, 129 278–286 (2019). doi:10.1016/j.ijheatmasstransfer.2018.09.104.
- 66) I.N. Rizki, and N. Okibe, "Size-controlled production of gold bionanoparticles using the extremely acidophilic fe(iii)-reducing bacterium, acidocella

- aromatica," *Minerals*, 8 (3) (2018). doi:10.3390/min8030081.
- 67) Hong-Ming Lin, "Fabrication of copper oxide nanofluid using submerged arc nanoparticle synthesis system (SANSS)," 2005.
- 68) L.C. Chen, "Preparation of tio2 nanoparticles by submerged arc nanoparticle synthesis system," *J Alloys Compd*, 495 (2) 476–480 (2010). doi:10.1016/j.jallcom.2009.10.215.
- 69) Liang-Chai Chen and Sheng-Hsin Pai, "In-situ measurement and control of electric discharge on submerged arc synthesis process for continuous tio2 nanoparticle fabrication.pdf," *Mater Trans*, 45 (10) 3071–3078 (2004).
- 70) O. V. Makarova, T. Rajh, M.C. Thurnauer, A. Martin, P.A. Kemme, and D. Cropek, "Surface modification of tio2 nanoparticles for photochemical reduction of nitrobenzene," *Environ Sci Technol*, 34 (22) 4797– 4803 (2000). doi:10.1021/es001109+.
- 71) T. Luo, X. Wei, H. Zhao, G. Cai, and X. Zheng, "Tribology properties of al2o3/tio2 nanocomposites as lubricant additives," *Ceram Int*, 40 (7 *PART A*) 10103–10109 (2014). doi:10.1016/j.ceramint.2014.03.181.
- 72) T. Luo, X. Wei, X. Huang, L. Huang, and F. Yang, "Tribological properties of al2o3 nanoparticles as lubricating oil additives," *Ceram Int*, 40 (5) 7143–7149 (2014). doi:10.1016/j.ceramint.2013.12.050.
- 73) J. Miyawaki, J. Yeh, H. Kil, J. Lee, K. Nakabayashi, I. Moshida, and S. Yoon, "Influence of pore size and surface functionality of activated carbons on adsorption behaviors of indole and amylase," *Evergreen*, 3 (2) 17–24 (2016). doi.org/10.5109/1800868.
- 74) R. Malik, N. Alvarez, M. Haase, B. Ruff, Y. Song, B. Suberu, D. Shereen, D. Mast, A. Gilpin, M. Schulz, and V. Shanov, "Carbon Nanotube Sheet: Processing, Characterization and Applications," Elsevier, 2013. doi:10.1016/B978-1-4557-7863-8.00013-X.
- 75) R. Wang, I. Bowling, and W. Liu, "Cost effective surface functionalization of gold nanoparticles with a mixed dna and peg monolayer for nanotechnology applications," *RSC Adv*, 7 (7) 3676–3679 (2017). doi:10.1039/C6RA26791B.
- 76) B. Veriansyah, H. Park, J.D. Kim, B.K. Min, Y.H. Shin, Y.W. Lee, and J. Kim, "Characterization of surface-modified ceria oxide nanoparticles synthesized continuously in supercritical methanol," *Journal of Supercritical Fluids*, 50 (3) 283–291 (2009). doi:10.1016/j.supflu.2009.06.007.
- 77) J. Zhu, Y. Su, J. Chai, V. Muravev, N. Kosinov and E. Hensen. "Mechanism and nature of active sites for methanol synthesis from co/co2 on cu ceo2," ACS Publications, 10 (19) 11532–11544 (2020).
- 78) N. Alzate-Carvajal, E. V. Basiuk, V. Meza-Laguna, I. Puente-Lee, M.H. Farías, N. Bogdanchikova, and V.A. Basiuk, "Solvent-free one-step covalent functionalization of graphene oxide and

- nanodiamond with amines," *RSC Adv*, 6 (114) 113596–113610 (2016). doi:10.1039/c6ra22658b.
- 79) S. Pati, M. Vellaichamy and J Philip, "A simple approach to produce stable ferrofluids without surfactants and with high temperature stability," *Journal of Nanofluids*, 19 (3) 14–16 (2013). doi:10.1016/s0965-2590(07)70060-9.
- 80) I. Popa, G. Gillies, G. Papastavrou, and M. Borkovec, "Attractive and repulsive electrostatic forces between positively charged latex particles in the presence of anionic linear polyelectrolytes," *Journal of Physical Chemistry B*, 114 (9) 3170–3177 (2010). doi:10.1021/jp911482a.
- 81) Y. Aiman , M. Firdaus, M. Musa, and S. Syahrullail. "The effectiveness of jet impingement cooling system on various flat plate surface," *Evergreen*, 8 (*I*) 187–192 (2021). doi.org/10.5109/4372277.
- 82) V. Pérez-Luna, C. Moreno-Aguilar, J.L. Arauz-Lara, S. Aranda-Espinoza, and M. Quintana, "Interactions of functionalized multi-wall carbon nanotubes with giant phospholipid vesicles as model cellular membrane system," *Sci Rep*, 8 (*I*) (2018). doi:10.1038/s41598-018-36531-9.
- 83) E.S. Budilarto, and A. Kamal-Eldin, "The supramolecular chemistry of lipid oxidation and antioxidation in bulk oils," *European Journal of Lipid Science and Technology*, 117 (8) 1095–1137 (2015). doi:10.1002/ejlt.201400200.
- 84) A.C. Opia, M.K.A. Hamid, S. Syahrullail, C.C. Johnson, S.C. Mamah, A.I. Ali, M.I. Izmi, C.D.Z. Hilmi, M.S. Khan, and A.B.A. Rahim, "Effect of surfactants on the tribological behavior of organic carbon nanotubes particles additive under boundary lubrication conditions," *Tribology Online*, 17 (1) 19–31 (2022). doi:10.2474/trol.17.19.
- 85) G. Liu, X. Li, B. Qin, D. Xing, Y. Guo, and R. Fan, "Investigation of the mending effect and mechanism of copper nano-particles on a tribologically stressed surface," *Tribol Lett*, 17 (4) 961–966 (2004). doi:10.1007/s11249-004-8109-6.
- 86) A. Kotia, K. Chowdary, I. Srivastava, S.K. Ghosh, and M.K.A. Ali, "Carbon nanomaterials as friction modifiers in automotive engines: recent progress and perspectives," *J Mol Liq*, 310 1–39 (2020). doi:10.1016/j.molliq.2020.113200.
- 87) J. Zhou, Z. Wu, Z. Zhang, W. Liu, and H. Dang, "Study on an antiwear and extreme pressure additive of surface coated laf3 nanoparticles in liquid paraffin," *Wear*, 249 (5–6) 333–337 (2001). doi:10.1016/S0043-1648(00)00547-0.
- 88) B. Li, X. Jiang, H. Wan, L. Chen, Y. Ye, H. Zhou, and J. Chen, "Fabrication and tribological behaviors of a novel environmental friendly water-based pai-ptfelaf3 bonded solid lubricating composite coating," *Tribol Int*, 121 400–409 (2018). doi:10.1016/j.triboint.2018.01.068.
- 89) Y. Gu, X. Zhao, Y. Liu, and Y. Lv, "Preparation and

- tribological properties of dual-coated tio2 nanoparticles as water-based lubricant additives," *J Nanomater*, 2014 (2014). doi:10.1155/2014/785680.
- 90) L. Rapoport, N. Fleischer, and R. Tenne, "Applications of ws2 (mos2) inorganic nanotubes and fullerene-like nanoparticles for solid lubrication and for structural nanocomposites," *J Mater Chem*, 15 (18) 1782–1788 (2005). doi:10.1039/b417488g.
- 91) D.X. Peng, Y. Kang, R.M. Hwang, S.S. Shyr, and Y.P. Chang, "Tribological properties of diamond and sio2 nanoparticles added in paraffin," *Tribol Int*, 42 (6) 911–917 (2009). doi:10.1016/j.triboint.2008.12.015.
- 92) K.E. Ojaomo, S. Syahrullail, F.M. Zawawi and M.Z. Yusop. Potential of palm oil with tert-Butylhydroquinone in place of mineral oil lubricant for reducing environmental degradation. Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology. 237(6):1342-52 2023 doi:10.1177/13506501221151100.
- 93) A.C. Opia, A.H.M. Kameil, S. Syahrullail, S.C. Mamah, M.I. Izmi, C.D.Z. Hilmi, A.A. Saleh, A.B.A. Rahim, and C.A.N. Johnson, "Effect of concentration on the tribological behavior of cyclic heated formulated organic carbon nanotubes in base lubricant under boundary conditions," *Tribology Online*, 16 (4) 199–209 (2021). doi:10.2474/trol.16.199.
- 94) D. Jiao, S. Zheng, Y. Wang, R. Guan, and B. Cao, "The tribology properties of alumina/silica composite nanoparticles as lubricant additives," *Appl Surf Sci*, 257 (13) 5720–5725 (2011). doi:10.1016/j.apsusc.2011.01.084.
- 95) Yu et al., "Preparation and tribological properties of surface-modified nano-y2o3 as additive in liquid paraffin," *Appl Surf Sci*, 263 (15) 655–659 (2012).
- 96) A. C. Opia et al., "Tribological behavior of organic anti-wear and friction reducing additive of zddp under sliding condition: synergism and antagonism effect," *Evergreen*, 09 (02) 246–253 (2022). doi.org/10.5109/4793628.
- 97) N.A. Jamaluddin, N. Talib, and A.S.A. Sani, "Performance comparative of modified jatropha based nanofluids in orthogonal cutting process," *Evergreen*, 8 (2) 461–468 (2021). doi:10.5109/4480729.
- 98) A.C. Opia, A.H.M. Kameil, S. Syahrullail, C.A. Johnson, M.I. Izmi, C.D.Z. Hilmi, and A.B.A. Rahim, "Eichhornia crassipes nanoparticles as a sustainable lubricant additive: tribological properties optimization and performance under boundary lubrication regime," *Ind Crops Prod*, 175 114252 (2022). doi:10.1016/j.indcrop.2021.114252.
- 99) A.C. Opia, A.H. Mohd Kameil, S. Syahrullail, A.B. Abd Rahim, and C.A.N. Johnson, "Eichhornia crassipes transformation from problems to wide unique source of sustainable materials in engineering application," *IOP Conf Ser Mater Sci Eng*, 1051 (1)

- 012100 (2021). doi:10.1088/1757-899x/1051/1/012100.
- 100) A.K. Jain, and A. Suhane, "Capability of biolubricants as alternative lubricant in industrial and maintenance applications," *International Journal of Current Engineering and Technology*, 3 (1) 179–183 (2013).
- 101) M.V. Thottackkad, R.K. Perikinalil, and P.N. Kumarapillai, "Experimental evaluation on the tribological properties of coconut oil by the addition of cuo nanoparticles," *International Journal of Precision Engineering and Manufacturing*, 13 (1) 111–116 (2012). doi:10.1007/s12541-012-0015-5.
- 102) S. Arumugam, and G. Sriram, "Preliminary study of nano- and microscale tio2 additives on tribological behavior of chemically modified rapeseed oil," *Tribology Transactions*, 56 (5) 797–805 (2013). doi:10.1080/10402004.2013.792977.
- 103) M. Kumar, A. Afzal, and M.K. Ramis, "Investigation of physicochemical and tribological properties of tio2 nano-lubricant oil of different concentrations," *Tribologia*, 35 (3) 6–15 (2017).
- 104) Z.Y. Xu, Y. Xu, K.H. Hu, Y.F. Xu, and X.G. Hu, "Formation and tribological properties of hollow sphere-like nano-mos2 precipitated in tio2 particles," *Tribol Int*, 81 139–148 (2015). doi:10.1016/j.triboint.2014.08.012.
- 105) B. Chen, K. Gu, J. Fang, W. Jiang, W. Jiu, and Z. Nan, "Tribological characteristics of monodispersed cerium borate nanospheres in biodegradable rapeseed oil lubricant," *Appl Surf Sci*, 353 326–332 (2015). doi:10.1016/j.apsusc.2015.06.107.
- 106) M. Gulzar, H. Masjuki, M. Varman, M. Kalam, R.A. Mufti, N. Zulkifli, R. Yunus, and R. Zahid, "Improving the aw/ep ability of chemically modified palm oil by adding cuo and mos2 nanoparticles," *Tribol Int*, 88 271–279 (2015). doi:10.1016/j.triboint.2015.03.035.
- 107) Rani S, "The tribological behavior of tio 2, ceo 2 and zro 2 nano particles as a lubricant additive in rice bran oil," *Int J Sci Eng Res*, 7 (8) 708–712 (2016).
- 108) Suthar et al., "Experimental evaluation of the friction and wear of jojoba oil with aluminium oxide (al2o3) nanoparticles as an additive.pdf," *Material Today: Proceedings*, 25 (4) 699–703 (2020).
- 109) V.H. Rajubhai, Y. Singh, K. Suthar, and A.R. Surana, "Friction and wear behavior of al-7% si alloy pin under pongamia oil with copper nanoparticles as additives," *Mater Today Proc*, 25 695–698 (2019). doi:10.1016/j.matpr.2019.08.149.
- 110) Kumar et al., "Improving the tribological performance of canola oil by adding cuo nanoadditives for steel/steel contact," *Material Today: Proceedings*, 28 (3) 1392–1396 (2020).
- 111)C. Rajaganapathy, D. Vasudevan, and S. Murugapoopathi, "Tribological and rheological properties of palm and brassica oil with inclusion of

- cuo and tio2 additives," *Mater Today Proc*, 37 (*Part 2*) 207–213 (2020). doi:10.1016/j.matpr.2020.05.032.
- 112) Y. Singh, V. Chaudhary, and V. Pal, "Friction and wear characteristics of the castor oil with TiO₂ as an additive," *Mater Today Proc*, 26 2972–2976 (2019). doi:10.1016/j.matpr.2020.02.612.
- 113) M. Zaid, A. Kumar and Y. Singh. "Lubricity improvement of the raw jojoba oil with TiO₂ nanoparticles as an additive at different loads applied," *Material Today: Proceedings*, 46 (9) 3165–3168 (2021).
- of sio2 nanoparticles on the tribological characteristics of jatropha oil," *Material Today: Proceedings*, 46 (20) 10109–10112 (2021).
- 115) Y. Singh, A. Sharma, N.K. Singh, and W.H. Chen, "Development of bio-based lubricant from modified desert date oil (balanites aegyptiaca) with copper nanoparticles addition and their tribological analysis," *Fuel*, 259 (2020). doi:10.1016/j.fuel.2019.116259.
- 116) V. Cortes, K. Sanchez, R. Gonzalez, M. Alcoutlabi, and J.A. Ortega, "The performance of sio2 and tio2 nanoparticles as lubricant additives in sunflower oil," *Lubricants*, 8 (*I*) (2020). doi:10.3390/lubricants8010010.
- 117) E. Sneha, V.S. Sarath, S. Rani, and K. Bindu Kumar, "Effect of turmeric oil and halloysite nano clay as anti-oxidant and anti-wear additives in rice bran oil," *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 235 (6) 1085–1092 (2021). doi:10.1177/1350650120945074.
- 118) B. Lu HaiZhou, Xi ChengWei, Zi JianMa, "Anti-friction performance of FeS nanoparticle synthesized by biological method," *Appl Surf Sci*, 407 21–28 (2017).
- 119) S. Syahrullail, S. Kamitani, and K. Nakanishi, "Experimental evaluation of refined, bleached, and deodorized palm olein and palm stearin in cold extrusion of aluminum a1050," *Tribology Transactions*, 55 (2) 199–209 (2012). doi:10.1080/10402004.2011.648826.
- 120) C.I. Tiong, Y. Azli, M.R. Abdul Kadir, and S. Syahrullail, "Tribological evaluation of refined, bleached and deodorized palm stearin using four-ball tribotester with different normal loads," *Journal of Zhejiang University: Science A*, 13 (8) 633–640 (2012). doi:10.1631/jzus.A1200021.
- 121) T. Chiong Ing, A.K.M. Rafiq, Y. Azli, and S. Syahrullail, "Tribological behaviour of refined bleached and deodorized palm olein in different loads using a four-ball tribotester," *Scientia Iranica*, 19 (6) 1487–1492 (2012). doi:10.1016/j.scient.2012.10.027.
- 122) P. Zulhanafi, and S. Syahrullail, "The tribological performances of super olein as fluid lubricant using four-ball tribotester," *Tribol Int*, 130 85–93 (2019). doi:10.1016/j.triboint.2018.09.013.

- 123) S. Syahrullail, N. Nuraliza, M.I. Izhan, M.K. Abdul Hamid, and D.M. Razaka, "Wear characteristic of palm olein as lubricant in different rotating speed," *Procedia Eng*, 68 158–165 (2013). doi:10.1016/j.proeng.2013.12.162.
- 124) A.C. Opia, M.K.B. Abdul Hamid, and S. Samion, "Antioxidant property of eichhornia crassipes in oil samples," *Int J Eng Adv Technol*, 8 (6) (2019). doi:10.35940/ijeat.F8529.088619.
- 125) Amit Jain and A. Suhane, "Review article "Research approach & prospects of non-edible vegetable oil as a potential resource for biolubricant a review," *Engineering*, 3 32–44 (2012).
- 126) Willey Liew Yun Hsien, "Towards Green Lubrication in Machining.pdf," 2015.
- 127) M.Z. Shaari, N.R. Nik Roselina, S. Kasolang, K.M. Hyie, M.C. Murad, and M.A.A. Bakar, "Investigation of tribological properties of palm oil biolubricant modified nanoparticles," *J Teknol*, 76 (9) 69–73 (2015). doi:10.11113/jt.v76.5654.
- 128) M. Gulzar, H. Masjuki, M. Kalan, M. Varman, N. Zulkifi, R. Mufti and R. Yunus. "Dispersion stability and tribological characteristics of tio2/sio2 nanocomposite enriched biobased lubricant," *Tribology Transactions*, 60 (4) 369–374 (2017).
- 129) D.I. Ahmed, S. Kasolang, R.S. Dwyer-Joyce, K.I. Sainan, and N.R.N. Roselina, "Formulation and physico-chemical characteristics of biolubricant," *Jurnal Tribologi*, 3 1–10 (2014).
- 130) Farhanah A. N and Syahrullail S., "Evaluation of lubrication performance of rbd palm stearin and its formulation under different applied loads," *Jurnal Tribologi*, 10 1–15 (2016).
- 131) N. Sapawe, S. Samion, P. Zulhanafi, C.S. Nor Azwadi, and M.F. Hanafi, "Effect of addition of tertiary-butyl hydroquinone into palm oil to reduce wear and friction using four-ball tribotester," *Tribology Transactions*, 59 (5) 883–888 (2016). doi:10.1080/10402004.2015.1118584.
- 132) S.S.K. Kiu, S. Yusup, V.S. Chok, A. Taufiq, R.N.M. Kamil, S. Syahrullail, and B.L.F. Chin, "Comparison on tribological properties of vegetable oil upon addition of carbon based nanoparticles," *IOP Conf Ser Mater Sci Eng*, 206 (1) (2017). doi:10.1088/1757-899X/206/1/012043.
- 133) N.W.M. Zulkifli, M.A. Kalam, H.H. Masjuki, and R. Yunus, "Experimental analysis of tribological properties of biolubricant with nanoparticle additive.," *Procedia Eng*, 68 152–157 (2013). doi:10.1016/j.proeng.2013.12.161.
- 134) S. Amiril, E. Rahim, Z. Embong and S. Syahrullail. "Tribological investigations on the application of oil-miscible ionic liquids additives in modified jatropha based metal working fluid," *Tribol Int*, 120 520–534 (2018).
- 135) A.E. Atabani, I. Ali, S.R. Naqvi, I.A. Badruddin, M. Aslam, E. Mahmoud, F. Almomani, D. Juchelková,

- M.R. Atelge, and T.M.Y. Khan, "A state-of-the-art review on spent coffee ground (scg) pyrolysis for future biorefinery," *Chemosphere*, 286 (*July 2021*) (2022). doi:10.1016/j.chemosphere.2021.131730.
- 136) R. Danell, and J.W. Schneider, "How to use bibexcel for various types of bibliometric analysis," (*May*) (2017).
- 137) M.U. Bin Khawer, S.R. Naqvi, I. Ali, M. Arshad, D. Juchelková, M.W. Anjum, and M. Naqvi, "Anaerobic digestion of sewage sludge for biogas & biohydrogen production: state-of-the-art trends and prospects," *Fuel*, **329** (*July*) 1–9 (2022). doi:10.1016/j.fuel.2022.125416.
- Nees Jan Van Eck and Ludo Waltman, "Software survey: vosviewer, a computer program for bibliometric mapping," *IOP Conf Ser Mater Sci Eng*, 7 (1) 1–6 (2022). doi:10.1088/1757-899X/496/1/012060.
- 139) M.C. Menkiti, O. Ocheje, and C.M. Agu, "Production of environmentally adapted lubricant basestock from jatropha curcas specie seed oil," *International Journal of Industrial Chemistry*, **8** (2) 133–144 (2017). doi:10.1007/s40090-017-0116-1.