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Prospects of Plant-Based Trimethylolpropane Esters in the Biolubricant Formulation for Various Applications: A Review

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Biodegradable lubricants from renewable feedstocks have been successfully developed to meet the demands of new machines with stringent requirements of the global standards, which address sustainability and environmental policy. Trimethylolpropane ester (TMPE) has been extensively evaluated as a biolubricant base stock and occasionally used as an additive, due to their low toxicity and excellent biodegradability. The formulation of high-performance TMPE-based lubricants involves addition of surface additives, multifunctional additives, and solid nano particles. This review focuses on the development of plant-based TMPE formulation for various applications, namely food-grade lubricant, engine oil, drilling fluid, insulating fluid, metal working fluid, hydraulic and heat transfer fluids. Even though plant-based TMPE lubricants have huge advantages over mineral oils, they have other challenging issues such as limited load-bearing capacity, hygroscopic properties, and high risk of toxic emission owing to additives selection. The details on the performance characteristics of TMPE as base stocks and additives are discussed, including the current prospects and challenges in the respective areas. This review concludes with a brief discussion on suggestions and recommendations for future advancement in the usage of TMPE and the remaining issues that must be overcome to allow for its full potential to be realized.

Keywords: biolubricants, trimethylolpropane ester, environmentally friendly lubrication, formulation, additives

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INTRODUCTION

Formulations of lubricants by using a conventional mineral oil and additives have raised crucial drawbacks, such as global scarcities due to a rapid exploitation of fossil oil resources, high toxicity, and non-biodegradability. The usage of mineral oil-based lubricants as the end products could adversely affect the environment due to an accidental loss, spillage, or a poor lubricant handling or management. In this case, due to its renewable, low eco-toxicity, biodegradable, and safer attributes, biolubricants derived from plant oil have become a great interest. While plant-based oils have long been used as lubricants, they were rapidly overshadowed in the 20th century by mineral oils, which are significantly cheaper. However, with the present increase in plant-based chemistry and skyrocketing petroleum crude oil prices, biolubricants are regaining popularity. The performance of biolubricants, however, particularly in terms of friction, wear prevention, and lubricity, remains debatable. One of the main attributes for an excellent lubrication is high affinity toward metal surfaces. A plant-based oil with a long chain fatty acid is normally required to increase lubrication and protection against friction and wear (Arumugam et al., 2014; Kotturu et al., 2020; Tulashie and Kotoka, 2020). The majority of research to date has looked at the friction and wear properties of vegetable oils alone or in the addition of particular additives. (Nair et al., 2017) has reported on the thermal and tribological performance of sesame oil as a lubricant base stock. While sesame oil is shown to have exceptional thermal and tribological characteristics, its viscosity range and oxidative stability should be enhanced. An extensive review on the use of palm oil and its challenges as a lubricant base stock has been reported by Dandan et al. (2018). The experimental findings showed that the palm oil suffers poorer thermal and oxidative stability and is also less effective under extreme loads (Dandan et al., 2018). Recently, Salaji and Jayadas (2021) have reported on the potential of nonedible chaulmoogra oil as the lubricant base stock. Although the lubricant displays a lower coefficient of friction, the wear scar diameter was significantly larger. The reported pour point of only 15°C needs to be further improved too.

In summary, the use of plant oils as lubricating oil is always associated with certain limitations such as poorer low-temperature properties and poor oxidative stability during usage (Owuna, 2020; Yunus et al., 2004; Yunus et al., 2005). The alteration of plant oils' molecular structures or a blending with commercial oil, chemical additives, or nano-particles would further envisage the physicochemical properties of biolubricants, especially along boundary and hydrodynamic lubrication regimes (Chan et al., 2018; Hamdan et al., 2018; Gul et al., 2020; Kotturu et al., 2020; Srinivas et al., 2020). The chemical modifications of plant oil such as by epoxidation (Afifah et al., 2021; Bashiri et al., 2021), transesterification (Robiah et al., 2003; Aziz et al., 2014; Hamid et al., 2016; Zulkifli et al., 2016; Raof et al., 2019a), esterification (Fernandes et al., 2018; Kim et al., 2019; Rochmat et al., 2020), hydrogenation (Troncoso and Tonetto, 2022), and estolide formation (Salimon et al., 2011; Hoong et al., 2019) have been carried out to overcome the limitations by plant oils. In esterification/transesterification reactions, the acids or alcohols used have a direct impact on the physicochemical properties of the produced esters, known as synthetic esters. Synthetic esters, generally, have better properties than their corresponding plant oils. Synthetic esters exhibit better low-temperature properties, higher flash and fire points, lower volatility, and higher oxidative stability (Cecilia et al., 2020). Compared with plant oils that is also a natural ester, the substitution of the glyceride moiety with a polyhydric alcohol such as neopentylglycol (NPG), trimethylolpropane (TMP), pentaerythritol (PE), or dipentaerythritol (diPE) can substantially increase plant oil's thermal and hydrolytic stabilities. The reaction of either monobasic acid or monoesters (usually methyl) with any polyhydric alcohol in the presence of a catalyst will produce polyol ester and is commercially available in the market in the wide range of viscosities and other physical properties (Randles, 2013). Among these polyol esters, trimethylolpropane ester (TMPE) has been more widely used in many applications since it has been more available and less costly.

The main role of lubricants is to reduce friction and to prevent wear and seizure. The other two major functions of lubricants are to provide a cooling effect between two-contact surfaces and to circulate between surfaces as a cleaning aid from external dusts, deposits, or wear particles. An excellent lubricant performance is obtained by the blending of lubricant base oil with selected additives (Rao et al., 2018). Lubricant additives could be categorized into several large groups based on their working functions (see **Figure 1**), which are tribology-improving additives, rheology-improving additives, condition-maintaining additives, and auxiliaries (Minami, 2017). The tribology-improving additives that directly improve the tribological performance of lubricants are friction modifiers, anti-wear agents, and extreme-pressure additives. Meanwhile, an enhancement of a base oil fluidity in a hydrodynamic regime is usually by using rheology-improving additives such as nano particles of viscosity modifiers and pour point depressant. For a prolonged lifetime of lubrication system and in certain cases, an improved lubrication performance, condition-maintaining additives were added. The additives of this group are such as antioxidants, detergents, dispersants, corrosion inhibitor, anti-foam agents, and demulsifiers. In addition, the last group of additives for a specific purpose other than working functions that are mentioned earlier are categorized as auxiliaries. Excellent lubricant performance can often be obtained using suitable additive technology (Rao et al., 2018). For the development of sustainable lubricants, biodegradability and toxicity are two most important criteria to be considered. While the first concern is usually addressed by utilizing a biodegradable base fluid, low toxicity requires the use of environmentally friendly additives. It should be emphasized that several additive classes are toxic and may bioaccumulate in the environment.

Table 1 highlights some of the review articles that have been published in the last 5 years that discuss the potential of plant-based oils as an alternative in the production of lubricants for numerous industrial applications. Various biolubricant feedstocks have been discussed including specifically from vegetable oils (Masripan et al., 2020; Owuna, 2020; Wang X et al., 2020; Rasep et al., 2021) and nonedible oils (Singh et al., 2017; Singh et al., 2019; Almasi et al., 2021). Recently, Owuna et al. (2020) presented a short review on the use of TMPE as biolubricants. A detail and comprehensive review on the specific application of TMPE can be a new and valuable addition to the current literature. Therefore, in this article, the application of TMPE as a synthetic lubricant base oil or as a major component in biolubricant formulations is thoroughly reviewed.

BIOLUBRICANT MARKET AND DEMANDS IN THE POST-COVID-19 ERA

Biolubricants are typically employed in niche markets, where recovery is difficult or where they are likely to be discharged into the environment. First, biolubricants are used in the lubrication of oven chain, chainsaw chains, bars, etc. During the use of the tools, oil is subjected to high temperature and virtually all of the lubricant ends up in the environment. Engine lubrication is

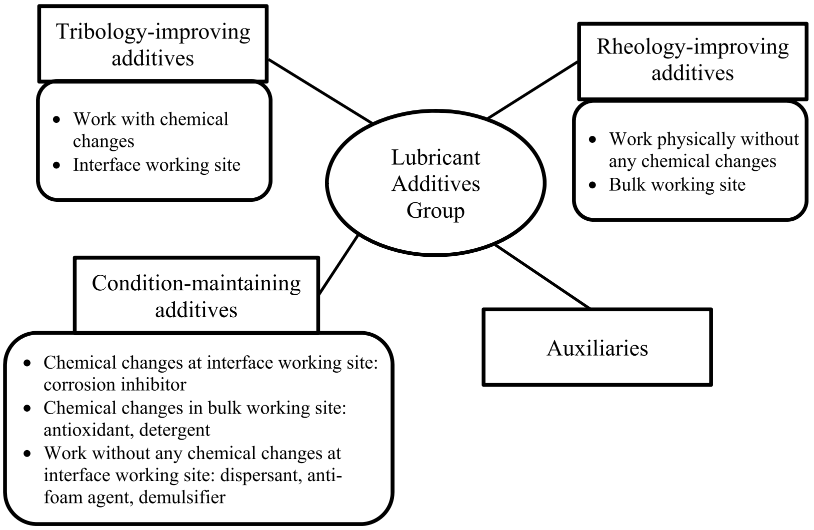

FIGURE 1 | Working function groups of lubricant additives (Minami, 2017).

TABLE 1 | Summary of a previous review paper that highlighted the potential of vegetable oil as bio lubricant in general/specific application.

References	Types of biolubricant feedstock	Types of biolubricant application focused	Remarks
Rasep et al. (2021)	Edible oils	Journal bearing	Highlighted on the performance of mineral and vegetable oil in the method of analysis through experimental and numerical studies in journal bearing application
Almasi et al. (2021)	Nonedible oils	General	Highlighted the production of nonedible oil-based biolubricants in Iran
Bolina et al. (2021)	General	General	Focused on the application of lipases as catalyst in biolubricant production
Negi et al. (2021)	General	General	Discussed production and characterization methods of bio-based lubricants
Wang K et al. (2020)	Edible oils	Cutting fluids	Reviewed works related to nanofluid application in vegetable oil and minimum quantity lubrication (MQL)
Masripan et al. (2020)	Edible oils	General	Mostly highlighted on the studies in properties and tribological by using vegetable oil as lubricant
Owuna (2020)	Edible oils	General	Emphasized on the thermal-oxidative stability studies of vegetable oils
Owuna et al. (2020)	General	General	Also reviewed on the use of TMPE as biolubricants but not in detail
Cecilia et al. (2020)	General	General	Concentrated on the production routes, certain properties, prospects, and challenges
Singh et al. (2020)	Nonedible oils	Internal combustion engine	Also highlighted on the different additives utilized in the internal combustion engine
Ho et al. (2019)	General	General	Reviewed on the commercially available biolubricants and its production technologies, emphasized more on the renewable hydrocarbon
Hossain et al. (2018)	General	Automotive	Discussed in detail the potential of homogeneous and heterogeneous supported metal complexes toward the synthesis of biolubricants
Chan et al. (2018)	General	General	Highlighted formulation of biolubricants and the tribological performances of various types of biolubricant base stocks and their related additives
Singh et al. (2017)	Nonedible oils	General	Highlighted most on the advantages/disadvantages and prospects of nonedible vegetable oil-based bio-lubricants
Reeves et al. (2017)	General	General	Also discussed on the issues and limitation when incorporating biolubricants against widespread use in industrial application
Pathak et al. (2019)	Edible oils	Automotive	Reviewed on the sources, advantages, disadvantages, prospects, and challenges of vegetable oil-based biolubricants

another application for biolubricants. Indeed, plant-based oil-based motor lubricants have been created to better withstand severe thermal stresses. Plant-based lubricants are also utilized as hydraulic fluids to improve the performance of forest equipment such as harvesters, cranes, tractors, and load carriers. Some machines and electrical components also require insulating lubricants or also known as insulating fluids, to avoid electrical discharges between surfaces at various electrical potentials, which can be found within transformers, for example. Because of their specific heat and thermal conductivity characteristics, lubricants can assist in the removal of heat generated by these systems. Finally, the application of biolubricants can also be found in the area of machining and metal working (cutting oils, cooling parts, corrosion protection, etc.), marine oils, drilling fluids, gear oils, etc. (Aranzabe et al., 2011).

The growing prospects for sustainable solutions, such as green buildings and sustainable lubricants, are expected to drive worldwide biolubricant demand, particularly in the post-COVID-19 era. According to the recent report by Global Industry Analyst Inc., the global market for biolubricants is expected to reach united States$ 2.6 billion with a post COVID-19 CAGR of 5.2%, over the analysis period of 2020–2027 (Global Industry Analysts, 2021). Biolubricants remain popular, notably in Europe, where demand is fueled by subsidies, tax incentives, and national and international labeling systems (Global Industry Analysts, 2021). According to the industry analyst, biolubricants in Asia are unlikely to take off unless governments give incentives or regulations for their usage. Malaysia looks to be taking moves in this direction as more grants have been disbursed by the government to upgrade and establish more biolubricant plants for automotive and industrial uses (LubesNGreases.com, 2021).

The global consumption of TMPE is expected to see a significant growth in the coming years owing to the fast-growing markets for end-user industries of polyol esters (Persistance Market Research, 2017). The market for food grade lubricant is expected to increase at a compound annual growth rate (CAGR) of 7% from the united States$182.8 million in 2016 to united States$256.5 million by 2021. Globally, the market is anticipated to reach 64.5 kilotons by 2021, with a CAGR of 6.7% from 2016 (Salih and Salimon, 2021). The selection and preparation of raw materials, intermediates, and finished products for food grade lubricants is more stringent and acute. One of the issues that engineers have is determining the qualification of food grade lubricant, which is determined by the chemicals and processing methods used. The lubricant should not change food performance and achieved high-speed machinery standards in food processing and packaging.

For transformer insulating oil, the global market is expected to grow at a CAGR of 6.5% from an anticipated market value of USD 1.9 billion in 2021 to USD 3.3 billion by 2030. The expansion in the industrial and commercial factors has resulted in the increase in demand for electricity and power generation capacity (MarketsandMarkets, 2021). Among that, ester-based transformer oil market is expected to reach USD 94 million by the end of 2027, growing at a CAGR of 1.8% during 2021–2027. The next few years will witness the increasing popularity of bio-based and naphthenic transformer oil in the market, mainly due to the increase in fire accidents in mineral oil-based transformers and the nonbiodegradable nature of mineral oil. The innovation involving fire-resistant transformer oils is expected to open new growth opportunities for the ester market over the foreseeable period (MarketsandMarkets, 2021).

Despite the negative impact on the biolubricant market during COVID-19 pandemic, a global metalworking market is forecasted to reach USD 11.6 billion by 2027, with a CAGR of 4.3% during a projected period of 2020–2027 (Fortune Business Insights, 2020). The biolubricant market is moving toward bio-based metalworking fluid from synthetic esters and plant oils although it currently still holds a low share as compared with the mineral oil-based metalworking fluid. This forecasted market is due to stringent regulations of related agencies, such as Environmental Protection Agency (EPA), Occupational Safety and Health Administration (OSHA), The National Institute of Occupational Safety and Health (NIOSH), and Canadian Centre of Occupational Safety and Health (OSH). In addition, increasing demands mainly in automotive sectors and transportation during post COVID-19 pandemic become the driving factors to the expected market growth. The other potential applications in the future market of bio-based metal-working fluids include machining in construction or agriculture, electrical and power, telecommunication, and healthcare.

On the other hand, a moderate projection of the global drilling fluid market size has been forecasted to achieve USD 11.1 billion from 2020 to 2027, with a CAGR of 4.2% (Grand View Research, 2020). Nowadays, biolubricant drilling additives are increasingly being used to develop bio-based drilling fluids, which becomes the main driving factor to a drilling fluid additives market. According to Data Bridge Market Research, it is expected that the market is growing at a rate of 9.2% from 2021 to 2028. The potential commercial bio-based drilling additives include surface modifiers, dispersants, corrosion inhibitors, fluid viscosifiers, biocides, and defoamers (Data Bridge Market Research, 2021). An intensifying activity of oil exploration and production in Asia Pacific countries such as China, Australia, Brunei, and Indonesia leads to a highest forecast growth rate over a period from 2020 to 2027. Meanwhile, a significant growth rate over the forecast period of synthetic-based fluids is due to its low toxicity, low bioaccumulation potential, and lower fluid loss when compared with other drilling fluid products such as water-based fluids and oil-based fluids (Grand View Research, 2020).

CHARACTERISTICS OF TRIMETHYLOLPROPANE ESTER FOR DEVELOPMENT AND SELECTION

TMPE is a hydrolytically stable and biodegradable polyol ester. TMPE contains three branches of ester functional groups that are attached to a TMP polyol molecule. TMP polyol is an organic alcohol that contains 3 hydroxyl functional groups and appears as clear to white solid phase in an ambient condition. TMPE can be synthesized mainly via esterification of fatty acids or transesterification of methyl esters with TMP alcohol. For optimum application performance, fatty acids or methyl esters of appropriate chain lengths and degree of unsaturation are utilized in the synthesis methods. The increase in branch length in the TMP structure increases the molecular weight and improves the lubricity properties at low temperature (Mahmud et al., 2015; Samidin et al., 2021). A significant branching group near the midpoint of a fatty acid chain from TMP's backbone causes a steric hindrance, which slows the crystallization process. As a result, the pour point and cloud point of the TMPE would be significantly improved. For example, Samidin et al. (2021) modified the chemical structure of TMPE to

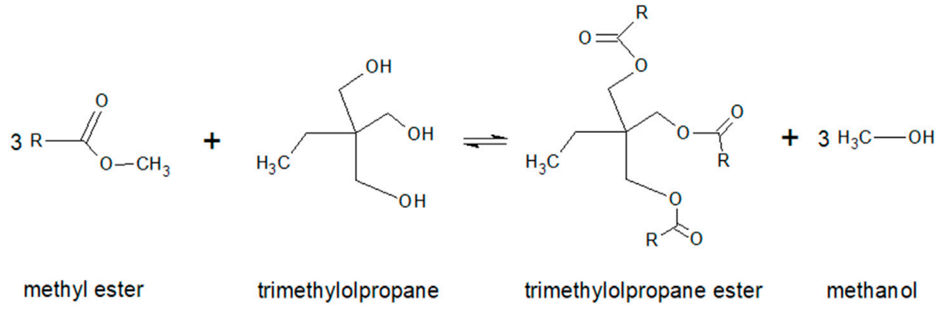

FIGURE 2 | Transesterification of plant oil-based methyl ester with trimethylolpropane (Raof et al., 2019a).

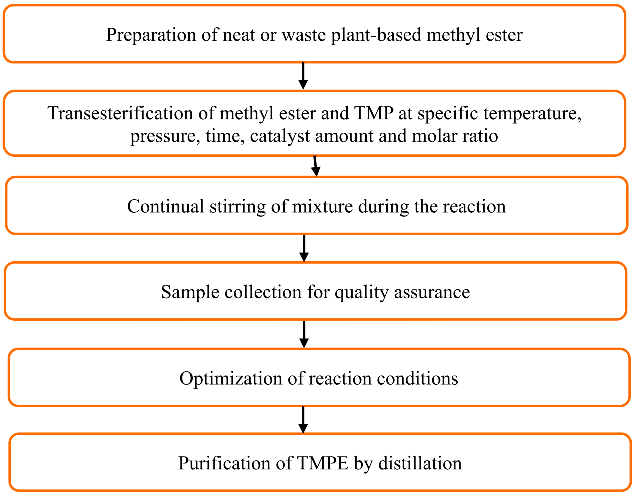

FIGURE 3 | TMPE production via transesterification reaction flow chart (Zulkifli et al., 2013).

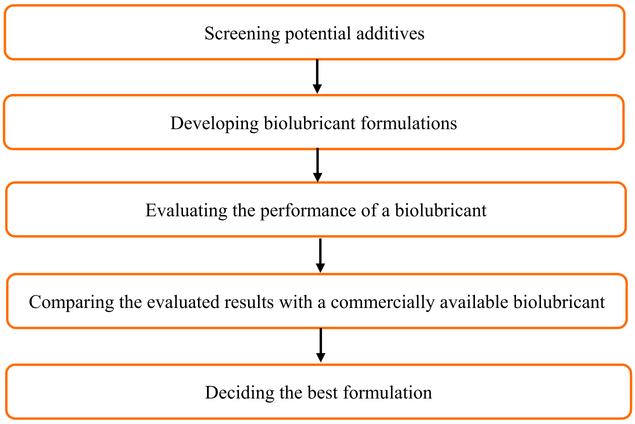

FIGURE 4 | TMPE as a base oil or an additive in a biolubricant formulation flow chart (Aziz et al., 2016).

hyper-branched nonaoleate TMP (NOTMP) through epoxidation, ring-opening reaction and further esterification reaction for improved thermal stability. NOTMP has a viscosity index of 237, which is quite high. The inclusion of polar groups in the ester increased its polarity, which was claimed to reduce wear and confirm its ability to be utilized without additives. According to Salih et al. (2013), the polar end groups will increase the adsorption of TMPE onto the metal surfaces and reduce the surface energy, which will further enhance the lubricity.

The most important lubricating function for an adequate protective film thickness is highly dependent on fluid viscosity, making it the most important characteristic for lubricant selection and application (Rashmi et al., 2017; Zulkifli et al., 2013). The viscosity should be high enough to provide a thick film between moving components even at high temperature and pressure, yet low enough to keep the lubricant fluid around each component part (Sharma and Sachan, 2019). For an example, palm oil that is known as a biodegradable resource has a viscosity and viscosity index of 40.0 mm^2/s (at 40°C) and 191, respectively (Kotturu et al., 2020). A transesterification of methyl ester that is derived from palm oil with TMP to produce TMPE (**Figure 2**) has shown better lubricity properties, with a viscosity of 42.5 mm^2/s (at 40°C) and a viscosity index of 221 (Kotturu et al., 2020; Qiao et al., 2017). In a different study, Kamarudin et al. (2020) produced TMPEs from nonedible oils such as waste cooking oil and rubber seed oil via two-stage transesterifications and found that the viscosities of both TMPEs satisfied ISO VG46 lubricant standard. The modification of the structure of vegetable oil to remove the β-hydrogen that is susceptible to oxidation improved the lubricity of a biolubricant in terms of oxidative and thermal resistance (Aziz and Atiqah, 2015). Furthermore, an esterification of Moringa *oleifera* oil with TMP has interestingly shown a high viscosity index of 170 and high thermal stability (Moreira et al., 2020). The synthesis studies of TMPE from other plant oils such as palm kernel oil, crude Jatropha oil, and castor oil also exhibited enhanced viscosity indices, pour points, and lubricities, which were comparable to the standards and commercial lubricants (Owuna et al., 2020). A flowchart of the transesterification procedure used to produce biolubricants is shown in **Figure 3**. Researchers investigated a variety of factors to produce a high yield and quality of biolubricant. The synthesized product was purified prior to formulation. In the case of TMPE as an additive, it was mixed with a base oil and submitted to a variety of assays to determine its performance. The baseline of a produced biolubricant is often compared to a standard grade and a commercially available biolubricant (Zulkifli et al., 2013). The flowchart for TMPE as a base oil or an additive in a biolubricant formulation is shown in **Figure 4**.

The properties of the stand-alone TMPE base stock are already superior as compared with most of other biodegradable synthetic esters. However, its lubricant performance could be further improved by formulation with other types of base oil and various additives technologies. With the same objective, the addition of TMPE to polyalphaolefin has reduced wear effectively (Zulkifli et al., 2013). The dispersion of nanoparticles in the synthetic ester base stock could potentially replace the conventional additives that could be harmful to the environment (Jason et al., 2020). Owing to the nano-sized solid particles, the asperities of the contacted surfaces could be filled. The addition of graphene nanoplatelets (GNP) in biolubricants, for example, is in line with the recent advances of nanotribology (Azman et al., 2016). Owing to nano solid's small size, the material can reach a constricted area for protective layering and bearing force during motion (Rashmi et al., 2017). Azman et al. (2016) proposed that only a small amount was required to prevent agglomeration behavior caused by particle interaction and forces at high concentration. Furthermore, an excess amount of GNP disrupts dispersion stability and increases the acidity of the oil. When large aggregates cannot fit in valleys between asperities, they may contribute to abrasive wear. Sufficient GNP aided in the formation of a protective layer for the prevention of asperities contact. Liñeira del Río et al. (2018) also investigated the performance of GNP in TMPE, as well as the speed of sound for pure oil and dispersions. The speed of sound values indicated the oil's quality in terms of chemical interaction between the pure oil and the nanoparticles. By forming thin protective graphene layers between rough surfaces, nanodispersants in oil were able to reduce the coefficient of friction. Because of TMPE's superior properties, less contentious additives such as ZDDP are added to the oil because it produces ash and poisonous emission during combustion (Hamdan et al., 2018).

Globally, regulations limiting the contents of hazardous additives such as sulfated ash, phosphorus, and sulfur have been implemented (Azman et al., 2016; Rashmi et al., 2017). These bearing additives could reversely affect the performance of devices, in particular diesel engines. Centers (1992) reported that a neurotoxin substance from lubricant decomposition may be produced at extreme temperature (350—700°C). For turbine engine oil application that used synthetic oil, when trimethylolpropane and phosphorus from the additive combines during thermal combustion, trimethylolpropane phosphate was formed. In addition, the decomposition of trimethylolpropane ester roduced carboxylic acid (Kalman et al., 1985). Phosphorus was presented in anti-wear additives, such as tricresyl phosphate (TCP, which is from tritolyl phosphate isomers) (Centers, 1992).

INDUSTRIAL APPLICATIONS OF BIOLUBRICANTS

Food Grade Biolubricant

Leaks and maintenance of lubricants are inevitable in many industries. Thus, the food processing and pharmaceutical industries often face additional challenges, especially with the selection of the right lubricants. Food-grade lubricants must fulfill the same technical requirements as conventional lubricants. According to the United State Department of Agriculture (USDA), food grade lubricants are categorized into three groups: H1, H2, and H3. H1 is a food grade lubricant used in food processing industry; it is colorless, odorless, tasteless, and low hazard. H2 is a biolubricant that should not come into contact with food. Edible oils make up the H3 category and the feedstock is mostly derived from vegetable oils such as coconut, sunflower, canola, palm, palm kernel, soybean, rapeseed and jatropha oil, and cashew nuts (Bahadi et al., 2019; Bhaumik et al., 2019; Attia et al., 2020; Masripan et al., 2020). However, due to the limitations of vegetable oils, modifications to the chemical structures were made since vegetable oil remains the safest and most cost-effective raw material (Salih and Salimon, 2021). Agricultural and animal substances are subjected to a variety of processes in a manufacturing plant, including cleansing, mixing, cooking, canning, and packaging. Tanks, pumps, gears, mixers, chain drives, and conveyor belts in a large-scale food processing facility confront identical tribological and lubricating issues as non-food processing plant (Fitch et al., 2009). Food grade gear oils are ideal for lubricating drive chains, conveyor chains, gearboxes, and reduction units. **Table 2** shows the commercially available food-grade gear oils from mineral, semisynthetic, and full synthetic. Full synthetic gear oil has excellent physicochemical properties, including a high viscosity index, kinematic viscosity at 100°C, and the lowest pour point, −43°C.

Tribology of food grade lubricants can be improved by the modification of fatty acid structure, such as with the use of levulinic acid (LA). LA is feasibly produced from glucose, fructose, starch, and lignocelluloses residues and is widely used in a variety of applications, including food flavoring, composites, and fuel (Zhu et al., 2020). The esterification between TMP and LA produced a trimethylolpropane trilevulinic (TMP-tri-LA) ester with viscosity index, flash point, and pour point being 49, 223°C, and −27°C, respectively. As 10% of TMP-tri-LA was added to mineral oil, the WSD (0.62 mm) improved by 21% when compared with mineral oil alone (0.78 mm). TMP triester based on palm kernel fatty acids is also suited for a food processing machine (Bahadi et al., 2019). TMPTE with a viscosity index of 154, a flash point of 320°C, and a pour point of −10°C were obtained (Bahadi et al., 2019). Di-trimethylolpropane tetraester (PKO-di-TMPTE) was proposed for food-grade hydraulic oil from the transesterification reaction of palm kernel oil and di-TMP, with viscosity index, flash point, and pour point of 140.1, 392°C, and -6°C, respectively (Bahadi et al., 2021). The

TABLE 2 | Basic physicochemical properties of mineral oil, natural ester, and synthetic-based for food-grade gear oils.

Test Parameter/ISO 220	Method	Mineral-based	Synthetic ester	Natural ester
Density at 20°C, kg/l	ASTM D 1298	0.89	0.844	NA
Kinematic viscosity at 40°C, cSt	ASTM D 445	217	198/242	198/242
Kinematic viscosity at 100°C, cSt	ASTM D 445	17.9	28.2	21.1
Viscosity index	ASTM D 2270	89	160	116
Flash point, °C	ASTM D 93	200	240	254
Pour point, °C	ASTM D 97	-21	-43	-12
4-Ball EP, weld point, min	ASTM D 4172	NA	NA	160
FZG test	DIN 5136	NA	>12	>12
Copper corrosion	ASTM D 130	NA	1a	1a

NA: not available.
Mineral-based: H1 Quinplex® White Gear Oil.
Synthetic: Repsol FG, gear synth.
Natural ester: Repsol FG, Gear Industry (Semi synthetic).

TABLE 3 | Tribological improvement of food grade biolubricants.

Source of biolubricant	Major findings	References
Levulinic acid (LA) + TMP + mineral oil	Function: Biodegradable lubricant 10% of TMP-tri-LA in mineral oil improved 21% of WSD (0.62 mm)	Zhu et al. (2020)
DiTMP esters	Exhibited the smallest WSD (0.64 mm) Up to 3450 N load for anti-seizure properties Thermally stable at 400°C	Nowicki et al. (2019)
TMPE from crude palm kernel fatty acids	Improvement in viscosity index compared to commercial ISO VG 46	Bahadi et al. (2019)

TABLE 4 | Allowable composition of food grade additives in biolubricant.

Additives	Allowable composition	References
Antioxidant	Irganox L-57 (aromatic amine): 0.07–1 wt% BHT and Irganox 135 (phenolic): 0.3—1 wt% Phenolic to aromatic amine ratio: 4:1 or 1:1	Alias et al. (2011) Wolf, (1992)
Anti-wear	Irgalube 349 (multifunctional): 0.1—1.0 wt% Irgalube TPPT: 0.3—1.0 wt% Antioxidant to anti-wear: 4:1 or 1:1	Corbett et al. (2008) Wolf, (1992)
Corrosion inhibitor	Sarkosyl O, Irgamet 39, Span 80: 0.05 to 1.0 wt%	Corbett et al. (2008) Wolf, (1992)

development of TMPE as a food grade biolubricant is summarized in **Table 3**.

Aside from producing oil with high lubricating capabilities, additives are utilized to compensate for the inadequacies of food grade lubricant. Food grade lubricant additives should adhere to the acceptable composition and be composed of safe chemicals compounds. In the event of accidental interaction with food products, the additives should not harm consumers' health. Antioxidant, anti-wear, and corrosion inhibitor are common additives. Antioxidants are required to inhibit the oxides derivatives. Sharma et al. (2007) stated that butylated hydroxyl toluene (BHT) is the second most effective antioxidant after zinc diamyl dithiocarbamate (ZDDC). BHT, a phenolic antioxidant, acts as a radical scavenger, preventing the phase of propagation. Furthermore, BHT is commercially available at a low cost and is HX-1 certified (Corbett et al., 2008). ZDDC acts as a peroxide decomposer and metal deactivator, preventing the commencement of the oxidation chain. To minimize environmental issues, heavy metal compounds such as lead, zinc, barium, and chlorine should not be used in lubricants (Waara et al., 2001; Zhan et al., 2004).

Irganox L-57, an aromatic amine type additive, has been approved by the Food and Drug Administration FDA/united States and can be used in food grade lubricants. It enhances antioxidant efficiency and can be used for long life span (Ciba, 2003). Wolf (1992) suggested that the best antioxidant ratio between phenolic and aromatic amine was 4 to 1 or 1 to 1. However, at high concentrations, an aromatic amine additive may generate sludge. Another formulation consists of 0.3–1 wt% and 0.07 to 1 wt% for phenolic (for example BHT and Irganox 135) and aromatic amine additives, respectively. Sharma et al. (2007) stated that hindered phenols and diphenylamine demonstrated radical scavenger behavior and boosted oxidative stability at high temperatures. Alias et al. (2011) have documented Irganox 135 as an antioxidant in the hydraulic lubricating system with a 1 wt% composition did not improve WSD. Untreated oil oxidizes and thickens as a result of the polymerization process (Salih and Salimon, 2021).

TABLE 5 | Basic physicochemical of mineral oil, natural ester, and synthetic ester for 10W-40 engine application.

Test Parameter/10W-40	Method	Mineral-based	Synthetic ester	Natural ester
Density at 20°C, kg/l	ASTM D 1298	0.855	0.87	0.866
Kinematic viscosity at 40°C, cSt	ASTM D 445	93.1	67.8	90.9
Kinematic viscosity at 100°C, cSt	ASTM D 445	13.9	12.5	13.9
Viscosity index	ASTM D 2270	152	193	136
Flash point, °C	ASTM D 93	218	223	230
Pour point, °C	ASTM D 97	-36	-42	-42
Base number, mm KOH/g	ASTM D 2896	4.4	NA	8.25
Sulphated ash, wt%	ASTM D 874	0.62	NA	NA

NA: not available.

Mineral-based engine oil: Eurol Special 10W-40.

Fully synthetic-based engine oil: Chemlube Organic Ester-based Motor Oil.

Vegetable ester-based engine oil: Motul 300v 10W40.

Previous research looked at the safe limit of additives in food grade lubricant as presented in **Table 4**. There has been a limited study into the effect of food grade additives on TMPE for machinery application. Finally, the food grade lubricant should be nontoxic and nonhazardous to one's health. Aziz (2016) reported that an acute toxicity test might be performed to validate toxicity of a product. After 14 days of evaluation based on OECD Guideline 423, no adverse toxic response impact was observed for the administration of 2000 mg/kg body weight of pentaerythritol ester with anti-wear (0.15% of Irgalube and 0.15% Irgalube TPPT) and corrosion inhibitor (0.1% Irgamet 39) in Sprague-Dawley rats. Current toxicity testing covers advanced life stages of zebra fish (*Danio rerio*) (Poopal et al., 2020; van der Ven et al., 2020) and brine shrimp (*Artemia salina*) (Camargo et al., 2017; Rozaki et al., 2017).

Based from the previous findings, the use of TMPE in the formulation of food grade lubricants has successfully improved the physicochemical and tribological properties. TMPE that is a non-Newtonian shear-thinning and high viscosity index fluid reduces wear and friction between two moving parts. This is important to ensure the lubricant can provide a sufficient film thickness to protect the equipment or engine from wear. Selecting and applying high-quality food-grade biolubricants are critical elements in ensuring a safe working environment and hygienic processing facility.

Engine Oil

Engine oil is critical for protecting parts from excessive heat formation and preventing corrosion (Kotturu et al., 2020). Engine oil consumed 48% of world market application (Mobarak et al., 2014). The engine's operating conditions were divided into two categories: high-load and low-speed, and low-load and high-speed. In high-load and low-speed conditions, boundary friction dominates, whereas nonboundary friction governs in low-load and high-speed conditions. These two conditions were critical components of the endurance test, yielding useful results in terms of fuel consumption and wear loss at respective parts assigned. The viscosity index for engine oil should be greater than 90. EL-magly et al. (2018) stated that for gas turbine engine lubricants, their viscosity at 98.9°C and military or civil specifications must be abided to be listed as suitable base oil. Based on various analyses, including kinematic viscosity, pour point, flash point, fire point, total acidity, and others, the study confirms that polyol ester performance was comparable to that of commercial lubricants (El-magly et al., 2018). **Table 5** compares the physicochemical properties of commercially available products for engine application. All types of base oil have high viscosity index ranging from 152 to 193. Diester's full synthetic ester-based product outperforms the viscosity of vegetable ester-based and mineral-based engine oil. Each product has a flash and pour point that is higher than 200°C and lower than −30°C.

Polyol ester-based engine oil, in particular TMPE, is a blooming and convincing base stock. Evolution of TMPE is observed to be utilized with commercial oil, and some research broadens to the addition of nano particles and surfactant to improve the lubricity of engine oils. Since 2002, TMPE has started to become an interesting subject and the effect of TMPE in poly alpha olefin (PAO) has been investigated by Rico et al. (2002). It was found that 5% of TMPE demonstrated the smallest wear scar for 264–490 N of loads. Pure TMPE recorded 0.533 mm of WSD and 0.612 mm for PAO. Rico et al. (2002) postulated that the lubricity of low polarity oil (such as PAO) was further improved with the presence of high-polarity TMPE. The findings of smaller WSD of 0.5 mm with 5% TMPE in PAO verified the function of TMPE as a wear reducer. Zulkifli et al. (2013) evaluated the efficacy of TMPE in a commercial oil (CO). The results highlighted that the addition of 3–7% of TMPE in CO is enough for improved WSD and COF. 0.28 mm of WSD was obtained for the tested 3% of TMPE in CO, compared with 0.36 mm of pure CO, and 0.78 mm in pure TMPE. Severe abrasive wear was also reported in the study for pure TMPE. Reduction in COF increases the efficiency of machinery component and thus increases the lubricant and machine lifespan. Zulkifli et al. (2013) also stated that 3% of TMPE acted as an active surface material and gave a sufficient protection layer on the rubbing surface contact. 7% of TMPE exhibited the lowest friction torque (0.02 Nm) up to 1569 N (160 kg). However, more addition of TMPE with fatty acids content may be added up to the corrosive acid accumulation during the oxidation process (Zulkifli et al., 2013).

Other studies on nonedible oil-based TMPE from *Calopyllum inophyllum* bring about interesting findings (Chebattina et al.,

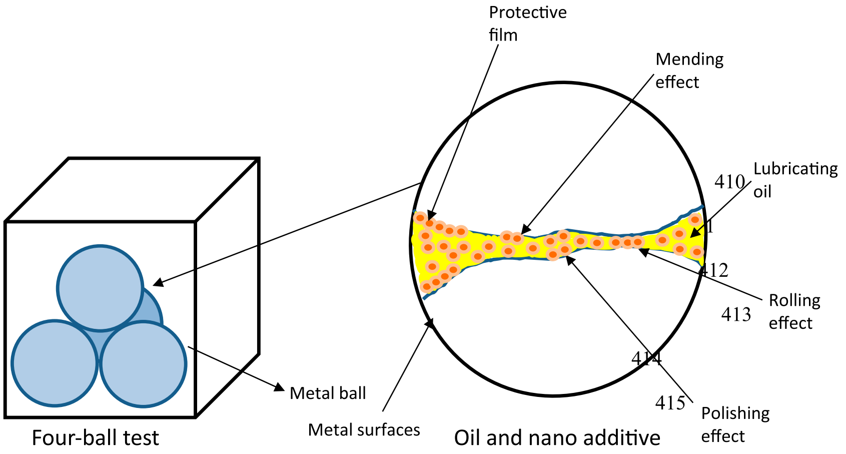

FIGURE 5 | Mechanism of nano additive between contacting surfaces (Shafi et al., 2018).

2019; Kotturu et al., 2020; Srinivas et al., 2020). When 20% of *Calopyllum inophyllum*-based TMPE was added to a commercial lubricant, higher WSD was observed than using only 10% of TMPE for 392 N of loads. Chebattina et al. (2019) obtained 428.23 μm of WSD at 20% of TMPE, whereas Kotturu et al. (2020) and Srinivas et al. (2020) got 396.11 and 391.36 μm, respectively. Almost similar results obtained by the researchers proved that 10% was adequate to reduce wear and abrasion rate. The COF values were almost the same, around 0.0727 to 0.0788. Srinivas et al. (2020) highlighted that the formulated engine oil could not bear higher than 785 N (80 kg) of loads before the protection layer was completely broke down.

Nano additives have the potential to increase machine lifespan, reduce friction and wear, and thus improve the environment and reduce energy loss (Singh et al., 2020). The mechanisms of nano additives between contacting surfaces include rolling, mending, and polishing effects, as well as the formation of a protective film (Rapoport et al., 2002; Ali et al., 2018, 2019; Shafi et al., 2018; Kotia et al., 2020; Radhika et al., 2021). **Figure 5** depicts the mechanism by which nano additives work.

0.25% of graphene nano particles (GnP) in TMPE gave the smallest WSD (48 nm) for 2.5N load testing conducted by Liñeira del Río et al. (2018). The smallest COF, 0.105, was achieved at 0.5% of GnP in TMPE because of the thin protective graphene layer covering rough surfaces. The authors also suggested maintaining the GnP at smallest amount possible since high concentrations on GnP might increase the tendency of agglomeration which might worsen WSD (Liñeira del Río et al., 2018). In a different study, the addition of 0.05% of GnP together with 5% of TMPE in PAO showed enhancement of 5% of COF (0.0737) and 15% of WSD (0.42 mm) (Azman et al., 2016). Rashmi et al. (2017) also investigated the effect of tribological properties on the addition of nano graphene platelets in TMPE base oil. At 392 N load, 0.1 wt% of GnP and 5% of phosphate ester reduced WSD by 16.2% compared with pure TMPE. This demonstrated that the GnP in the ester provided a stronger protective film that was resistant to oxidation attack. Based on 7% reduction in COF at 785 N load, a consistent film thickness that separated the metal surface from asperities was achieved. Yunus et al. (2020) thoroughly evaluated another intriguing combination of nano glass powder, palm oil, semisynthetic engine oil (commercial oil, CO), and TMPE. 0.5 wt% of nano glass powder in 70 wt% of CO and 30 wt% of esters (98% of palm oil and 2% of TMPE) use the high viscosity of CO to provide sufficient film thickness that separates metal surface in the engine at high temperature and loads. This combination simultaneously reduces the high viscosity of CO, which is a disadvantage for additional friction. Additional friction caused by the viscosity of the oil can raise the COF. Because of their high viscosity index, esters served an essential purpose in improving viscosity-temperature behavior. This contributed to the formulations' stability. A minimum amount of nano glass powder was used because it could degrade the thermal stability of the blends. The lowest COF and WSD obtained were 0.057 and 295 μm, respectively. The findings were comparable to those of other studies (Yunus et al., 2020).

Gulzar et al. (2017) investigated the effect of nano particles size [1% of molybdenum disulphide (MoS_2)] and surfactant (oleic acid) on wear protection in TMPE. The results were compared with the similar composition of nano particles and surfactant in commercial PAO. MoS_2 was effective as anti-wear additives. It was found that surfactant increases the stabilization by the adsorption onto nano particles. Large size of nano particles (50—2000 nm) studied showed reduced agglomeration tendency than small size (20—150 nm). Without dispersant, large-size GnP was found to disperse better in oil than small size of GnP. The addition of surfactant promoted better suspension in both GnPs sizes. Higher average improvement 14.28%, 37.5, and 25% was observed for formulated TMPE to pure oil, than formulated PAO to its pure oil in terms of last non-seizure load (LNSL), initial seizure load (ISL), and weld point (WP), respectively. Mean WSD at ISL 2.48 mm for small GnP size, 2.66 mm for large size of GnP were achieved for formulated TMPE where pure TMPE yielded 2.68 mm of WSD. Nano particles tend to

TABLE 6 | Tribology properties of TMPE-based engine oil.

Source of biolubricant	Major findings	References
TMPE + Poly alpha olefin (PAO)	5% of TMPE in PAO exhibits best wear performance under load (264—490 N)	Rico et al. (2002)
Palm-based TMPE + Commercial oil (CO)	3% of TMPE reduces 30% of COF (0.05) and WSD (0.28 mm) 7% of TMPE gives lowest friction torque (0.02 Nm)	Zulkifli et al. (2013)
Calopyllum inophyllum-based TMPE + CO	20% of TMPE in CO shows the best result of smallest COF (0.0727) and 428.23 µm of WSD for 392 N load	Chebattina et al. (2019)
Calopyllum inophyllum-based TMPE + CO	10% of TMPE in CO provides sufficient protection layer for the smallest WSD (396.11 µm for 392N, 485.11 µm for 588 N) and COF (0.0788)	Kotturu et al. (2020)
Calopyllum inophyllum-based TMPE + CO	10% of TMPE in CO yields 391.36 and 467.62 µm of WSD for 392 and 589 N load, respectively. The formulation gave small COF but failed at 785 N	Srinivas et al. (2020)
TMPE + GNP	0.25% GNP in TMPE produced the minimum wear width (48 nm) 0.5% GNP in TMPE provided the lowest COF (0.105) (2.5N)	Liñeira del Río et al. (2018)
Palm-based TMPE + PAO + graphene nanoplatelets (GNP)	5% of TMPE in 95% of PAO and 0.05% GnP improves 5% of COF (0.0737) and 15% of WSD (0.42 mm)	Azman et al. (2016)
Palm-based TMPE + GNP + Phosphate ester (PE)	5% of PE and 0.1% of GNP gave 16.2% reduction in WSD (0.34 mm for 392 N load) 6.9% reduction of COF (0.48 for 785 N) was achieved	Rashmi et al. (2017)
Palm-based TMPE + Palm oil + nanoglass	0.5% nanoglass + 30% (98% Palm oil + 2% TMPE) + 70% CO achieved 33% of WSD (295 µm) reduction and improved 40% of COF (0.057)	Yunus et al. (2020)
Palm-based TMPE + Molybdenum disulfide (MoS_2) nano particle + surfactant (oleic acid)	1 wt% of MoS_2 and 1 wt% of surfactant in TMPE Mean WSD at ISL 2.48 mm for small GnP size 2.66 mm for large size of GnP. Pure TMPE yielded 2.68 mm of WSD.	Gulzar et al. (2017)

TABLE 7 | Basic physicochemical and dielectric properties of mineral oil, natural ester, and synthetic ester.

	Units	IEC 61099 specification[a]	Mineral oil	Natural ester	Synthetic ester
Kinematic viscosity at 40°C	mm^2/s	<35	8	36	24
Flash point	°C	≥250	150	316	260
Pour point	°C	≤-45	-50	-21	-60
Acidity	mg KOH/g oil	<0.03	0.001		
Moisture content	ppm	<200	2.4		
Biodegradability	%		10	97	89
Breakdown voltage (2.5 mm gap)	kV	>45	70	>75	>75
Dielectric dissipation factor ($\tan \delta$ at 90°C)	-	<0.03	<0.002	<0.003	<0.008
Permittivity	-	N/A[b]	2.2	3.1	3.2

[a] *IEC, 61099 - Insulating liquids - Specifications for unused synthetic organic esters for electrical purposes.*

[b] *N/A—not available.*

cover the rubbing surfaces and make up for the worn surfaces. Thus, GnP attends and polishes the interacting surfaces simultaneously (Gulzar et al., 2017). **Table 6** summarizes the development of TMPE as an engine oil.

Addition of 3–20% of TMPE in various synthetic stocks has been evaluated. Researchers agreed in unison that TMPE does have a wear reducer effect. Improvement of the COF efficacy denotes that lubricant and machine usage could be prolonged. However, the fatty acids content in vegetable oils-based TMPE is a concern due to corrosive acids that may be produced during the machine or engine operations. The advances of nano particles in engine oil have broader prospect in engine applications. As most of the research extensively study on the tribological aspects from WSD and COF point of view, the hydrolytic, thermal, and oxidative stability in engine applications should be investigated in depth.

Transformer Insulating Liquid

Another major growth area for TMPE over the last 2 decades has been in environmentally acceptable insulating liquids. Mineral-based transformer insulating liquid has long served the purposes of insulating and cooling in an electrical power transformer. In recent years, substantial efforts have been explored to develop high-performance eco-friendly insulating liquids to replace mineral oil. Polychlorinated biphenyl (PCB)-based insulating liquids were once marketed for high fire safety requirements but were outlawed in the 1970s due to the health and environmental risks (Fofana, 2013). The phasing out of a PCB led to development of other halogenated insulating fluids, such as benzyltoluene, perchorethylene, trichlorobenzene, and dichlorotoluene, which are considered nonflammable. "Less flammable" insulating liquids have been established for transformers at major fire risk locations and are primarily high molecular weight hydrocarbons, silicone oil, synthetic esters, and natural (vegetable) esters (McShane et al., 1999). **Table 7** compared the basic parameters for fresh mineral oil, natural ester, and synthetic ester to the IEC 61099 specifications.

As tabulated in **Table 8**, there are several studies in the literature reporting the application of TMPE as the insulating liquids (Kanoh et al., 2008; Kanoh et al., 2012; Hof et al., 2008;

TABLE 8 | Previous studies on the application of TMPE as a transformer-insulating liquid.

References	Fatty acid	Flash point (°C)	Pour point (°C)	Viscosity (mm²/s)	Acidity (mg KOH/g of oil)	Moisture content (ppm)	Breakdown voltage (kV)	Tan δ Permittivity Resistivity (Ω cm)	Oxidation stability
Wang et al. (2019)	C6, C8 and C10 blend (coconut and castor)	248	-45	23.3	0.028	N/A	72.6 (2.5 mm spacing)	0.02 3.2 10^{13}	OIT at 130°C: 38 h
Capuzzi et al. (2019)	C9 and C10	220	-54	21.4	0.01	46.7	86	0.03 N/A 6.3^{12}	N/A
Raof et al. (2019b); Raof et al. (2019a)	C18:1 (palm oil)	310	-18	42.5	0.084	146	95	0.01 2.8 2.4^{13}	435°C (TGA onset temperature)
Qiu and Brown (2013)	C18:1 (soybean)	318	-38	41.8	0.015	25	N/A	N/A 0.9 6^{13}	OSI at 110°C: 14 h
Hof et al. (2008)	C5 to C11	273	-49	19.3	0.01	100	75 (2.5 mm spacing)	0.025 N/A 8.3^{13}	N/A

N/A: not available.

Qiu and Brown, 2013; Raof et al., 2016). TMPEs produced from saturated fatty acids of C5 to C11 have been patented by Hof et al. (2008) and claimed to satisfy all requirements for transformer oil. The ester produced exhibited excellent properties of transformer oil, such as low viscosity and low pour point as well as excellent oxidation and dielectric properties. The reported biodegradability corresponds to "readily biodegradable" limit (more than 60% BOD/COD or CO2 evolution or >70% DOC removal after 28 days). They incorporated 0.1wt% of antioxidants (preferably BHT or phenyl naphthylamines or diphenylamines) and 0.1wt% of metal deactivator (preferably triazoles or tolyltriazoles or dimercaptothiadiazolines).

In a different study, Qiu and Brown (2013) synthesized TMPE from high-oleic soybean oil and showed remarkable insulating properties such as high flash point and low moisture content. However, the major drawback of this invention was its very low oxidative stability index (OSI) compared to Midel 7131. The reported OSI at 110°C for high-oleic TMPE and Midel 7131 were 14 and >100 h, respectively. It was suspected that the low OSI is the result of the high content of linoleic and linolenic fatty acid content in the soybean oil. Capuzzi et al. (2019) invented a low pour point TMPE particularly for insulating oils in the electrical equipment that requires an effective cooling action. They exceptionally found that the addition of about 10% of branched C9 acids (3,5,5-trimethylhexanoic acid) to linear C9 monocarboxylic acids (nonanoic acid) brings about an appreciable fall of pour point to less than −50°C. To minimize the acidity and water content, the TMPE product was purified further using Fuller's earth (sepiolite) and A4 molecular sieves. They also discovered the slight reduction in water content, acidity, and dielectric loss with the addition of 0.3wt% of primary phenol antioxidant (Irganox® 1010, marketed by BASF SE) (Capuzzi et al., 2019).

In three reports by our group (Raof et al., 2019b; Raof et al., 2019a; Raof et al., 2019c), the high oleic TMPE was synthesized from palm oil methyl ester. We studied the effect of molecular structure on the physicochemical and electrical properties in detail. We found that the palm-based TMPE has a superior flash point compared to PFAE, mineral oil, and some other esters. In terms of electrical properties, TMPE exhibited excellent breakdown voltage, relative permittivity, dissipation factor, and resistivity. The only drawbacks of this ester are its physical properties such as high viscosity and pour point which does not conform to the IEC standard. Thus, in a different study, we blend the TMPE with mineral oil and 80%/20% blend (TMPE/mineral oil) was found to be promising with properties nearest to the standard values for transformer liquid insulation (Raof et al., 2019c). The blend provides significant benefits to utilities in terms of improved fire safety, biodegradability, and performance properties. Most importantly, the blend can reduce the oxidization issues associated with copper/steel corrosion caused by conventional mineral oil.

Wang et al. (2019) synthesized TMPE by the esterification of the mixture of C6, C8, and C10 acids blend with TMP alcohol. High-performance TMPE was prepared using a purification method that included washing with ultrapure water and absorption with a molecular sieve. The ester was washed with ultrapure water to reduce the ionic and polar impurities. Then the molecular sieve was added to reduce the moisture content and the product was further filtered and dried. Although the electrical properties improved significantly during the purification processes, it is not economical and would impair future mass production significantly. Recently, the same group of researchers found a new purification method for the mass production of TMPE. The addition of 3 wt% alkaline Al_2O_3 and 5wt% activated clay as adsorbents managed to reduce more than 80% of acidity and dielectric loss (Wang K et al., 2020). Alkaline Al_2O_3 successfully reduce the acidity to 0.028 mg KOH/g. After subjected to absorption with 5% of activated clay (at 90–95°C and 0.2–0.6 kPa for 30 min) and multiple filtrations, the dielectric loss (tan δ) decreases and resistivity increases significantly. Wang X et al. (2020) also proposed that additives that do not contain oxygen, fluorine, or chlorine should be prioritized when formulated with TMPE. These negative ions would greatly

TABLE 9 | Previous studies on the application of TMPE as a biodegradable hydraulic fluid.

References	Uosukainen et al. (1998)	Alias et al. (2009)	Alias et al. (2011)	Gunawidjaja et al. (2019)
Feedstock for TMPE	Rapeseed oil methyl ester	Palm oil methyl ester	Palm oil methyl ester	High oleic canola oil
Fluid formulation	—	TMPE with 0.5, 1, 1.5 and 2% of additive (Irganox L135 and Irgalube F10A)	TMPE + 1% of Irganox L135	52% TMPE + 15% canola oil + 15% PAO + 15% PAG + other additives
Viscosity at 40°C (mm^2/s)	32.9	42.0	42.0	N/A
Viscosity index	220	N/A	N/A	205
Filterability (%)	92		N/A	—
Pour point (°C)	-41		10	-45
Wear and friction	0.4		0.46	N/A
Wear scar diameter (mm)			0.08	
Coefficient of friction, μ			—	
Biodegradability (%)	>90 (based on CEC-L-33-A-93)		N/A	N/A
Oxidation stability	—		N/A	302 min (RPVOT)
Corrosion	—		N/A	1b (slight tarnish)

induce space charges in electric fields and increase the streamer propagations. A shift to renewable and biodegradable fluids requires a greater need for new effective additives to meet the challenges of formulating insulating fluids for transformer applications. Given that impulse pre-breakdown and breakdown characteristics are linked to the chemical composition of the liquid, the use of esters (which have a different chemical composition than mineral oil) requires a detailed study under impulse voltage (Rozga et al., 2020).

Hydraulic Fluid

Environmentally friendly hydraulic fluid is another important development area for TMPE in biolubricant application. Hydraulic fluids transfer power to the moving parts of many machines, including automobiles, bulldozers, tractors, and the majority of heavy construction equipment (Mendoza et al., 2011). Therefore, they must meet particular specifications in order for the machines to function properly. A good hydraulic fluid should have the following properties: low loss power transmission, lubrication of moving surfaces, oxidation resistance, tribological and anticorrosion properties, compressibility, compatibility with seal, etc. (Alias et al., 2009). The vegetable-based hydraulic fluids suffer several issues mainly related to oxidative stability, incompatibility with bearing materials, low friction torque, and low temperature properties (Syahrullail et al., 2013). Under extreme loads, vegetable oil also loses its effectiveness.

The useful lives of the hydraulic fluids can be extended by the use of higher oleic oils and appropriate additives. In a report by Åkerman et al. (2011), the high conversion to high oleic TMP triester (with low diester and monoester contents) is important to fulfill the required pour point for hydraulic fluids requirements. The transesterification of rapeseed oil methyl ester with TMP which was performed by Uosukainen et al. (1998) exhibited good cold stability, friction and wear characteristics, and resistance against oxidation at elevated temperatures. The TMPE prepared in their work had a viscosity grade of 32, and contained (w/w) 0.5–2.5% antioxidant, 1.0–5.0% pour-point depressor, 0.4–2.0% anti-wear agent, and 0.1–0.5% antifoam agent.

Gunawidjaja et al. (2019) studied the effect of adding PAO and PAG in the formulation containing TMPE derived from high oleic canola oil as the base stock. PAO significantly increases the oxidative stability and maintains a low pour point, but it has an adverse effect on hydrolytic stability. PAG improves the hydrolytic stability and slightly increases the oxidative stability, but undesirably increases the pour point. The synergistic interaction between PAO, PAG, and TMPE (with other additives) managed to produce hydraulic fluids with a high viscosity index, a low pour point, and a good hydrolytic and high oxidative stability (Gunawidjaja et al., 2019).

To study the oxidative stability and wear properties of hydraulic fluid formulation, the "Lab-scale Hydraulic Test Rig" was developed by a group of researchers from UPM (Alias et al., 2009). The performance of palm-oil-based TMPE was studied at temperature range of 80–100°C for 800 h (without and with the presence of additives) while monitoring the changes in acidity and oil viscosity. The results revealed that Irganox L135 additive outperforms Irgalube F10A additive. The ultimate TAN value for the formulated oil was just 0.32 mg KOH/g after 800 h of exposure, compared to 4.88 mg KOH/g for the oil without addition. The findings suggest the compatibility of TMPE with Irganox L135 as an antioxidant and this is a great contribution to the future studies involving the formulation of TMPE as a biolubricant base stock. Similar authors then conducted wear and friction test to the TMPE formulation with 1% of Irganox L135 and found reduction in coefficient of friction (from 0.08 to 0.06) compared to the unadditived TMPE base oil (Alias et al., 2011). However, the formulated TMPE exhibited quite high WSD compared to the unadditived TMPE and this suggests further addition of anti-wear additive to improve the formulation. **Table 9** summarizes the previous studies that involved in the application of TMPE as hydraulic fluids. TMPE found its application as a hydraulic fluid due to its improved oxidative stability, viscosity index, and tribological properties. Hydraulic fluids, like any other application, must be carefully designed with additives to protect the base stock and components in the hydraulic system while also ensuring optimum system performance.

Heat Transfer Fluid

Heat transfer fluid, also known as thermal fluid, is a heat transmission fluid with excellent oxidation resistance. It is used for cooling or heating or as a thermal storing medium in a process heating, metal working, and machine cooling applications. Water is naturally an efficient heat transfer medium; but, due to its processing temperature and pressure limits, water is no longer practical (Qazi, 2017). Water can also create corrosion on the system piping, which is a disadvantage. The heat of vaporization, thermal conductivity, and specific heat are the design parameters in every heat transfer fluid. A reduction in the heat transfer would result in the reduction of energy efficiency. There are several types of heat transfer fluids available which include refrigerants, anti-freezes, chiller fluids, hot oils, etc. The main synthetic fluids are ester and diester compounds, polyglycol and water-glycol fluids, and silicone-based greases and oils. The thermal conductivity of TMPE and other esters are slightly higher than hydrocarbons, therefore improving the heat transfer properties of the oils (Shah et al., 2021).

More stringent emission rules, the need to minimize oil dependency, and the need to increase transportation energy efficiency are all driving the increasing interest in the application of ester in electric vehicle technology. The main challenge associated with the electric vehicles is the optimization of the thermal management system which requires efficient cooling and heating methods. To avoid breakdown, the system must be able to maintain a steady temperature across the operational temperature range of components such as the battery. Despite the fact that the water/glycol mixture has outstanding heat transfer capabilities, its high electrical conductivity may cause electivity leakage and power losses in the fluid. Among other factors, the diester and trimester-based heat transfer fluid provides a heat transfer fluid that is biodegradable and environmentally friendly, has low flammability, and is therefore safe. The application of triester as a heat transfer fluid in the electric vehicles is described in United States 2012/0164506 A1 Patent by Claeys et al. (2012). The ester was derived from a mono-unsaturated fatty acid and biomass. The coolant exhibits an electrical volume resistivity at 25°C of at least 10^{10} Ω-cm, and generally at least 10^{12} Ω-cm. The specific heat of the present coolantas exhibited at 20°C is generally at least 2.00 kJ/kg.K., and can be at least 2.30 kJ/kg.K. The present coolant composition also generally exhibits a thermal conductivity at 20°C. of at least 0.170 W/m.K., and even at least 0.200 W/m.K. The ester samples have electrical resistivities significantly higher than the water/glycol mixtures and the magnitude of the electrical resistivity is of the order that it can be used as a dielectric fluid in applications with low conductive requirements (Claeys et al., 2012).

TABLE 10 | Comparison of properties of trimethylolpropane ester (TMPE) and mineral oil as MWF (Benedicto et al., 2017).

Performance	TMPE	Mineral oil
Biodegradability	Better	Poor
Toxicity	Low	High
Oxidative stability	Moderate	Better
Lubrication	Better	Good
Heat exchange	Good	Good
Viscosity index	Better	Moderate
Hydrolytic stability	Moderate	Very good
Thermal stability	Good	Good
Seal compatibility	Moderate	Better
Relative cost to mineral oil	2	1

In a different study, United States Patent United States5494597A discloses refrigeration working fluids made of TMPE which is prepared from branched C7 to C10 monocarboxylic acids (Krevalis et al., 1996). This carbon chain length is said to produce satisfactory miscibility values, when admixed with the R152a and R125 refrigerants compared with other higher or lower alkyl carbon chain length. For instance, the formulation of 10wt% iso-decanoic/TMP (acid/polyol) and 90wt % of R152a resulted in a viscosity of 46.8 mm2/s and −60°C miscibility value. The patent also mentioned to avoid the use of esters with lower carbon chain length (C2 to C6) since they are more volatile, more hydrophilic and exhibit more solvation power. These are all the undesired properties in the formulation of good refrigeration working fluids (Krevalis et al., 1996).

Metal Working Fluid

In metal working fluids (MWF), fatty acid esters have found application as a lubricant additive and TMPE is the most common ester used (Mathiesen, 1998). MWF plays a crucial role as a cutting fluid in machining to facilitate lubrication by providing a thin layer between interfaces of metal working tools and work pieces. It also acts as a coolant to reduce heat of tools and pieces for an optimum efficiency and productivity. Continuous efforts in developing a sustainable plant oil-based MWF have been done to replace the hazardous mineral oil-based MWF. It was due to an evaluation result in 1987 by International Agency for Research on Cancer that has determined the conventional MWF as a carcinogen (Li et al., 2003). Hence, for an environmentally friendly and sustainable machining process, a combination of low toxicity, biodegradable lubricant, dry machining, and minimum quantity lubrication (MQL) conditions are required (Talib and Rahim, 2016).

Investigations on tribology characteristic and metal working process have revealed the potential of TMPE to replace mineral oil as MWF, as summarized in **Table 10**. Long polar fatty acid chains of plant oil-based TMPE (C16 to C18) have contributed to a strong, thin, and sufficient lubrication on the contact surfaces, which was also great in adsorption on the metal surfaces (Talib

TABLE 11 | Additives related to MWFs.

Additive type	Function	Chemical compounds
Anti-aging additive, oxidation inhibitor	Prevention of oxidation of base oil at high temperatures and stabilization	Aromatic amines, organic sulfide, zinc dialkyldithiophosphate
Anti-wear additive	Reduction of abrasive wear of rubbing surfaces by physisorption	Acid and nonionic phosphoric acid ester, zinc dialkyldithio-phosphate
Biocides	Prevention of excessive microbial growth	Phenol derivatives, formaldehyde releasers, isothiazolinones
Dispersant	Prevention of varnishes build-up on surfaces and agglomeration of particles to form solid deposit	Sulfonate, phenolate, salicylate
Emulsifier	Emulsion formation and stabilization	Anionic sulfonates, potassium-soap, alkanolamine-soap, nonionic fatty alcohol
Extreme pressure additive	Protection against wear by formation of adsorption or reaction layers, prevents micro fusing of metallic surfaces	Chlorineparaffine, sulphuros ester, phosphoric acid, ester, polysulfide
Foam inhibitor	Destabilization of foam in oil	Silicone polymers, tributyl phosphate
Friction modifier	Friction and wear reduction, enhancement of lubricating film adhesion	Glycerol mono oleate, natural fats, synthetic ester
Metal-deactivators	Adsorptive film formation	Heterocycles, di-amine, triaryl phosphite

References (Lawal et al., 2012; Brinksmeier et al., 2015; Wickramasinghe et al., 2020).

and Rahim, 2014). Furthermore, its high viscosity has produced low WSD and COF, which also reduced the vaporization volume as compared with a commercial synthetic ester (Talib and Rahim, 2014).

The tribology characteristic as well as physicochemical properties of TMPE can be further improved with the formulation of MWFs in which the surfactants and additives modify the chemical structure to withstand special environmental conditions for better performance. The additives and surfactants as listed in **Table 11**, in the range of 5–15%, could be added to improve seal compatibility, oxidative and hydrolytic stabilities as shown in comparison of TMPE and mineral oil MWFs (Wickramasinghe et al., 2020). An evaluation on machining process with an MQL technique was carried out by using Jatropha oil-based TMPE, or modified Jatropha oil (MJO), with an addition of 0.05wt% hexagonal boron nitride (hBN) nanoparticle (Talib et al., 2019). MJO with 0.05 wt% hBN had the lowest cutting force (383 N) and cutting temperature (210 °C) as compared with the pure MJO and synthetic mineral oil MWFs. Moreover, the addition of nanoparticle to the MJO also greatly reduced tool-chip contact length on the cutting inserts.

An application of the plant oil-based TMPE with miscible ionic liquids additives via the MQL technique could also greatly reduce excessive usage of MWF, as studied by Abdul Sani et al. (2019). The additions of fully oil-miscible and biocompatible ionic liquids, 10% (N1,8,8,8)(NTf2) (AIL) with MJO as the base oil and 1% (P6,6,6,14) [i (C8)2PO2] (PIL) with MJO showed the highest cutting performance and required low specific cutting energies. They have successfully reduced cutting forces and specific cutting energy by 4–5%, cutting temperatures by 7–10%, friction coefficient by 2–3%, tool-chip contact length by 8–11%, chip thickness by 22–25%, friction angle by 1–2% and increased shear angle by 25–29% compared to the benchmark synthetic ester lubricant. Hence, the study revealed the highly potential and sustainable green alternative to the mineral oil-based MWF.

An adaptability and performance of formulation of high oleic palm oil-based TMPE (HO-TMPE) with different additives was also investigated by Chang et al. (2015), specifically for the tapping oil formulations. The research study revealed that the formulation of 88.8% HO-TMPE base oil with 5% high molecular polymer ester GY-25, 1% alkyl phosphate 360-P (extreme pressure, EP and anti-wear AW), and 5% L5333 (a sulfurized vegetable oil with 10 wt% active sulfur as a lubricity improver) and 0.2% KSP-93 (triazole derivative as a metal passivator) additives, had potential as MWF for heavy-duty applications in hard metals such as stainless steel, duplex stainless steel, and hastealloy®. Other research studies that had used high oleic palm oil-based TMPE with synergy of additives such as nanoparticles and ionic liquids also revealed its technological competitiveness and commercially viable MWF (Sani et al., 2017; Kathamore and Bachchhav, 2021).

Drilling Fluid

In drilling fluid application, TMPE was examined as an additive, specifically, as a nonionic surfactant, along with other potential polyol esters such as neopentyl glycol ester (NPGE) and pentaerythritol ester (PEE) (Kania et al., 2021). The polyol esters act as a thinner to prevent flocculation of uncharged macro-molecules and finally to stabilize the colloidal particles (Napper, 1977; Luckham and Rossi, 1999). It was found that by using Monte-Carlo and Molecular descriptor calculations, polyol esters with more hydrophobic fatty acid chains had high possibility to enhance rheology of drilling fluids and stability of mud emulsions. Moreover, the hydrophobic chains in TMPE provide the affinity to attract molecules on the organoclay and its high molecular mass also contributes to a maximum adsorption density. Hence, TMPE with three hydrophobic chains is suitable as a drilling mud with moderate solid content, as compared with PEE that has four hydrophobic chains that is more apt for high solid-content mud (Kania et al., 2018; Kania et al., 2021).

PROSPECTS AND CHALLENGES

Modern machine and engine advancements have presented numerous challenges in terms of the effectiveness and performance of current biolubricant base oils and formulations. Some of the challenges include the need for more cost-effective production plant, the need to reduce the dependence on the current plant oil feedstocks, the specialized performance requirements of emerging end-use applications, and many more (Rudnick, 2017). Development of biodegradable fluids with the necessary high oxidative and thermal stability has been a major challenge for the industry. Synthetic ester, particularly TMPE, often defines the maximum performance in terms of thermal and oxidative stability due to the absence of beta hydrogens in its structures (Frauscher et al., 2017; Rudnick, 2017). However, like any other organic compounds, the oxidative stability of TMPE can be compromised. Previous studies have reported that the degradation of TMPE is significantly enhanced by catalytic surface reactions by several dissolved metals, including copper, iron, and zinc (Kauffman, 2006; Randles, 2013; Urness et al., 2016). Raof et al. (2019a) conducted an oxidation study on trimethylolpropane tricaprylate/tricaprate (TMPE C8/C10), trimethylolpropane trilaurate (TMPE C12), and trimethylolpropane trioleate (TMPE C18) in the presence of copper/steel catalyst. The ED-XRF analysis revealed a highly dissolved copper concentration (>700 ppm) in the TMPE C8/C10 and TMPE C12 base oils compared with TMPE C18 (<10 ppm). In the presence of metal surfaces, the presence of water and contaminants caused by incomplete esterification/transesterification of the starting polyol also contributes to catalytic decomposition. Randles (2013) mentioned the suitability of using phosphate additive to passivate the iron surfaces. The studies on the catalytic decomposition of TMPE on metal surfaces are still lacking and further works need to be done to help us establish a greater degree of understanding on this matter.

Malaysia, the world's second largest palm oil producer after Indonesia, contributes nearly half of global palm oil production each year. Although less than 10% of palm oil is used in the biodiesel and biolubricant streams (Salih and Salimon, 2021), it may eventually arouse concerns about food chain supply. Based on their oil content, both edible oils such as palm, olive, soy, con, and so on, as well as nonedible oils such as Jatropha, karanja, castor, and neem have high potential as neat oil (Singh et al., 2017; Jimenez-Lopez et al., 2020; Salih and Salimon, 2021). According to Salih and Salimon (2021) advanced separation techniques can also extract nonedible constituents from oil to make it food grade. Exploration of nonedible oil as a raw material to produce polyol ester could lead to the production of a stable food grade biolubricant (Gunam Resul et al., 2012; Gul et al., 2020). For example, Ng et al. (2022) evaluated an 80% yield of NPG ester from palm fatty acid distillate (PFAD) for the use in a two-stroke engine. In a different study, Cheryl-Low et al. (2021) reported 100% purity of polyol ester synthesized from lignocellulosic biomass. Also, to avoid competing with food value chain, many companies and private sectors are now seeking into re-processing or re-refining technologies for used vegetable cooking oils. The idea is to recycle this feedstock into useable base oils for use in lubricant formulations, therefore adding value to the core business. This would allow major food companies to cover all disposal expenses and, in the long run, produce a "green" revenue stream for the company. The challenge is to find new and innovative technologies that can fully integrate the refining and pretreatment of used cooking oil into base oils that can be used as a feedstock in the TMPE production. The presence of heavy impurities and solid particles and also inconsistent quality of used vegetable cooking oils present other challenges in realizing this idea.

One common issue in developing a food grade lubricant is that some additives are not approved for use in food (Sherman and Totten, 2018). Globally, regulations limiting the contents of hazardous additives such as sulfated ash, phosphorus, and sulfur have been implemented (Azman et al., 2016; Rashmi et al., 2017). These bearing additives could reversely affect the performance of devices, in particular diesel engines (Rashmi et al., 2017). Centers (1992) reported that a neurotoxin substance from lubricant decomposition may be produced at extreme temperature (350–700°C). For turbine engine oil application that used synthetic oil, when trimethylolpropane and phosphorus from the additive combines during thermal combustion, trimethylolpropane phosphate was formed. In addition, the decomposition of TMPE produced carboxylic acid (Kalman et al., 1985). Phosphorus was presented in anti-wear additives, such as tricresyl phosphate (TCP, which is from tritolyl phosphate isomers) (Centers, 1992).

Sherman and Totten (2018) discovered differences between food grade and non-food grade water glycol hydraulic fluids. Because amine additives, which are essential for corrosion inhibitors, are prohibited for contact with food, approved additives with lower performance were used instead. Furthermore, food-grade hydraulic fluids frequently fail to meet ISO VG 46 specification (Sherman and Totten, 2018). According to Canter (2020), two commonly used antioxidants such as diphenyl amine and hindered phenolic derivatives could cause aquatic toxicity. When propylene glycol was used instead of diethylene glycol, which has superior lubricity properties, the results showed higher wear scar diameters as well as changes in oil density, pH, and pour point. Furthermore, product recalls would occur when food products were contaminated by non-food grade lubricant, gear oil, or grease, which could cause off-odor, off-flavor, irritation, and intestinal discomfort (Gebarin, 2009). Because of its improved viscosity index and ability to withstand high temperatures, research into food grade additives in polyol ester, in particular, TMPE could be expanded. If modified with appropriate additives, TMPE has greater potential. Toxicity test is a method of confirming the claim of food grade, thereby assuring consumers and industry for the alternatives of mineral-based lubricant.

Other challenges related to the development of TMPE as food grade lubricants are the selection of catalyst during base oil synthesis. The impurities generated from the use of acidic catalyst during the incomplete esterification process (such as unreacted raw materials) or catalyst residue could contaminate the produced lubricant (Papadaki et al., 2018). Nowicki et al. (2019) acknowledged that homogeneous acid catalyst had disadvantages for instance, high corrosivity and difficult product recovery. As a result, a similar catalyst used in the food sector, Tin (II) *bis*(2-ethylhexanoate), which is neutral and noncorrosive, was selected for the investigation. The produced TMPE exhibited the smallest WSD (0.64 mm), the greatest anti-seizure properties (3450 N), and outstanding thermal stability at 400°C, according to studies on high TMP dimers. The most crucial aspect was that proper catalyst selection enables the manufacturing of high-quality products without the requirement for high vacuum distillation operations (Nowicki et al., 2019). Papadaki et al. (2018) investigated the production of TMPE from a two-step bioprocess microbial oil and TMP. The esterification process used lipase enzyme, which yielded 83% of TMPE after 72 h. However, of the TMPE's physicochemical properties were not disclosed. Therefore, it is recommended that the future research in TMPE production could opt for more environmentally friendly catalyst and green synthesis.

For engine oil application, the load-bearing capacity of pure bio lubricants was limited and eventually failed when subjected to higher loads (Kotturu et al., 2020). Most lubricants' performance reports focused on various speed and load conditions at short durations of testing, but there were few reports on long-term and continuous endurance testing under extreme load and speed conditions. Furthermore, the improvements in the engine and emission performance for alternative bio lubricants could have been investigated. Less study on the oxidative, thermal, and hydrolytic stability test is conducted on TMPE in engine oil application. The synergistic and adverse effect studies in particular additives could benefit the industry and engineers in the future.

Despite the many advantages of using TMPE, its usage as insulating fluids is often linked to several challenges too. Regardless of the fluid used to produce a transformer's insulation system, network operators confront challenges related to the system's moisture after many years of operation (Cybulski and Przybylek, 2021). Unfortunately, throughout the transformer's long-term operation, which can last up to 50 years, the water content in its insulating system gradually rises. If the moisture level is too high, the transformer can fail electrically. To reduce the risk of transformer failure, it is important to maintain the insulation moisture level low throughout the transformer's lifetime. A study by Cybulski and Przybylek (2021) shows a possibility of using 3A molecular for continuous drying of ester during transformer operation. It is estimated that for a free-breathing transformer filled with mineral oil, 200 kg of molecular sieve should be suffice for 10 years of continuous drying. Natural ester and synthetic ester like TMPE would require lesser volume than mineral oil due to its high moisture absorbance capacity.

Hydraulic fluids in particular are very prone to water contamination during service, especially when esters are being used (Rowland et al., 2017). Some base stocks interact with water or metals to create by-products such as sludge and make hydraulic fluids inefficient. Deciding on the most lucrative hydraulic fluid for companies is very challenging because many factors need to be taken into consideration. The turbine oil stability test (TOST) has been widely used to assess the oxidative stability of hydraulic fluids. The test run at 95°C, in the presence of water, metal catalyst, and air. The "dry" TOST method that operates at higher temperature (120°C) and in the absence of water has been developed later on and has found to be less discriminatory on vegetable oil and ester-based hydraulic fluids (Petlyuk and Adams, 2004; Rowland et al., 2017). It is also critical that the test distinguishes between thermal degradation, oxidative degradation, and volatility. Some oven-aging or thermogravimetric analysis has resulted in incorrect results since the loss in sample weight and increase in viscosity might be ascribed to volatilization of the lighter components rather than chemical degradation (Rudnick, 2013). More appropriate bench tests are needed to simulate real-time operating conditions for hydraulic fluid application.

Plant oil-based MWF has limitations in oxidation stability, hydrolytic stability, and heat-bearing capacity due to their chemical structure, especially for its polyunsaturated fatty acid profiles, while MWF strongly favors for lubricant that contains highly saturated fatty acids (Wickramasinghe et al., 2020). However, the most successful formulation method for plant oil-based water-soluble MWFs is emulsification, in which the aquatic and oleic phases are mixed together and strongly shaken to disperse the oil droplets in water and vice versa (Coker, 2007). For an industrial heat treatment, palm oil has shown as an effective bio-quench ant for industrial heat treatment, in addition to its highest thermal stability as compared with sunflower, coconut, and mineral oil-based MWFs (Chandrakar et al., 2014). It is expected that palm oil-based TMPE has better opportunity in MWF application due to its enhanced hydrolytic stability and oxidation stability than the original palm oil.

Plant oil-based TMPE with three-branched chains of ester groups has provided an excellent friction reduction and anti-wear performance although PEE was reported as the best candidate to the synthetic drilling mud formulation (Kania et al., 2018). As a recent off-shore regulations requirement, an enhancement of the synthetic drilling mud lubricity becomes crucial. Moreover, an addition of plant-based TMPE into the synthetic drilling mud also showed a lower force to initiate a fluid movement, for its shear-thinning rheology, instead of other improvements in drilling mud filtration properties. However, as mentioned in Section 3.7, TMPE as a biolubricant additive is not suitable for drilling mud with high solid content, which limits the application of TMPE only in low to medium solid-contents of drilling muds.

The question arises of how to convince industrial users to pay two-fold of the cost of mineral oil-based lubricants as the end products, no matter the excellent exhibited performance of formulated plant-oil-based lubricants. One can justify it from the standpoint of performance, warranty costs, avoiding early failure of the part, etc. despite evidence that costs can be cut by switching to synthetic lubricants. Their needs are so simple and petroleum oils and greases are so cheap that synthetics cannot compete for these applications, despite a widespread impression among industrial users that in general, synthetic lubricants protect well, last longer, and outperform their conventional counterparts. Thus, the conventional lubricants are currently still strongly entrenched.

The cost of producing biolubricant is not currently well established compared to the cost of biodiesel processing. Up to this point, biolubricant manufacturing has been scaled up to the pilot plant stage. Lubricant raw material costs are as essential as utility costs in determining annual operating cost of lubricant production (Kumar et al., 2020). The cost of raw material from neat resources to produce lubricant is approximately 2–4 times that of mineral and waste plant-based raw materials. As a result, the price of lubricant for bio-based oil is 2–3 times higher (Soufi et al., 2019). Moreover, bio-based and waste plant-based lubricants have lower carbon footprints than mineral oil lubricant. Thus, it is inferred that the waste management cost for mineral-based lubricant to reduce greenhouse gas emissions is higher.

CONCLUSION

The following conclusions can be drawn from the present review:

1. This review helps the readers to survey the potential formulation of TMPE with other base oils or additives. Since various functions of lubrication conditions are required in different lubricant applications, a scientific point of view of TMPE is also needed in terms of lubricant technology.
2. To date, research studies of lubricants formulation of plant oil-based TMPE are still vastly undergoing since TMPE has won the researchers' interest in the formulation of biolubricant for its enhancement of lubricant performance, qualities, and thermo-oxidative properties of biolubricant base oil.
3. TMPE was mostly studied as a biolubricant base oil in most potential applications such as engine oil, insulating fluid, heat transfer fluid, metal-working fluid, etc. except for the synthetic drilling mud application, where it is utilized as a lubricant additive.
4. The formulations of TMPE in numerous studies have considered the working functions to enhance tribology, rheology, as well as to maintain the condition of the lubricants itself.
5. The implementation of renewable resources in the production of lubricants could potentially reduce the carbon emissions associated with the process, packaging, and distribution, and eventually their whole life cycle. This effort is in line with the United Nation's target that is to achieve a truly global coalition for carbon neutrality by 2050. The present study can support and encourage research on using plant-based TMPE as biolubricants.

AUTHOR CONTRIBUTIONS

NR, HH, NM, and RY contributed to conception and design of the overall review. NR involved in planning, supervised and directed the work. HH and NM designed the figures and tables. NR, HH, and NM wrote the first draft and all sections of the manuscript. All authors discussed the results and commented on the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

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