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Review

Natural Esters for Green Transformers: Challenges and Keys for Improved Serviceability

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Abstract: The service of mineral insulating oils for power transformer insulation and cooling aspects cannot be disavowed. However, the continued use of mineral oils is questionable due to environmental unfriendliness and the divestment from fossil fuels. This has provoked the quest for green alternative insulating liquids for high-voltage insulation. Natural esters are among the remaining alternatives that are renewable and environmentally friendly. Regardless of their environmental and technical merits, natural esters have some limitations that are slowing down their total acceptance by transformer owners and utilities. Critical limitations and concerns include esters' pour point, viscosity, oxidative stability, and ionization resistance. In this work, the state of the art of "natural esters for transformers" is explored with the aim of potential improvements. The sections of the article are geared towards technical viewpoints on improving the overall workability and serviceability of natural esters in high-voltage applications. A comprehensive review of the existing literature is achieved, based on performance improvements of the natural ester using "additives" and "chemical modification". The authors hope that this report may be helpful to transformer owners as well as influence the progression of natural esters for power transformer applications.

Keywords: green transformers; natural esters; additives and chemical modifications

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1. Introduction

Power transformers are one of the significant pieces of equipment whose continued service is essentially related to the reliability of the electrical network. It is reported that 75% of high-voltage transformer failures are related to a dielectric/insulation issue [1]. These unforeseen failures in transformers that are largely caused by insulation problems cost a huge amount of money for transformer repairs or replacement [2,3]. The insulation system in the transformer is composed of solid (paper and pressboard) and liquid (oil) dielectric materials [4]. The elementary characteristics of the liquids used for insulation in the transformer are low acidity, high interfacial tension, high flash point, low viscosity, low volatility, low dielectric loss, high thermal conductivity, high dielectric strength, and impulse strength [2]. Pour point and density are important parameters too, and in cold regions, the discussion is concerns insulating liquids. In addition, the liquid should be nonflammable, compatible with the transformer tank without causing chemical corrosion, and cheaply available. However, with the rising interest in sustainable and environmentally friendly technologies, the biodegradability of the liquid has become a key concern. Of further engineering importance are towards materials that can withstand a high power density to serve the elevated electricity load demand. In addition, this also invite the requirement of the materials being able to withstand high thermal conditions. Thus, in a nutshell, future insulating liquids are expected to withstand high thermal and electrical stress while also being biodegradable [5–7].

The mineral oil typically used in liquid-filled transformers is non-biodegradable and hazardous to the environment [8]. In addition, mineral oil has a poor emission profile; the gasses released at ignition are usually carbon compounds, which may form acidic compounds when reacting with the atmospheric air. Due to the issues associated with mineral oil, researchers have placed attention on finding other materials with similar qualities as mineral oils, in addition to being biodegradable and environmentally friendly [8–10]. Synthetic ester is a well-fitting insulating liquid for transformer insulation; however, the cost of producing this liquid is high, and an environmentally friendly insulating oil that is also cheap is strongly desired. Research on natural esters started in the 1990s, and esters have attracted great interest as an alternative insulating material for power transformers due to their high moisture tolerance, biodegradability, sustainability, nontoxicity, high fire point, high flash point, etc. [10–13]. As natural esters are the target candidate for this study, the discussion in the paper is restricted to natural ester liquid alone.

The rate of biodegradability of natural esters according to the Co-ordinating European Council (CEC-L-33) is within the range of 97% to 99% in 21 days, and they display low or no toxicity relative to mineral oil [8]. This is attributed to the absence of halogen, poly-nuclear aromatics, and semi-volatile or volatile organics in vegetable-based dielectric liquid. Considering both aerobic and anaerobic conditions, the biodegradation rate of vegetable-based insulating liquids is relatively better than that of mineral oil [10]. It has been documented that vegetable-based insulating liquids undergo biodegradation of more than 70% in 28 days [2,10]. The fire point of natural ester dielectric liquid is greater than 360 °C, a good fire property that has led the oil to be classified under the "K" class according to [10,14,15]. The product of oxidation in mineral oil forms a sludge precipitate, but vegetable-based liquids oxidize differently. The oxidation product of vegetable-based liquids does not form sludge precipitate; instead, the liquid starts to thicken and polymerize by moving from a sol to a gel state, as reported in [16]. The different solubility levels of water in both esters and mineral oils have created a reasonable difference. Ester liquids can absorb up to 20–30 times more water than mineral insulating oil at similar conditions. With this unique property of natural esters, moisture impact on the insulating strength of natural ester liquids and insulating paper is reduced because of the higher water absorption ability of natural esters relative to mineral oil [10]. Due to this ability of natural esters, the rate of degradation of oil-paper insulation is much slower. In addition, it reduces the deterioration rate of the paper insulation by protecting it from absorbing water. This gives vegetable-based dielectric liquids an edge over traditional mineral insulating oils. However, natural ester dielectrics are facing issues with synthesis (high cost), poor ionization resistance, high pour point, and low thermo-oxidative stability, which has posed barriers to the general acceptability of vegetable-based insulating liquids, especially in the case of a free-breathing transformer [10,14,17]. The recent interest in green technologies for a sustainable planet and health safety aspects positions natural esters as an interesting technology. It is important to know that there is currently biodegradable hydrocarbon on the market with high biodegradability and non-ecotoxic properties, but the fire property of this oil is inferior to that of natural esters. Considering the technical merits summarized above and the environmental safety aspects, various researchers have given attention to the improvement of this alternative dielectric liquid [18].

This article aims to emphasize the major drawbacks and the state-of-the-art literature on improving these short falls of natural esters. It is apparent from the literature of the recent past that the addition of nanoparticles to natural esters has been a subject of interest to many researchers across the globe. It is reported and understood that few nanoparticles have the potential ability to alter the properties of natural esters for better functionality in transformers. Therefore, special attention has been paid to the role of nanoparticles in influencing the properties of natural esters. It is to be mentioned that there are various reviews reported in the literature focusing on the application of nanoparticles for improving the properties of transformer liquids. Although natural esters are also a candidate for transformers in the reported reviews, the properties of natural esters have been addressed in a general way. With the various investigations by Fofana et al. and Mohan Rao et al. on the topic of alternative liquid dielectrics, it is apparent that natural esters have been widely criticized in terms of their pour point, viscosity, oxidative stability, and ionization resistance. Therefore, these reported short falls of esters are the main concerns for the present review. It is believed that this review may encourage progress in natural esters research for applications in transformer insulation technology.

2. Plant-Based Liquids and Recent Progress

The search for alternatives to mineral insulating oils for use in liquid-filled high-voltage apparatuses began a few decades ago. The reasons behind the need for an alternative liquid have been discussed in the introductory section and are detailed in [4,7,18]. In the search for an alternate transformer dielectric liquid, attention has been placed on natural plant-based liquids because of their potential to serve as dielectric liquids. The demand for sustainable development and environmentally friendly solutions has been an instigating element for the rapid rise of interest in plant-based liquids. The 30-year development of plant-based liquids for use as engineering dielectric liquids is summarized in [18]. Despite the various advantages of plant-based liquids, the problem of synthesizing natural ester liquids with low pour points and high thermo-oxidative stability persists. The process of synthesizing vegetable-based dielectric liquids from bioseeds is illustrated in Figure 1.

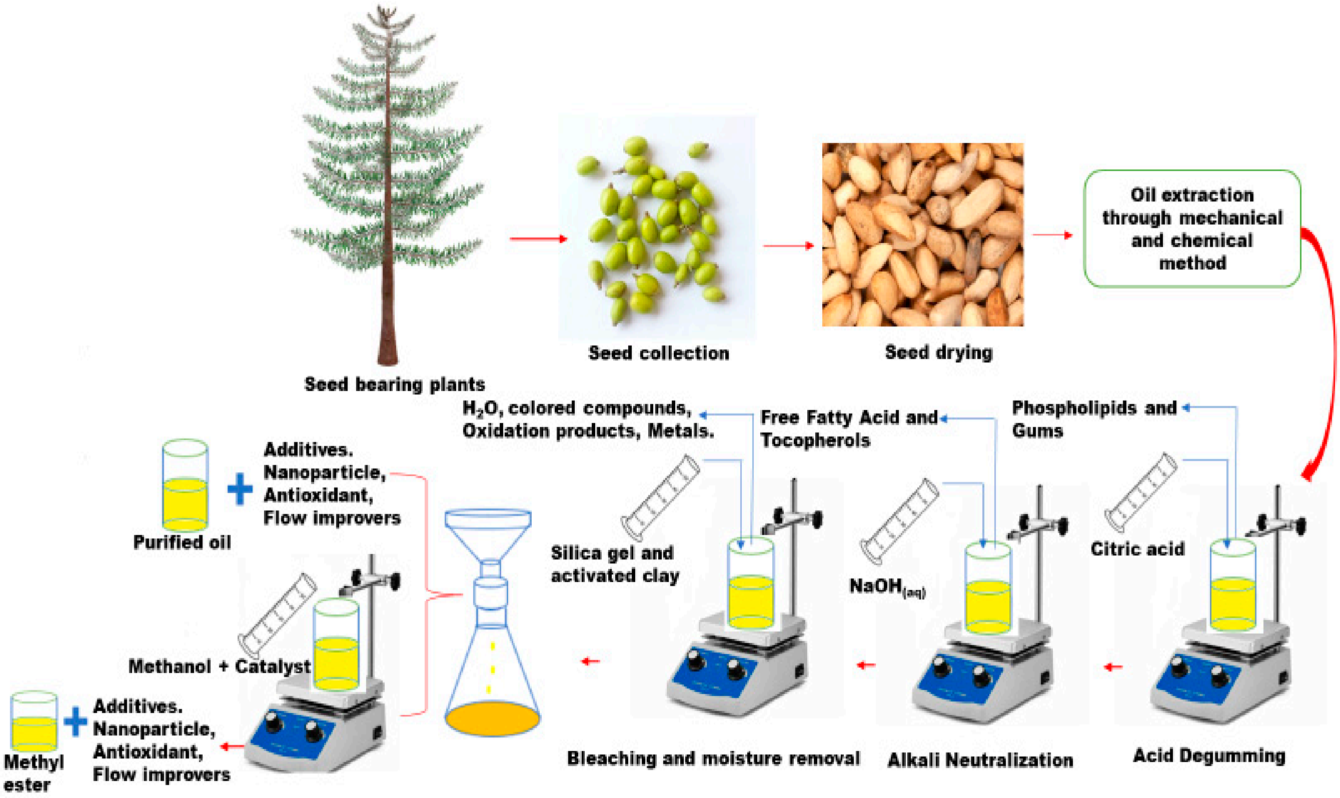


Figure 1. Synthesis of bio-based insulating oil.

Meanwhile, in the attempt to find a suitable dielectric liquid, great attention has been paid to vegetable oils such as sunflower, canola, coconut, soybean oil, etc., and synthetic esters as a liquid insulating medium [2,19]. It is reported in [20] that palm fatty acid esters (PFAE) possess some properties that position these as an alternative to mineral oils. PFAE has a flash point higher than mineral oil but lower than that of natural esters and therefore does not conform to the requirements in ASTM D6871-17, IEC 62770, or IEEE C57.147. The characteristics of the charge behavior in PFAE are similar to that of mineral oils. This is because the electric field strength in charged flowing liquid is the consequence of the space charge and the charges accumulated on the pressboard. However, there is a difference in the electric field distributions, and this has been attributed to variations in properties such as permittivity, relaxation time, and charge density. A similar study was conducted by Suzuki et al. [21], who reported that the resistance to the dielectric breakdown of fatty acid esters synthesized from vegetable-based liquid using an electrode gap of 2.5 mm was greater than conventional mineral oil. This could be attributed to the fact that water molecules in fatty acid esters are trapped by the ester group of these fatty acid esters. The work reported by Sitorus et al. on the electrical and physicochemical properties of jatropha curcas methyl ester liquid as a green alternative to mineral oil is promising [22]. The physicochemical and electrical properties along with the breakdown voltage were measured in the same experimental condition. It was reported that the methyl ester from jatropha oil and mineral oil had comparable AC breakdown voltages (acceptable limits), and this complies with the requirement of IEEE standard C.57.147 (for acceptance as an insulating liquid) except for the flashpoint. The dielectric properties of coconut oil and palm oil were investigated as potential green insulating oils [23]. Chemical modifications such as refining, bleaching, and deodorizing are some of the factors that improve both the physical and dielectric properties of vegetable-based liquids. Among these improved properties are the viscosity, dissipation factor, and resistivity.

Jatropha oil, a non-edible oil, was refined in [24] through degumming, neutralizing, and bleaching. The pour point and oxidation stability of the oil had to be enhanced through the addition of additives such as pour point depressants and oxidation inhibitors. It was expected that the addition of these additives might help the oil to meet the standard requirements of the American Society for Testing and Materials (ASTM D6871) and the International Electrotechnical Commission (IEC 62770).

Abdelmalik et al. reported that jatropha oil is a high-temperature liquid compared to mineral oil when considering flashpoints and fire points [25]. The viscosity of jatropha oil is almost the same as that of the natural esters available on the market. Further, jatropha oil was found to have good dielectric properties and a pour point less than 0 °C, which makes it usable in moderate-temperature regions. The compatibility of the prepared liquid sample with cellulose paper, both fresh and aged, showed that the impregnated paper had a low dielectric loss contrary to most reports on oil impregnation in the literature [25]. Due to the high affinity of ester groups to water molecules, the liquid might have absorbed some water molecules present in the paper. This consequently decreases the degree of aging that might have occurred because of thermo-hydrolytic degradation. The stability of jatropha oil to oxidation using an open beaker with a catalyst at 140 °C and 480 h showed that the liquid was not suitable for use in a free-breathing transformer, though it could be used in a hermetically sealed transformer. It was inferred that modification of this liquid through a chemical epoxidation procedure might improve the thermo-oxidative properties [25].

The effect of thermal aging on both the physical and dielectric properties of natural esters has to be properly monitored since the liquid is expected to serve for a long time. The characteristics of aged natural esters recently reported in [26] revealed that the moisture content, viscosity, turbidity, and dielectric loss of the liquid increase with aging. Further, the ionic mobility of the aged liquid increased, which caused an increase in the conductivity of the liquid and a decrease in the corona inception voltage of the aged liquid. The increase in ionic mobility and dielectric loss could be related to the negative impact of thermal aging temperature. The recent work on monitoring the sol and gel formation in natural esters under oxidative aging revealed that the breakdown strength of the gelled liquid was still within the scope for use as a liquid insulator. However, the high viscosity of the gel after the accelerated thermal aging might affect the cooling of the transformer, and this might lead to thermal breakdown of the system [27].

In spite of all the positive reports in the literature concerning natural esters, there is still a need for further research on natural esters by annexing all their characteristics and further improving the properties for a proper insulating liquid in high-voltage insulation. In this work, the current challenges affecting the general acceptability of natural esters as an insulating liquid are addressed, and previous efforts that have been made on addressing these issues are also discussed.

3. Major Critiques and Challenges

The choice of selecting natural ester over mineral oil has been a good decision to meet environmental requirements and for sustainability. However, there are some drawbacks associated with natural esters, viz., pour point, viscosity, oxidative stability, low resistance to ionization, and high dielectric loss [27]. These problems have hindered the general and widespread acceptability of this liquid by transformer owners. Table 1 compares some imperative properties of mineral oils and saturated/unsaturated vegetable-based liquids. It is vital to know that some of these properties are interwoven, and no insulating liquid is completely superior to another. It is now important to modify any type of selected liquid to suit the requirements of a good insulating material when considering both functionality and environmental friendliness. Most importantly, for environmental conditions and sustainability, natural esters have been considered over mineral oil [8]. In this section, these short falls of esters are discussed in detail. An overview of the previous attempts reported in the literature to overcome these drawbacks is organized in the subsequent sections.

Table 1. Some properties of mineral oils and vegetable-based liquid [14,28–30].

Properties	Conventional Mineral Oil	Vegetable Oil with Saturated Fatty Acid	Vegetable Oil with Unsaturated Fatty Acid	Standard Method of Testing
Density (g/cc) at 20 °C	0.895	0.917	0.886	ASTM 1298, ISO 3675
Moisture content, ppm	≤30	-	-	ASTM D1533, IEC 60814
Pour point (°C)	−40	20	−22	ASTM D 5949
Flash point (°C)	154	225	260	ASTM D 92, ISO2719
Viscosity (cSt) at 40 °C	13	29	37.6	ASTM D445, IEC 61868
Conductivity (S/m) at 20 °C	10^{-13}	10^{-11}	10^{-10}	-
Oxidation onset temperature (°C)	207	282	192	-
Breakdown voltage (kV)	45	60	56	IEC 60156, ASTM D 1816
Sustainability	NO	YES	YES	
Emission profile	Unacceptable	Acceptable	Acceptable	
Biodegradability Classification	Not biodegradable	Fully degradable	Fully degradable	IEC 61039

3.1. Pour Point

The fluidity of the dielectric liquid used in electrical insulation depends on its pour point. The minimum temperature at which there is no observable flow of liquid or the temperature at which the liquid becomes semi-solid is referred to as the pour point of the liquid. It is important to know that liquids intended for insulation in an electrical appliance are often expected to flow under any temperature conditions and to act as a perfect coolant. The pour point of the insulating liquid is largely determined according to the ASTM D 5949 standard [31,32].

The pour point of natural esters has been a challenging factor that is hindering the use of this liquid, especially in extremely low-temperature regions. This issue is due to the easy crystallization of the oil at low temperatures, which can lead to clogging in the transformer system. The rate of crystallinity varies in natural esters due to their saturation level. The percentage increase in the unsaturated fatty content from mono-unsaturation to poly-unsaturation has a great influence on the melting and pour point of the oil. The higher the percentage of unsaturated fatty acid content, the lower the melting and pour point, and vice versa. Generally, unsaturated fatty acids have lower melting and pour points than saturated fatty acids [33]. The uniform molecular shape of the saturated fatty acid is the main reason for its high pour point, because these molecules pack up easily as it solidifies. The carbon–carbon double bonds in unsaturated fatty acids introduce bends and kinks, which affect the rate at which the unsaturated fatty acids are crystallized [6]. As a result, the more unsaturated fatty acids, the harder it becomes for the molecules to crystallize. The triglycerides (C16:0, C18:1, and C18:3) in [34] show different types of fatty acids according to their level of saturation and unsaturation. The pour point requirement for a good insulating oil corresponds to IEC 60296 is −40 °C [35]. However, the pour point of natural esters is within a range lower than that of the requirement and lower than that of mineral oil. This invariably indicates that the application of natural esters in an extremely low-temperature region is challenging, since they solidify easily as compared to mineral oils. Several attempts have been made on the modification of natural esters' pour point, viz., modification through a chemical process (transesterification) and the addition of pour point depressants (flow improvers).

3.2. Oxidation Stability

Among the critical technical issues that have slowed the general application of natural esters is their poor oxidation stability. Despite this persisting issue, some parts of the world have been able to successfully utilize natural esters as insulating liquids both in sealed, free-breathing transformers and in power transformer retro-filling. However, the oxidation stability of dielectric liquids used in high-voltage insulation is highly essential, because most of the power transformers in use across the globe are free-breathing [36]. A condition-monitoring assessment of the long-term use of vegetable-based dielectric liquid can be found in [37]. The report of 17 power transformers revealed that there were no evident changes in the properties of the liquid used over 10 years. However, in [27], the impact of gelling in natural esters in the case of open beaker aging conditions was reported. The authors reported the impact of oxidation stability issues on the overall performance of the insulation system. Liquids that are not stable to oxidation become oxidized easily, and the products of oxidation are detrimental to the health of transformers. When natural liquid becomes oxidized, the viscosity and acidity of the liquid increase, making viscosity and acidity prominent factors that can be used for monitoring oxidation progress in natural esters. These factors affect the cooling and the dielectric properties of the liquid, respectively [38].

The oxidative stability of natural esters varies due to variations in the fatty acid composition. It varies from saturation to poly-unsaturation, and due to the presence of a high percentage of double bonds in unsaturated triglycerides, natural esters are more prone to an oxidation reaction. Unsaturated fatty acids polymerize and degrade after oxidation, and this is an undesirable condition, as it may cause damage to the transformer. When a natural ester is exposed to oxygen, it develops into a polymerized product. This process is known as gelling, and it affects the cooling and insulation properties of the oil. On the contrary, saturated fatty acids are relatively stable to oxidation due to the existence of a single bond existing in the oil. However, this oil is not often considered for insulation due to its high pour point temperature. Partial discharge activity in high-voltage systems has a relatively high percentage of occurrence whenever there is a solidification of insulating liquids in transformers during a cold start. Partial discharge initiation weakens the insulation and may eventually lead to electrical breakdown. The relationship between the concentration of oleic acid and the oxidation stability of natural esters has been established by Viertel et al. [39]. The presence of a high concentration of oleic acid in natural esters can extend the oxidation induction time of the oil. In a nutshell, a high concentration of oleic acid in natural esters could serve as an anti-oxidizing agent in the natural ester. This could help in the selection of natural base liquids for insulation in transformers. The stability enhancement of natural esters to oxidation has been addressed in diverse ways, viz., chemical structure modification and the addition of antioxidants [11,13].

3.3. Viscosity

Transformers generate a specific amount of heat during operation. This heat comes from the core and windings of the transformer; therefore, the liquid used for convectional cooling must have a low viscosity. The viscosity of natural esters has been reported to be very high by several researchers [13,24,40]. It is dependent on three main factors, which are the degree of unsaturation, the structural block of the fatty acid chain being connected to the glycerol, and the length of the chain. Neem oil has a dynamic viscosity of about 38 mPa.s, palm kernel oil has a viscosity of about 40.01 mPa.s, and jatropha has a viscosity of about 39.8 mPa.s [13,35,40,41]. The values reported here are higher than the viscosity of mineral oil but in the range of values recommended by the IEEE C57.147 [28]. From Equation (1), by implication, the heat transfer coefficient of natural ester is lower than that of mineral oil. Since the heat transfer coefficient and dynamic viscosity are inversely proportional, this can cause the thermal breakdown of an energized power transformer.

$$h = C \times \left(\frac{\Delta T_{Oil}}{\mu(T)} \right)^{n} \tag{1}$$

where h is the heat transfer coefficient; T is the temperature in kelvin; C is dependent on the thermal conductivity, density, thermal expansion coefficient, and specific heat of the oil; μ is the dynamic viscosity; and ΔT_{oil} is the oil temperature difference [42,43].

Further, the heat exchange property of oil can be assessed considering the Reynolds number, which is inversely proportional to the dynamic viscosity, as seen in Equation (2) [35]. The Reynolds number is a parameter that can be used to determine the flow type of liquids (laminar or turbulent flow). It is reported in [35] that liquid with a Reynolds number greater than 4000 has a turbulent flow, and liquid with a Reynolds number less than 2000 is a laminar flow. The turbulent flow has more effective cooling than the laminar flow.

$$R = \frac{\omega\ d}{\mu} \tag{2}$$

where ω is the velocity of the oil, μ is the dynamic viscosity of the oil, and d is the diameter of the channel. Natural esters with a viscosity this high do not perform better than mineral insulating oil as a cooling liquid in a transformer, since they have a Reynolds number that is relatively low compared to mineral oil.

3.4. Ionization Resistance

Low ionization resistance has been one of the critical challenging issues that needs proper attention when considering the use of vegetable-based liquids as an insulating material in transformers [27]. Chemistry reveals that reactions are faster as you go down a group due to a fall in ionization energy, which is proportional to a fall in activation energy. Ionization energy is the minimum energy required to remove the loosely held electron from one mole of a neutral gaseous atom, and activation energy is the minimum energy needed before a reaction takes place [44]. At a high electric field, the liquid dielectric becomes ionized, and the dynamics of ions in the electric field lead to the current generation in the liquid. The current in the system is conserved, and there is energy generated in the system with respect to time. This may eventually lead to a thermal and electrical breakdown in the transformer system. The least attention has been placed on the ionization resistance of natural ester insulating oil. The low activation energy of natural ester relative to mineral oil has been reported by [42,45]. Abdelmalik reported that the activation energy of mineral oil is almost twice that of vegetable oil [42]. In [46], it was also reported that the activation energy of mineral oil is higher than that of the natural ester. In this regard, the higher the activation energy, the higher the energy required to dissociate the molecules of the oil. Therefore, a high activation energy prevents a fast rise in ionic mobility [47]. The low ionization resistance of natural esters could be attributed to weak intermolecular bonds existing between the molecules. This poor ionization resistance of natural ester oil needs proper attention, as it could lead to the thermal and electrical breakdown of the transformer.

4. Chemical Modifications to Improve the Workability

4.1. Pour Point and Viscosity Enhancement

A "transesterification" reaction is the chemical reaction between the triglycerides of natural esters and alcohol to give fatty acid methyl ester and glycerol [48]. This reaction takes place in the presence of a base catalyst, be it a homogenous or heterogeneous catalyst. Examples of these catalysts are NaOH, CaOH, and KOH. A diagrammatic illustration of the chemical reaction is presented in Figure 2. The separation of glycerol from the triglyceride causes a drastic decrease in the pour point temperature of natural esters, and this can be attributed to the removal of glycerol, which is the backbone of easy crystallization of the oil. Even more so, removing glycerol reduces the percentage of O-H hydrogen bonding in the oil, which, consequently, reduces the average molecular mass of the oil and in turn decreases the rate at which the fatty acid crystallizes [5,46].

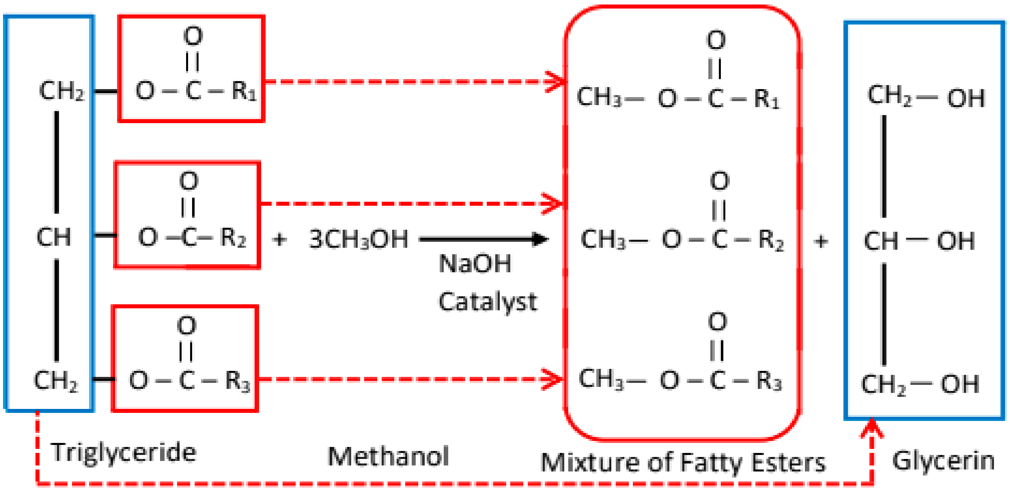


Figure 2. Chemistry of fatty acid methyl ester production.

Oparanti et al. [46] and Aransiola et al. [40] reported a reduction in the pour point of purified palm kernel oil and jatropha oil, respectively. The pour point of palm kernel oil was reported to decrease from 25 °C to −4 °C, and jatropha oil decreased from 2 °C to −6 °C after transesterification. This is an indication that the transesterification process improves the pour point property of the vegetable oil, and this places them on the verge of being used as insulating oil in a low-temperature region. Furthermore, this transesterification reaction has also been used to treat the problem of viscosity associated with natural esters. The transesterification process is an attempt at reducing the viscosity of natural ester oil [35,40,49]. The removal of glycerol from the oil reduces the average molecular weight and consequently leads to a reduction in the dynamic viscosity of the liquid. This is theoretically shown in Equation (3), where the dynamic viscosity and average molecular weight have a direct proportionality [5]. In addition, the removal of glycerol also reduces the resistive frictional force that exists between the layers of the methyl ester [5,49].

$$\mu = K\overline{M}^{\alpha} \tag{3}$$

where $[\mu]$ is the dynamic viscosity, $\overline{M}$ is the average molecular weight, and K and α are constant, which directly depends on the temperature and the solvent. It is important to notice that modifying the viscosity of natural esters has some detrimental effects on other physical properties such as the fire and flash points. This reduces the fire safety potential initially attributed to natural esters [22,50]. Further, electrical properties such as conductivity and dielectric loss of the natural ester increase after transesterification. This could be attributed to the reduction in the viscosity of the ester liquid, which gives easy transport to streamers. The increase in conductivity could also be related to the dissociation of some impurities in the oil during the process of transesterification [5,51]. Table 2 shows some properties of different vegetable liquids before and after transesterification. The process of improving conductivity and dielectric loss has been investigated by several researchers using some additives, and this is addressed in the next section of the paper.

Table 2. Some properties of oil before and after transesterification.

Vegetable Oil	Viscosity Before	Viscosity After	Dielectric Loss Before	Dielectric Loss After	Pour Point Before (°C)	Pour Point After (°C)	Flash Point Before (°C)	Flash Point After (°C)
Rapeseed refined oil [52]	36.14 mm^2/s	4.615 mm^2/s	0.0016	0.005	−8	−18	297	175
Jatropha oil [50]	32.44 mm^2/s	10.45 mm^2/s	-	-	3	0	≥240	191
Palm kernel oil [5,46]	44.49 mm^2/s	4.57 mm^2/s	0.0063	0.044	26	−6	239	148
Neem oil [35,53]	43.75 mm^2/s	5.53 mm^2/s	-	-	7	3	209	175
Canola oil [54,55]	33.4 mm^2/s	3.9 mm^2/s	-	-	-	−15	280	167

4.2. Oxidative Stability Enhancement

Research has shown that the oxidation stability of natural esters can be improved through the attachment of molecular side chains to the esters [5]. The report made by Abdelmalik shows that chemical modification of natural esters can be carried out in two steps. The first step involves the reaction of the double bonds in the unsaturated fatty acid of natural ester with peracids to form epoxides. The epoxide is a tri-membered ring with oxygen that has a highly reactive epoxy ring. The second step involves the grafting of side chains to the epoxy group. A systematic flowchart and reaction scheme of the first and second steps can be seen in Figures 3 and 4, respectively.

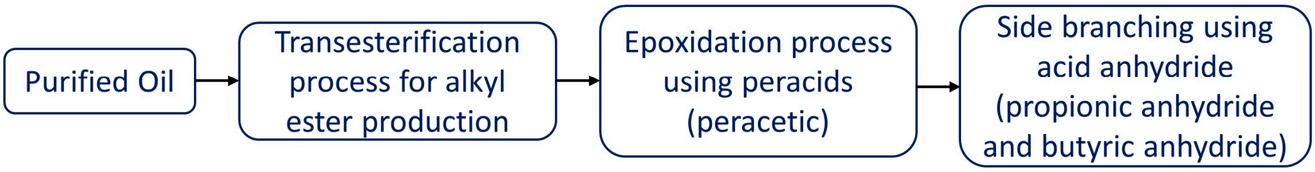


Figure 3. Systematic flow chart of epoxidized and grafted ester.

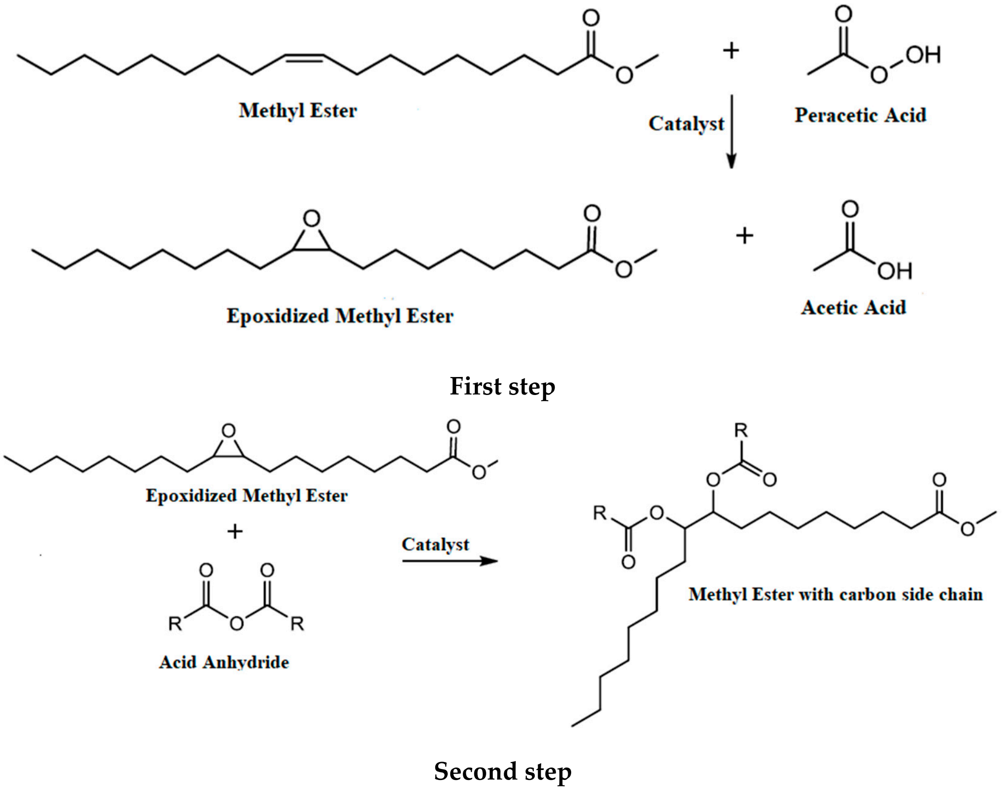


Figure 4. Reaction scheme of the first and second steps for epoxidation and grafting [5].

The chemical modifications performed on the alkyl ester reveal that the epoxidized alkyl ester has the highest stability to oxidation. However, the oxidative onset stability of mineral oil is still better than that of epoxidized oil. The further attachment of side carbons reduces the oxidative stability, which could be a result of the instability of the side-branched carbon molecules or the deposit of some oxidizing chemical element [5].

5. Additives to Improve the Properties

5.1. Pour Point Depressants

The addition of a certain type of pour point depressants to natural esters has also proven to be an alternative means of reducing natural esters' pour point to a fitting value that can withstand low-temperature performance. The addition of pour point depressants into the base liquid does not by any means affect the temperature of crystallization of wax in the solution, and it also has nothing to do with the percentage of wax that precipitates. The pour point depressant co-crystallizes with the wax of the base oil and reforms the structure of the wax crystal's growth pattern [56]. It also keeps the wax crystals apart and prevents them from forming a three-dimensional structure that could resist the flow of the liquid. The most common depressant used by oil manufacturers is poly methyl methacrylate (PMMA). This has been reported to reduce the pour point of natural insulating oil by 10 °C when less than 1 % weight of it is applied [11]. The depressant helps in suppressing the development of large crystals during the solidification of the natural ester at low temperatures. Polymethacrylate, among others, stands out as a good pour point depressant. It has little or no effect on the chemical and dielectric properties of the base liquid (natural ester). It has a negligible effect on the acid value and dielectric loss of natural esters. The comparison of other pour point depressants with polymethacrylate can be seen in [56]. The Evonik Viscoplex 10 series is designed for use as an environmentally friendly depressant [57]. This depressant makes vegetable oil stable for 15 days without losing its fluidity, but the fresh oil (untreated) solidifies after 24 h. However, the temperature details are not discussed by authors.

A thermomechanical method known as crystalizing fractionation is also a systematic method of improving the pour point of natural esters. In this method, freezing crystallization is used to separate triglycerides with high melting points from those with low melting points [56,58]. In this method, a diatomite can be added to increase nucleation. This process is performed in two steps, viz., crystallization and filtration, respectively. The fractionation process is reversible, and the steps can be seen in Figure 5.

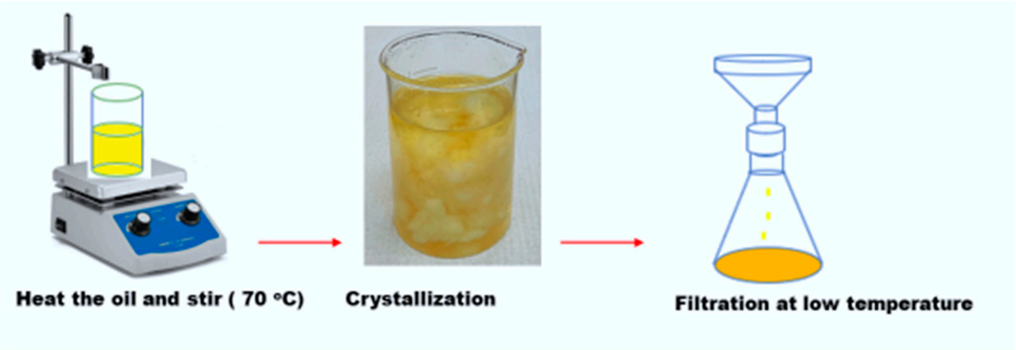


Figure 5. Fractional crystallization of natural esters.

Recently, crystallizing fractionation used on soybean oil drastically reduced the pour point of the oil from −13.5 °C to −20.3 °C [56]. However, the problem with this method is the reduction in the oxidation resistance due to the removal of triglycerides with high melting points [56]. The pour point property of an insulating oil needs proper study after aging to understand the potential of the pour point depressant even after aging. The pour point in [56] had a positive effect on oil crystallization properties after aging. This prevents the crystallization of the wax and the agglomeration of oxidation polar molecules. However, the effect of this pour point depressant on other physicochemical or dielectric properties of natural ester liquid has not yet been explored. Further, despite the enhancement of the pour point property, there is still a need for further study on the compatibility of pour point depressants with impregnated cellulose paper.

5.2. Oxidation Inhibitors

The oxidation in vegetable oil occurs in three different stages, viz., initiation, propagation, and termination. At the initiation stage, the alkyl free radical is formed due to some external factors such as heat, metals, or light. In the propagation stage, the free alkyl radicals react with oxygen molecules to form peroxyl free radicals. Thereafter, the peroxyl free radicals react with oil molecules to form hydroperoxide and a new alkyl free radical [59]. This process can be a continuous one in a cyclic manner. The peroxide generated in this stage is often termed a primary oxidation byproduct, which can be decomposed into a secondary oxidation byproduct (acids, ketones, and aldehydes) when subjected to thermal and electrical stress. The last stage is the termination stage. At this stage, the free radicals are joined together to form a stable compound [60]. Figure 6 shows a schematic diagram of the oxidation process. A radical hydroperoxide scavenger additive known as an antioxidant is used to protect materials from free radicals and oxidation. The antioxidant can be a donor or an acceptor. The chemistry of the reaction between the antioxidant (acceptor and donor) and the free radicals in the oil can be seen in Figure 7. The letters with asterisk mark in Figures 6 and 7 are the radicals.

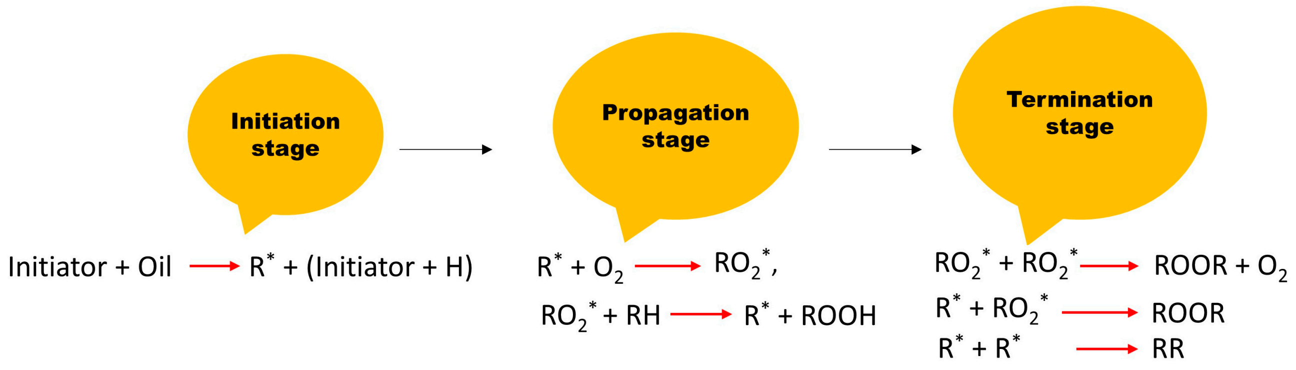


Figure 6. Stages of oil oxidation in vegetable oil.

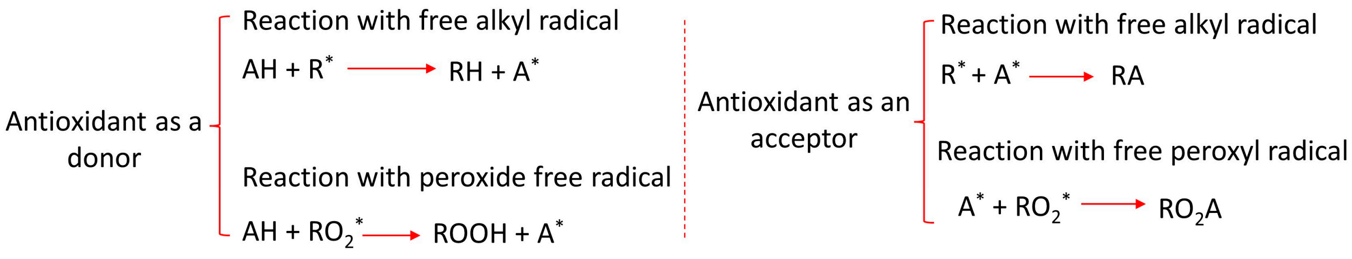


Figure 7. Reaction between antioxidant and the free radicals in the oil.

Over the decades, butylated hydroxytoluene (BTH) has been the main choice of manufacturers, because it increases the melting point and oxidative stability of insulating oil [61–63]. It is reported that despite the addition of this antioxidant to natural esters, the oxidative stability is still below that of mineral oil [9]. Researchers also utilized the tertiary butyl hydroxyquinone (TBHQ) as an antioxidant additive in alkyl esters. As reported, the choice of TBHQ was based on the fact that ester treated with TBHQ has less susceptibility to oxidation relative to butylated hydroxytoluene (BHT), butylated hydroxy anisole (BHA), and propyl gallate (PrG) α—tocopherols [42,64,65]. It is important to optimize the antioxidant loading, because excessive antioxidants can affect the quality of the base liquid. The optimization of TBHQ on palm kernel-based liquid was achieved in [13] by varying the percentage loading from 1 wt.% to 5 wt.%. It is reported that the optimum performance at 4 wt.% was observed when the alkyl ester was doped with TBHQ before epoxidation. In the same vein, a 3 wt.% optimum concentration was recorded for the epoxidized and side-branched alkyl esters. This is an indication that the antioxidant was able to protect the oxidative degradation of the long and branched carbon chains against much higher temperatures. In [66], the effect of different loading of antioxidants (BHT) on mineral oil, sunflower, and rapeseed oil was observed. Viscosity, AC breakdown analysis, dielectric dissipation factor, and partial discharge tests were used as factors for analyzing the rate of oxidation between inhibited and uninhibited samples. The sample preparation was achieved through the addition of a 0.25%, 0.3%, and 0.35% weight concentration into the base liquid, and copper metal was added to the glass vessel as a catalyst. An increase in the acidity of the uninhibited sample was observed, which was attributed to the oxidation products. This, consequently, increases the dielectric loss and decreases the breakdown voltage. The properties of the natural ester with inhibitors are moderately higher than base liquids, with an outstanding performance in sunflower oil apart from the viscosity value [66].

Several researchers have tried a mixture of different antioxidants, and the report showed a promising property [67,68]. The oxidation stability of rapeseed oil was enhanced in [68] through additive optimization using a two-level factorial design. Propyl gallate and citric acid were used as an antioxidant; the choice of selecting propyl gallate and citric acid was related to radical scavenging and hydroperoxide scavenging, respectively. The loading of equal proportion of antioxidants (0.25 wt%) gave an optimum performance based on the average oxidation induction time. The work reported in [67] also confirmed the possibility of mixing antioxidants for the oxidation stability enhancement of natural esters. A 0.3 wt.% of T501 (2, 6-ditert-butyl-4-methylphenol) and a 0.3 wt.% of L06 (high purity alkylation-α- naphthylamine) were mixed with natural ester liquid, and an increase in the oxidation onset temperature was reported. The effect of the addition of antioxidants on other properties, especially the dielectric properties of transformer insulating oil, also needs a proper inspection.

The effect of antioxidants on the dielectric properties of natural ester insulating liquid has been explored, and it was reported that antioxidants enhance the AC dielectric strength of the liquid as well as some physical properties such as viscosity, fire point, and flash point [11]. The improvement in the dielectric strength is attributed to the nature of the antioxidants being mono-aromatic compounds. It is proved beyond a reasonable doubt that mono-aromatic compounds enhance the dielectric strength of natural ester insulating liquid and give a low partial discharge, since they could enhance gas absorption under electrical stress [49,69–71]. In this regard, it may be concluded from the previous research that the enhancement of the oxidative stability of natural esters can be achieved by antioxidants without any pronounced negative effect on the electrical properties of the base liquid.

5.3. Electronic Scavengers

The challenges of natural esters' poor ionizing potential have been addressed using some additives such as dimethylaniline and azobenzene, which showed an improvement in streamer propagation and impulse breakdown [11]. Table 3 shows a summary of previous additives used on natural esters. Additives with low ionization potential and low first excitation energy are desired for proper enhancement of the base liquids. It was hypothetically stated that the streamer propagation and the impulse breakdown strength were increased due to the difference in ionization potential and the first excitation energy values that occur between the additive and the dielectric liquid [72]. Despite this outstanding enhancement, it is important to notice that the addition of low-ionization potential additives affects other properties of the insulating oil. Further, it is to be noted that some types of additives are toxic and highly harmful to humans and the environment [73].

It is highly imperative to seek another means of curbing the menace of poor ionizing potential using an environmentally friendly material. An attempt to mitigate this effect is considered in the next section of this paper.

Table 3. Some additives used in the literature and their effect on natural esters.

Reference	Additives	Factors	Percentage Increment
Unge et. al., 2013 [74]	dimethylaniline (DMA) (1 wt%)	Breakdown voltage and acceleration voltage	32% and 90%, respectively
Unge, et. al., 2013 [75]	dimethylaniline, azobenzene (5 wt.%)	Acceleration voltage	40%
Liang, et. al., 2019 [76]	(i) 4ethoxycarbonylphenyl-n-methyl-n-phenylformamidine, (ii) 2-(4′-diethylamino-2′-hydroxybenzoyl) benzoic acid hexyl ester (5wt.%)	Light impulse voltage and AC breakdown strength	(i) 15% and 60%, 17% respectively (ii) 4.7% and 18.4%.

5.4. Role of Nanoparticles

5.4.1. Development of a Nanofluid

The fundamental application of nanotechnology has shed more light on the field of dielectric engineering regarding the enhancement of dielectric properties of insulators used in transformer insulation systems with nanoparticles. The word nanofluid is commonly used when a nano-sized material (particles less than 100 nm) is mixed with a base liquid [77]. Nanofluid is a two-phase mixture generally used as a heat transfer liquid when a small fraction of nanomaterials is suspended in a conventional heat transfer liquid such as water, mineral oil, ethylene glycol, etc. [78]. The reason for adding nanoparticles to the liquid is to increase the heat transfer and electrical properties of the insulating oil. Several kinds of research exist in the literature about the enhancement of thermophysical properties of insulating liquids using nanoparticles [77]. In [79], graphene oxide (GO) and titanium oxide (TiO_2) nanoparticles were used to enhance the thermophysical properties of natural and synthetic esters, and it was reported that there was an enhancement in the thermal conductivity of the oil. GO nanoparticles showed the maximum performance by increasing the thermal conductivity of the base liquid by 3.77% at 0.05 wt% loading. Further, in [35], recent research conducted on the effect of two different nanoparticles, tungsten oxide and silicon oxide, reported that the nanoparticles had no negative effect on the thermal properties of natural ester. In [80], the report made on the addition of Cu nanoparticles or carbon nanotubes to ethylene glycol and oil showed an increase in thermal conductivity by 40% and 150%, respectively. Both experimental and theoretical predictions have been used to determine the effect of nanoparticles on the thermal properties of insulating oil, and these have been promising [81]. On the electrical properties of insulating oil, over 100 scientific publications reported an enhancement in the dielectric properties of both mineral oil and natural ester liquids. In [82], nanoparticles increased the trap density and reduced the velocity of streamer propagation in mineral- and vegetable-based insulating liquids. The addition of nanoparticles to insulating liquids at a specific concentration enhanced the breakdown, dielectric loss, and dielectric constant [29,47,78,83,84]. However, it is important to know that despite the current level of research on nanofluids for transformer insulation, a nanoparticle with the ultimate performance has not been pronounced. Therefore, it is important to continue research for the best-performing nanoparticles.

Nanofluid preparation is performed in two different ways, viz., a single-step method and a two-step method [30,78–80]. The single-step method has been reported to be the best method for the preparation of stable nanofluid, because the nanoparticle is simultaneously prepared with the base liquid without passing through the stage of vaporization drying, storage, and transportation [80]. However, the cost of achieving this process is high, which has rendered it ineffective for researchers. Further, the leftover reactant in the nanofluid due to an incomplete reaction makes it difficult to categorically predict the effect of the nanoparticle on the base liquid [80]. The two-step method, on the other hand, is cost-friendly, but the stability of the nanofluid is not as precise as in the one-step method, because many processes are involved, and particle agglomeration is inevitable. In this method, the nanoparticle is synthesized separately using physical or chemical methods before dispersion into the base liquid. The percentage stability of this method relative to the one-step method is low, but researchers still prefer this method, since it is not expensive relative to the former, and it can be produced in large quantities. For example, in [85], the dielectric properties of vegetable insulating liquids obtained from raw rapeseed were enhanced using oleic acid-coated Fe_2O_3 nanoparticles. The dried nanoparticles were dispersed in the oil at 0.004% and agitated for 20 min. The enhancement in the breakdown voltage was reported to be 19.8%. Enhancement in both positive and negative lightning impulse breakdown voltage was attributed to the trapping of free electrons through the polarization mechanism.

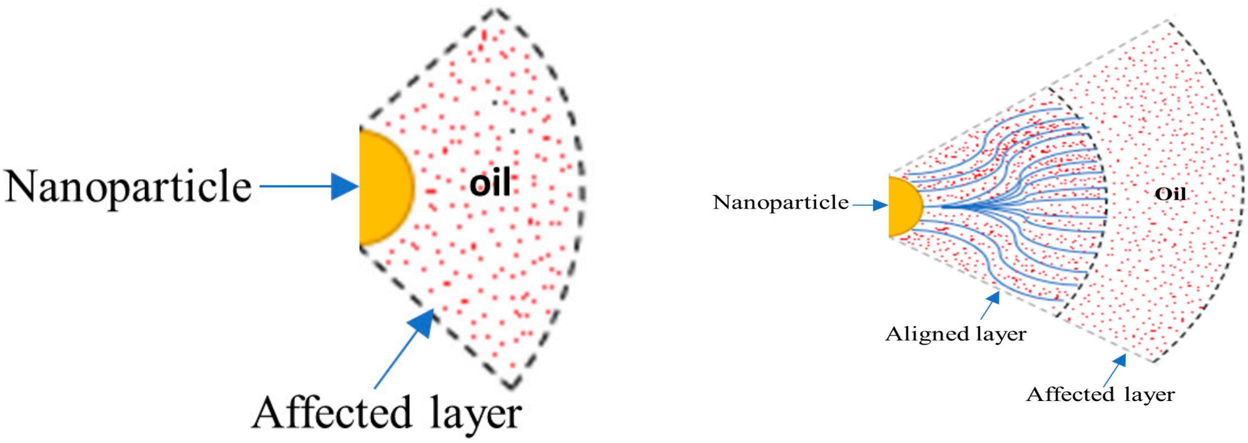
The effect of nanoparticles (TiO_2 and ZnO) on vegetable-based liquid was studied and reported in [86]. Since nanofluid is intended to be used for a long time, accelerated aging of the freshly prepared nanofluid is important. The nanofluid prepared in [86] was subjected to accelerate thermal aging at 150 °C for 312 h using a sample containing a 0.04% concentration of nanoparticles. It was reported that the breakdown voltage of the nanofluid increased as the aging time increased. However, deterioration in other measured parameters was observed after aging. Important parameters of a nanofluid prepared from sunflower oil using TiO_2 nanoparticles (20–30 nm) was examined in [87]. The breakdown voltage of the oil increased as the loading of the nanoparticle increased, with an optimum performance at 0.5 kg/m^3. Further, a slight increase in the viscosity and the dielectric loss of the oil were observed. The cooling properties of the nanofluid depreciated by 3.9%. Several nanoparticles exist in the literature, and they are categorized into groups. Sidik et al. classified nanoparticles into metallic and non-metallic nanoparticles [80]. Examples of metallic nanoparticles are gold (Au), silver (Ag), and copper nanoparticles. Non-metallic nanoparticles include silica, titania, alumina, zinc oxide, etc [80]. The non-metallic nanoparticles can be further classified into conductive, semiconductive, and insulating nanoparticles [83,88,89]. Methods of synthesizing nanoparticles can be classified into two kinds, viz., physical and chemical methods [90].

5.4.2. Challenges with Nanoparticles for Transformer Oil

The addition of particles in the nano-range to insulating oil has been facing a lot of problems, especially that of sedimentation. The non-lipophilic nature of nanoparticles prevents them from suspending in the oil. When the nanoparticle settles, it affects the dielectric and thermophysical properties of the insulating oil. To obtain stability of the nanofluid for the two-step method, two different methods have been explored; these are the surface modification of nanoparticles, known as functionalization, and the addition of surfactants to the base liquid before the addition of nanoparticles.

The addition of surfactants to the base liquid enhances the contact between the solid–liquid interface by decreasing the surface tension of the base liquid. At the interface, the surfactant establishes a continuity between the solid and liquid, thereby increasing the stability of the nanoparticles in the oil [90]. However, nanofluid with surfactants might not be able to withstand high-temperature operation due to the high tendency of bond breaking, which could consequently affect the properties of the nanofluid [83].

It is worth mentioning that there is a need for proper study on the effect of different surfactants on the dielectric and thermophysical properties of base liquids. In addition, the selection of a surfactant with the highest performance and the optimization of the quantity of surfactants needed are important. An investigation of the interfacial zone effect on dielectric properties in the nanofluid was detailed in [91]. The addition of surfactants to the base liquid enhanced the dielectric properties of the nanofluid, and this can be related to the influence of the interfacial zone. It has been proposed that the interfacial zone comprises two different layers: the aligned layer and the affected layer. The structure of the interfacial zone is presented in Figure 8.



(**a**) Sample without surfactant (**b**) Sample with surfactant

Figure 8. Interfacial zone structure in oil-based nanofluid.

Selection was performed in [47] by comparing the potential of different types of surfactants: cetyl trimethyl ammonium bromide CTAB, oleic acid, and Span-80 in silica-based synthetic esters. In the report, the addition of Span 80 to the base liquid showed the best stability among other surfactants, and the result was in good agreement with the corona inception voltage, showing better properties relative to other samples with different surfactants.

Surface modification, in this approach, the compatibility between the solid and liquid, is enhanced by modifying the surface structure of the nanoparticle. The modifier is physically or chemically adsorbed on the surface of the nanoparticle. The surface force of hydroxyl groups is reduced, and the hydrogen bonds between nanoparticles are removed to avoid the development of oxygen bridge bonds, which consequently enhances stability by limiting agglomeration in the liquid [83]. Several surface modification techniques have been explored to increase the stability and miscibility of the inorganic nanoparticle. A diverse selection of molecules have been considered as coating agents, viz., lauric acid, myristic acid, trioctylphosphine oxide, dodecanethiol, tetraoctylammonium bromide, dodecyl-benzenesulfonic acid, and oleic acid [92,93]. In [94], the enhancement of natural ester using oleic acid-coated Fe_3O_4 nanoparticles was performed, and a 20% improvement in the power frequency breakdown voltage of the ester was reported. In addition, the volume resistivity and relative permittivity of nanofluid are greater than the base liquid. The potential of oleic acid-coated magnetic iron oxide nanocrystals (MIONs) and oleate-coated colloidal MIONs was explored in [92]. The nanofluid containing oleate-coated MIONs had the optimum performance (77.8 kV at 0.012%), and this can be related to the stability of the nanofluid, as it was stable even after 10 months.

Since there are different types of nanoparticles according to the band gap energy, the application of different nanoparticles according to this criterion was explored in [29]. An oleic-coated nanoparticle was reportedly stable with an enhancement in the dielectric strength of the base liquid. Oparanti et al. [46] reported the enhancement of dielectric properties of fatty acid methyl ester using semiconductive and dielectric nanoparticles. The surface modification of the nanoparticle was performed using oleic acid, and the stability was observed using visual inspection. An optimum dielectric strength was observed in an oleic-Al_2O_3 nanofluid. The application of nanoparticles in enhancing the thermophysical and electrical properties of the base liquid has been positively reported. However, several issues hindering the usage of nanoparticles should be addressed, viz., the cost of production, the selection of nanoparticles, and the optimization of surfactants and nanoparticles.

5.4.3. Nanoparticles as Additives

Impact on Viscosity

Several reports on nanofluids show that the addition of nanoparticles to the base liquid has a negligible effect, and the viscosity of nanofluids decreases as the temperature increases. As the temperature increases, the frictional force that exists between the layer of nanofluids decreases, which consequently reduces the viscosity. The work in [95] investigated the effect of three types of nanoparticles on palm fatty acid esters, which was compared with mineral oil. The viscosity of PFAE oil was better relative to mineral oil, and the percentage difference between the PFAE nanofluids and the base liquid was less than 0.5%, which indicated an insignificant effect of the nanoparticle on the oil viscosity. A different percentage loading of nanoparticles to the base oil is always performed to optimize the performance of the nanoparticle; therefore, it is also important to investigate this effect on viscosity. The effect of nanoparticles on the base liquid was investigated in [96,97], and an increase in the concentration of nanoparticles increased the viscosity of the nanofluid. The effect of loading different types of nanoparticles was investigated in [98] by doping soybean esters and palm esters with TiO_2 and ZnO nanoparticles. The effect of nanoparticles on the viscosity of the base liquid was negligible, and the viscosity of the nanofluid decreased as the temperature increased.

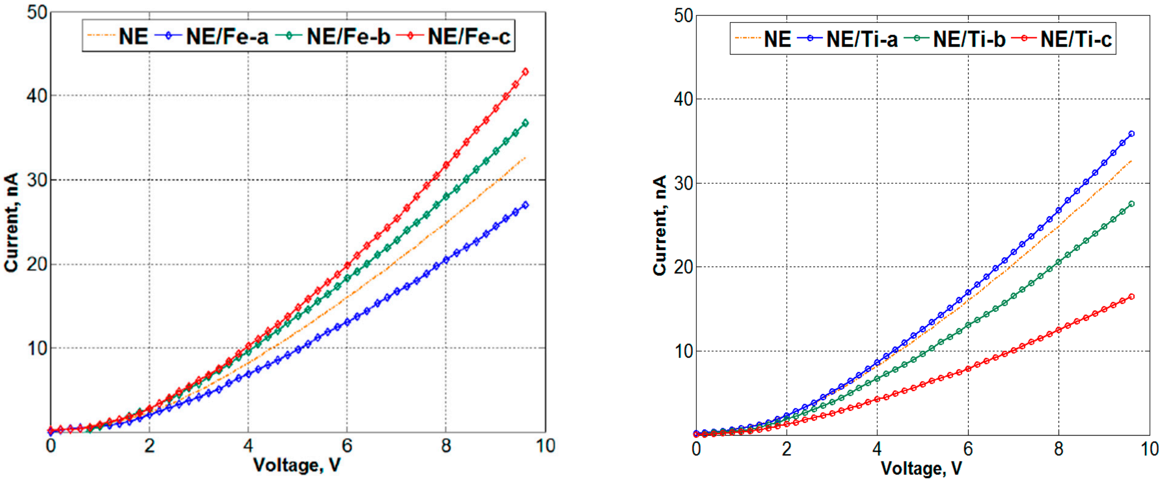
An experimental investigation on methyl ester from nonedible vegetable oil using SiO_2 and WO_3 nanoparticles was reported in [35]. The report showed a progressive increase in viscosity as the loading of nanoparticles increased, with a high percentage increment in WO_3 nanofluid. According to the report, at a 1 wt% loading of both nanoparticles, the viscosity of neem oil ester increased from 5.17 mPa.s to 5.55 mPa.s and 5.37 mPa.s for WO_3 and SiO_2 nanoparticles. respectively. The report made by Fernández et al. [89] also showed that the addition of TiO_2 and ZnO nanoparticles increased the viscosity of the base liquid. Analyzing the previous report on the effect of nanoparticles on the base liquids, it can be concluded that nanoparticles increase the viscosity of the base liquid with a relatively insignificant value.

Impact on Ionization Resistance

The poor ionization rate of natural esters has been a hindrance to the applications of natural esters; however, the application of nanoparticles to this oil has proven to be a positive enhancement on the ionization rate of the esters. Ionization rates can be related to a leakage current in the insulating oil. The molecules of the oil close to the electrode become ionized when a sufficient amount of energy is supplied through the electrode. At this point, more ions and electrons are created due to collision, which consequently forms a conductive path known as a streamer. The streamers become elongated and extend from the point of higher potential to the ground electrode, which is the lowest potential. This, in turn, forms a short circuit or bridge between the electrodes, which consequently leads to a breakdown [29]. The addition of nanoparticles has been reported to be a scavenger of electrons in an insulating liquid. It was reported in [29] that the aligned layers (Figure 8b) in the nanofluid created a rigid intermolecular structure that reduced electron and ion mobility, leading to a decrease in the conduction current, as seen in Figure 9a,b. The increase in the breakdown voltage and decrease in the dielectric loss of a nanofluid can be related to rigid intermolecular forces, which require sufficient energy to dissociate [29].

The AC breakdown of palm fatty acid ester nanofluid was studied using Fe_3O_4, TiO_2, and Al_2O_3 [95]. The conductive nanoparticles in the base liquid acted as an electron scavenger when the oil was subjected to electrical stress, and semiconductive nanoparticles produced shallow electron traps in the liquid, which captured the fast-moving electrons and converted them into slower electrons through the process of trapping and de-trapping [95]. This is an indication that the conversion of the fast-moving electron into a slower one caused the streamer process to take a longer time to break down under electrical stress. In another report, a decrease in the leakage current was observed after loading semiconductive and insulating nanoparticles into palm kernel oil methyl ester except for 1 wt% of Al_2O_3

nanoparticles [46,99]. The decrease in the leakage current could be attributed to the trapping and de-trapping of electrons and ions in the oil. Further, Jacob et al. reported that Al_2O_3 nanoparticles enhanced the breakdown properties of natural esters at 0.02 wt% and related the enhancement to trapping and de-trapping of mobile electrons and ions in the oil [100].



(**a**) (**b**)

Figure 9. Current–voltage curve for natural ester containing (**a**) conductive and (**b**) semiconductive nanoparticles [29].

The fundamentals and the theory behind the reduction in streamer propagation in insulating oil by nanoparticles have not been fully understood, especially in classical theory. The polarization and surface charge mechanism was proposed by Hwang et al. when they used Fe_3O_4 nanoparticles to enhance the insulating properties of the oil; a structural illustration can be found in [101]. A decrease in positive streamer velocity was reported, which was attributed to electron trapping by nanoparticles. The report revealed that fast-moving electrons that were generated through field ionization were converted into a slow-moving negative charge carrier by the influence of the nanoparticles [101]. This was theoretically addressed using the concept of charge relaxation time shown in Equation (4):

$$\tau = \frac{2\varepsilon_1 + \varepsilon_2}{2\sigma_1 + 2\sigma_2} \tag{4}$$

where τ is the relaxation time, ε_1 is the permittivity of mineral oil, ε_2 is the permittivity of nanoparticles, σ_1 is the dc conductivity of mineral oil, and σ_2 is the dc conductivity of nanoparticles [78,88]. In this theory, relaxation time is a determining factor. If the relaxation time of the nanoparticle is shorter than the time of development of streamers in the transformer oil, the nanoparticle will easily capture fast-moving electrons on its surface [102]. The nanoparticles are polarized and convert fast-moving electrons into a slow, negatively charged carrier. However, if the streamer development time scale is shorter than the relaxation time of the nanoparticle, the effect of the nanoparticles on the high-electron mobility will be minimal [78,101]. Further studies on the effect of nanoparticles on insulating oils showed the limitation of polarization and surface charge mechanisms. The reason that SiC mineral oil nanofluid had a decrease in the breakdown voltage value relative to the base oil despite the relaxation time constant of SiC being much shorter than the time scale of the streamer development in mineral oil was not explained [103]. In addition, the reason for the increase in the breakdown strength of the nanofluid prepared with nanoparticles (TiO_2) having a relaxation time longer than the timescale of streamer growth in mineral oil also could not be explained [103–106].

It is evident from previous research [29,100] that the addition of nanoparticles to natural esters at a certain percentage can reduce the conduction current and streamer generation in the oil. This can be attributed to the trapping of the electrons that would have caused the ionization of the neighboring molecules.

Impact on Pour Point

The pour point of vegetable-based liquid is high relative to mineral oil, and its application in an extremely low-temperature region might be challenging. Reports on the pour points of nanofluids using natural esters as the base liquid have been made in the literature, and the results are contradictory and do not follow the same trend. The effect of nanoparticles on the pour point of pongamia oil methyl ester (POME) was investigated in [107] with a 0.01 wt% of exfoliated hexagonal boron nitride (Eh-BN). The pour point of the mineral oil and POME decreased with the addition of a 0.01 wt.% exfoliated hexagonal boron nitride (Eh-BN), and this could be attributed to molecular interaction between Eh-BN and the oil. The reason for the decrease in the pour point value of the nanofluid could be attributed to the nano-dimensional scale of Eh-BN and high intermolecular interaction, which prevents the formation of wax crystals in the oil through dispersing the few crystals in the oil [107]. On the other hand, the report on non-edible methyl ester from neem oil by [35] revealed a slight increase in the pour point after dispersing SiO_2 and WO_3 nanoparticles. The size and shape of the nanoparticle can affect the physical properties of the base liquid, especially the pour point. The effect of the particle was investigated in [35], and the authors revealed that nanoparticles with a small size could easily be attached to the molecules of the oil and reduce the crystallization rate. Ahmadi et al. reported on the effect of CuO nanoparticles on lubricants. It was reported that the addition of CuO nanoparticles to the base oil increased the pour point at both 0.1 wt% and 0.5 wt% loading of the nanoparticles [108]. The effect of combined nanoparticles on soybean and mineral oil was analyzed in [109]. It was reported that the pour point of soybean nanofluid before aging was higher than the pour point of mineral oil and had the same value as mineral oil after aging. Though the pour point of mineral oil and soybean nanofluid was not within the recommended value, the addition of composite nanoparticles (aluminum and zinc oxide) to sunflower and olive oil had a pour point somewhat near to the recommended level.

Impact on Oxidation

The poor thermo-oxidative stability of natural ester is a setback that needs urgent attention if the liquid is to be used in free-breathing transformers. However, natural esters have been successfully used in distribution transformers for decades. Chemical modification and the addition of antioxidants have been performed, but little research exists in the literature regarding the oxidation stability of nanofluid from vegetable-based insulating liquids. Recently, it was reported in [110] that the dispersion of titanium oxide nanoparticles and graphite carbon nitrides (TiO_2/gC_3N_4) increased the oxidation stability of vegetable oil. The thermogravimetric curve of the base liquid in [110] showed an onset of oxidation at 128 °C, and the prepared nano-oil had an onset of oxidation at 165 °C. The nano additives acted as an inhibitor that slowed down the rate of reaction and improved the thermal stability of the nano-oil. In [107], nanoparticles from eggshell were used to enhance the oxidation stability of rice bran oil. The thermal stability of the base liquid was enhanced by 18.2% and 25% through the addition of 0.25 wt% and 0.5 wt% of CaO nanoparticles [111].

6. Conclusions

Research over the decades has revealed the potential of vegetable-based insulating liquids for transformers with promising results. Many applications around the globe are now rapidly adopting the use of natural ester liquid, especially in distribution transformers. With this progress and further research work, there is a bright future for the general acceptability of vegetable-based insulating liquids as an insulating liquid in both distribution and power transformers. However, it is highly imperative to further explore how to resolve the associated problem mentioned in the previous section before the liquid is generally accepted. In addition, in a situation in which additives are employed as an enhancer, it is important to consider the environmental friendliness of the additives, the long-term behavior of the additives, and the compatibility of the additives with other insulating materials in the transformer. The application of nanoparticles is still a wide field of research that needs proper attention, because the choice of nanoparticle, shape, and size are still critical challenges in nanofluids for transformer insulation. Moreover, the stability and aging of the nanofluid need to be properly addressed. Vegetable-based insulating liquids have the potential of replacing mineral insulating oil when both the physical and electrical properties are successfully enhanced.

The application of nanotechnology in the enhancement of thermophysical and electrical properties of natural esters has brought great hope for the successful application of ester-based nanofluids in high-voltage insulation. The addition of different kinds of nanoparticles into natural esters has shown an improvement in some of the problems hindering the application of natural esters, such as the ionization rate and oxidative stability. However, present research in the literature on ester insulating nanofluid is not sufficient or consistent. For example, there are some reports in which the addition of nanoparticles to a base liquid had both negative and positive effects simultaneously on the properties of the oil. In the report by Fernandez et al. [89], the acidity of the base liquid increased after the addition of TiO_2 and ZnO nanoparticles to the base. In the same vein, the report by Asse et al. also showed an increase in the acidity of the base liquid after the addition of FeO_3 nanoparticles [112]. The increase in the acidity of the base liquid is an undesired enhancement and is detrimental to the life of the transformer, as it increases the conductivity of the oil and the rate of aging of the transformer insulation system. Therefore, there is still a need for proper investigation on nanofluids regarding the optimization of nanofillers for optimum performance. Further, all the physical, chemical, thermal, and electrical properties of the synthesized ester-based nanofluid need to exhibit a balance for effective performance before consideration for use in power equipment. In addition, there is a great need for proper investigation of the stability of the nanofluid before its wide application. In the area of transformer design, a proper study is needed. Since the existing transformer is not configured for nanofluid, there might be a need for a design modification.

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