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Amélioration de la stabilité à l'oxydation des esters naturels par l'ajout d'antioxydants à l'aide d'une analyse statistique multi-réponses pour les applications dans les transformateurs

Par

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RÉSUMÉ

Le fonctionnement fiable des transformateurs de puissance dépend en grande partie de leur système d'isolation électrique (solide/liquide). Pendant longtemps, l'huile minérale, un fluide dérivé du pétrole, a été utilisée comme liquide isolant. Cependant, en raison de ses inconvénients environnementaux et de son inflammabilité, l'attention s'est progressivement tournée vers les huiles esters naturelles en tant qu'alternatives durables. Bien que les esters naturels présentent un fort potentiel, ils posent encore d'importants défis qui freinent leur adoption généralisée dans les équipements à haute tension remplis de liquide. Parmi ces défis, la stabilité à l'oxydation de ces liquides, principalement liée à leur composition en acides gras, est la plus préoccupante. Pour surmonter cette limitation et améliorer la stabilité à l'oxydation, divers antioxydants ont été étudiés.

Afin de contribuer à l'avancement des connaissances dans ce domaine, deux antioxydants (l'acide citrique et le tert-butylhydroquinone (THBQ)) ont été introduits dans deux liquides isolants à base d'esters naturels distincts. Ces échantillons ont ensuite été soumis à des tests de stabilité à l'oxydation et de vieillissement thermique accéléré pour évaluer la compatibilité entre les esters et les additifs antioxydants. Une méthodologie de réponse basée sur un plan factoriel complet a été utilisée pour déterminer la concentration optimale des mélanges d'antioxydants. Les principaux paramètres de réponse analysés étaient le facteur de dissipation, la viscosité et l'acidité.

Les résultats, évalués par une analyse de la variance (ANOVA), ont révélé que la combinaison de 0,2 % en poids de THBQ et d'acide citrique offrait la meilleure stabilité à l'oxydation pour l'Ester Naturel 1 (NE1), tandis que 0,2 % de THBQ et 0,15 % d'acide citrique étaient les plus efficaces pour l'Ester Naturel 2 (NE2). Ces conditions optimales ont été appliquées dans le cadre du test de vieillissement thermique accéléré, et les résultats ont démontré que les échantillons traités avec des antioxydants présentaient des améliorations significatives en matière de stabilité. Cette étude apporte des informations précieuses sur le rôle des antioxydants dans l'amélioration de la stabilité à l'oxydation des esters naturels, offrant ainsi des perspectives prometteuses pour leur utilisation dans les systèmes de transformateurs de puissance.

ABSTRACT

The reliable operation of power transformers largely depends on their electrical insulation system (solid/liquid). The liquid insulation for long has been the mineral oil, a petroleum-based fluid. However, due to its environmental drawbacks and flammability, attention has increasingly shifted toward natural ester oils as sustainable alternatives. While natural esters show great promise, they still possess significant challenges which represent the primary barriers to their widespread adoption in liquid-filled high-voltage equipment. Among these challenges, the most prominent is the oxidation stability of this liquid, which can be attributed to its fatty acid composition. To address this limitation and improve oxidation stability, various antioxidants have been explored. To contribute the advancement of knowledge in this field, antioxidants (Citric acid and Tert-butylhydroquinone (THBQ) were introduced into two distinct natural ester insulating liquids. This was further subjected to oxidation stability test and accelerated thermal aging in order to understand the compatibility between the esters and antioxidant additives. A full factorial design response methodology was employed to determine the optimal concentration of the antioxidant mixtures. The primary response parameters analyzed were dissipation factor, viscosity, and acidity.

The results assessed by analysis of variance (ANOVA), revealed that the combination of 0.2 wt.% THBQ and CA yielded the best oxidative stability in Natural Ester 1 (NE1), while 0.2 wt.% THBQ and 0.15 wt.% CA proved most effective for Natural Ester 2 (NE2). These optimal conditions were applied in the case of the accelerated thermal aging test and the results demonstrated that the antioxidant-treated samples showed significant improvements in stability. This study provides valuable information into the role of antioxidants in enhancing the oxidation stability of natural esters, offering promising advancements for their application in power transformer systems.

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NE1: Ester naturel 1
NE2 : Ester naturel 2
TBHQ: Tert-butylhydroquinone
CA : Acide citrique
LMA: Acides de faible poids moléculaire (Low Molecular Weight Acids)
HMA : Acides de haut poids moléculaire (High Molecular Weight Acids)
CIGRE: Conseil International des Grands Réseaux Électriques
IUPAC: Union Internationale de Chimie Pure et Appliquée
ROS: Espèces réactives de l'oxygène (Reactive Oxygen Species)
HAT : Transfert d'atome d'hydrogène
IEC: Commission Électrotechnique Internationale
FFAs : Acides gras libres
UN: Organisation des Nations Unies (United Nations)
DF : Facteur de dissipation
ROS : Espèces réactives de l'oxygène (Reactive Oxygen Species)
HAT : Transfert d'atome d'hydrogène (Hydrogen Atom Transfer)
SET : Transfert d'un seul électron (Single Electron Transfer)
OIT : Temps d'induction d'oxydation
ORAC : Capacité d'absorption des radicaux oxygénés
ppm: Parties par million
wt. % : Pourcentage en masse (% m/m)
GC-MS: Chromatographie en phase gazeuse–spectrométrie de masse
DAG : Glycérol diacétylé
BHT : Hydroxytoluène butylé
HORAC : Capacité d'annulation des radicaux hydroxyles
TRAP : Paramètre total de piégeage des radicaux libres
FRAP : Réduction ferrique du pouvoir antioxydant
CUPRAC : Capacité antioxydante cuprique
ASTM : Société Américaine pour les essais et les matériaux
RBOT: Test d'oxydation à la bombe rotative
TOST : Test de stabilité à l'oxydation de l'huile pour turbine
DSC : Calorimétrie différentielle à balayage
NMR : Résonance magnétique nucléaire
BHA: Butylated hydroxy anisole
DOE: Design of experiments
RSM: Response surface methodology
ANOVA: Analyse de la variance
AI: Intelligence artificielle
FTIR : Spectroscopie Infrarouge à Transformée de Fourier
CNN: Convolutional neural network
CIGRÉ: Conseil International des Grands Réseaux Électriques

DÉDICACE

Cette thèse est dédiée
à Dieu, à mon époux et à ma famille

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Je souhaite exprimer ma plus profonde gratitude à mon directeur de recherche, le professeur Issouf Fofana, pour m'avoir offert cette opportunité exceptionnelle, m'avoir accueillie au sein de son équipe de recherche et m'avoir apporté un soutien financier tout au long de ce parcours.

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CHAPITRE 1

INTRODUCTION GÉNÉRALE

1.1 INTRODUCTION

Le transformateur de puissance joue un rôle essentiel dans le réseau électrique. Il constitue l'équipement principal responsable de la production, du transport, de la transformation et de la distribution de l'électricité. Pour que les transformateurs fonctionnent de manière fiable tout au long de leur durée de vie, sous des conditions variables de température et de charge, une isolation adéquate est indispensable [1, 2]. Le transformateur est constitué de deux principaux types d'isolation : le papier isolant à base de cellulose et l'huile isolante liquide. L'huile joue un double rôle dans le transformateur, à la fois comme isolant et comme agent de refroidissement. Par conséquent, l'efficacité du transformateur dépend fortement de la qualité de l'huile isolante.

Depuis plus d'un siècle, l'huile minérale, dérivée du pétrole, est le liquide isolant le plus largement utilisé dans les transformateurs de puissance. Elle est reconnue pour améliorer la rigidité diélectrique du système d'isolation tout en agissant comme fluide caloporteur, en dissipant la chaleur générée au niveau du noyau et des enroulements du transformateur [3]. Malgré ses avantages tels que son faible coût et la facilité de production en masse, l'huile minérale présente certaines limites importantes, notamment sa non-biodégradabilité, sa forte inflammabilité et sa toxicité. De plus, la transition mondiale vers des sources d'énergie durables et respectueuses de l'environnement a renforcé la recherche de liquides isolants alternatifs dérivés de ressources renouvelables telles que les huiles végétales [4, 5].

Natural esters, developed in the early 1990s, are derived from various oil crop plants such as neem seed, jatropha, peanut, soybean, rapeseed, palm, and so many others. They are comprised of a complex mixture of fatty acids that fundamentally define their properties. Les esters naturels, développés au début des années 1990, sont issus de diverses plantes oléagineuses telles que les graines de neem, le jatropha, l'arachide, le soja, le colza, le palmier à huile, et bien d'autres. Ils sont composés d'un mélange complexe d'acides gras, qui déterminent fondamentalement leurs propriétés. Ces acides gras peuvent être classés en trois catégories : saturés, monoinsaturés et polyinsaturés [6]. Il est important de noter que les propriétés chimiques et physiques de ces huiles d'esters naturels sont principalement influencées par la composition de leurs acides gras. Elles sont largement reconnues pour leur faible toxicité, leur biodégradabilité élevée, leur grande sécurité au feu et leur bonne capacité d'absorption de l'humidité. Toutefois, elles ne sont pas exemptes de contraintes. Certaines caractéristiques insuffisantes, telles que la faible stabilité à l'oxydation, la mauvaise viscosité et les performances médiocres à basse température, limitent leur application dans les transformateurs à respiration libre [7].

La stabilité à l'oxydation constitue une préoccupation majeure pour tout fluide diélectrique. Elle est jugée faible dans le cas des diélectriques à base d'esters naturels. Les variations dans la composition en acides gras expliquent les différences observées en matière de stabilité à l'oxydation. De la saturation à la polyinsaturation, la présence d'un pourcentage élevé de doubles liaisons dans les triglycérides insaturés rend les esters naturels plus sensibles aux réactions d'oxydation [8]. L'application des esters naturels dans les transformateurs de puissance reste un défi pour les chercheurs, principalement en raison de leur faible stabilité à l'oxydation et de la formation de sous-produits indésirables durant le processus d'oxydation, tels que les acides, les aldéhydes et les cétones [9] . Ces sous-produits d'oxydation peuvent entraîner une augmentation de la viscosité et de la conductivité de l'huile, et accroître ainsi le risque de défaillance diélectrique [10].

Diverses avancées ont été développées pour faire face aux défis liés à l'utilisation des huiles à base d'esters naturels, en particulier leur faible stabilité à l'oxydation. Parmi celles-ci figurent la modification chimique de leur structure moléculaire, les améliorations de formulation, et surtout, l'introduction d'antioxydants, qui jouent un rôle clé dans l'amélioration de la résistance à l'oxydation et dans la prolongation de la durée de vie opérationnelle des fluides diélectriques à base d'esters [10].

1.2 PROBLÉMATIQUE

Le besoin croissant en sources d'énergie écologiques et durables est devenu une tendance dominante. Dans le secteur de l'énergie, on observe une adoption rapide des esters naturels comme liquides isolants, une stratégie visant à réduire l'impact environnemental des hydrocarbures sur le climat. Ces huiles isolantes à base d'esters naturels, issues de plantes et caractérisées par des compositions spécifiques en acides gras, sont proposées comme alternatives aux huiles minérales.

Cependant, en raison de la forte teneur en acides gras insaturés dans les esters naturels, ceux-ci présentent une susceptibilité plus élevée à l'oxydation comparativement aux huiles minérales. Parmi les produits de cette oxydation figurent les acides et l'humidité, qui jouent un rôle majeur dans la dégradation des systèmes d'isolation. Le taux de dégradation induit par l'oxydation peut toutefois être réduit grâce à l'ajout d'antioxydants.

Dans la littérature, plusieurs antioxydants ont été étudiés pour améliorer les performances des esters naturels. Toutefois, aucun d'entre eux n'a démontré une stabilité équivalente à celle des huiles minérales.

Ainsi, l'amélioration de la stabilité à l'oxydation des esters naturels représente une lacune importante dans les connaissances actuelles. La présente étude vise à évaluer la possibilité d'améliorer deux huiles d'esters naturels distinctes (NE1 et NE2), chacune caractérisée par un profil unique en acides gras, par l'utilisation combinée du tert-butylhydroquinone (TBHQ) et de l'acide citrique (CA), dans des conditions d'oxydation accélérée.

1.3 OBJECTIFS DE LA RECHERCHE

L'objectif principal de ce travail est d'améliorer la stabilité à l'oxydation de deux esters naturels distincts par l'ajout de différents antioxydants, à l'aide de techniques statistiques. Plus précisément, l'étude vise à :

I. Améliorer la stabilité à l'oxydation et les performances des huiles d'esters naturels par l'intégration et l'évaluation d'antioxydants.
II. Évaluer et comprendre la compatibilité entre l'huile et les antioxydants sur le long terme à travers un vieillissement thermique accéléré.

1.4 ORIGINALITÉ DE LA RECHERCHE

L'originalité de cette recherche réside dans son approche novatrice et systématique visant à optimiser la charge en antioxydants en fonction de la composition spécifique en acides gras des huiles de base à base d'esters naturels, un aspect largement négligé dans la littérature scientifique. Bien que de nombreuses études aient exploré l'utilisation d'antioxydants pour atténuer la dégradation oxydative des esters naturels, peu, voire aucune, n'a procédé à une optimisation systématique des concentrations d'antioxydants tout en tenant compte du profil en acides gras de l'huile de base.

De plus, les études existantes appliquent généralement des concentrations fixes ou n'adoptent pas une démarche rigoureuse d'optimisation. À ce jour, aucune recherche n'a étudié de manière approfondie comment les variations dans les profils en acides gras influencent le comportement synergique et l'efficacité des systèmes antioxydants. Cela représente une lacune critique dans la littérature, puisque différents esters naturels peuvent réagir de manière distincte aux traitements antioxydants selon leur composition chimique propre.

Cette recherche répond directement à cette lacune en combinant deux antioxydants et en appliquant un plan d'expériences statistique (plan factoriel complet) pour déterminer leurs concentrations optimales sur deux huiles d'esters naturels présentant des compositions en acides gras différentes. En adaptant les stratégies antioxydantes à la structure moléculaire de l'huile de base, cette étude propose une approche plus ciblée et plus efficace pour l'optimisation des antioxydants.

Les résultats de cette recherche sont particulièrement pertinents pour le développement de liquides isolants à haute performance et respectueux de l'environnement pour les transformateurs de puissance. L'amélioration de la stabilité et de la durée de vie des huiles isolantes à base d'esters naturels permet non seulement d'accroître la fiabilité et la sécurité des équipements électriques, mais aussi de soutenir la transition vers des alternatives durables et biodégradables dans le secteur de l'énergie.

1.5 ORGANISATION DE LA THÈSE

Cette thèse, rédigée selon le format « thèse par publication », est structurée en quatre chapitres.

Le premier chapitre présente une vue d'ensemble du projet, en exposant la problématique de recherche, les objectifs visés, la nouveauté de l'étude, ainsi que l'approche méthodologique adoptée pour la réalisation du projet.

Le deuxième chapitre, consacré à la revue de la littérature, aborde plusieurs thématiques clés liées à ce travail. Il traite notamment de la composition chimique des esters naturels en lien avec leur stabilité à l'oxydation, des antioxydants, de leur classification et de leur influence sur diverses propriétés des liquides isolants. Ce chapitre est présenté sous forme d'un article de revue intitulé : « Amélioration des performances des liquides isolants à base d'esters naturels dans les transformateurs de puissance : une revue complète sur les additifs antioxydants pour une meilleure stabilité à l'oxydation ».

Le troisième chapitre (Expériences et méthodes) décrit les matériaux, les méthodes, les pratiques expérimentales employées, les résultats obtenus ainsi que leur interprétation. Il est présenté sous forme d'un article intitulé : « Amélioration de la stabilité à l'oxydation des esters naturels : une approche d'analyse statistique multi-réponses ».

Le quatrième chapitre présente la conclusion générale de la thèse et formule des recommandations pour des recherches futures en vue d'approfondir ce domaine d'étude

CHAPTER 2

REVUE DE LITTÉRATURE

ENHANCING THE PERFORMANCE OF NATURAL ESTER INSULATING LIQUIDS IN POWER TRANSFORMERS: A COMPREHENSIVE REVIEW ON ANTIOXIDANT ADDITIVES FOR IMPROVED OXIDATION STABILITY

TITRE: Amélioration des performances des liquides isolants à base d'esters naturels dans les transformateurs de puissance : une revue complète des additifs antioxydants pour une meilleure stabilité à l'oxydation.

JOURNAL : MDPI ENERGIES.

LES AUTEURS: E. O. Obebe, Y. Hadjadj, S. O. Oparanti and I. Fofana

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RÉSUMÉ: La fiabilité du réseau électrique est essentielle à la prospérité économique et à la qualité de vie. Les transformateurs de puissance, éléments clés des systèmes de transmission et de distribution, représentent des investissements en capital majeurs. Traditionnellement, ces équipements utilisent de l'huile minérale dérivée du pétrole comme liquide isolant. Toutefois, avec la transition mondiale vers la durabilité, les matériaux isolants renouvelables tels que les esters naturels suscitent un intérêt croissant en raison de leurs avantages environnementaux et de sécurité incendie. Ces liquides biodégradables sont appelés à remplacer les huiles à base d'hydrocarbures dans les transformateurs, en s'inscrivant dans les Objectifs de Développement Durable 7 et 13, qui visent à promouvoir l'énergie propre et l'action climatique. Malgré leurs atouts, les esters naturels présentent certaines limites dans les applications à haute tension, notamment en raison de leur faible stabilité à l'oxydation, liée à leur composition en acides gras. Divers antioxydants ont été étudiés pour remédier à cette problématique, les antioxydants synthétiques s'avérant généralement plus efficaces que les naturels, en particulier à haute température. Leur meilleure stabilité thermique permet aux esters naturels de conserver leurs propriétés de refroidissement et d'isolation diélectrique, indispensables au bon fonctionnement des transformateurs. Par ailleurs, l'intégration de l'intelligence artificielle et de l'apprentissage automatique dans le développement et la surveillance des antioxydants offre une perspective innovante et prometteuse. Cette revue apporte un éclairage sur le rôle des antioxydants dans les équipements électriques à base d'esters naturels, en soutenant leur adoption à plus grande échelle et en contribuant à un avenir énergétique plus durable.

2.1 Abstract

The reliability of the electrical grid is vital to economic prosperity and quality of life. Power transformers, key components of transmission and distribution systems, represent major capital investments. Traditionally, these machines have relied on petroleum-based mineral oil as an insulating liquid. However, with a global shift toward sustainability, renewable insulating materials like natural esters are gaining attention due to their environmental and fire safety benefits. These biodegradable liquids are poised to replace hydrocarbon-based oils in transformers, aligning with Sustainable Development Goals 7 and 13 by promoting clean energy and climate action. Despite their advantages, natural esters face challenges in high-voltage applications, particularly due to oxidation stability issues linked to their fatty acid composition. Various antioxidants have been explored to address this, with synthetic antioxidants proving more effective than natural ones, especially under high-temperature conditions. Their superior thermal stability ensures that natural esters retain their cooling and dielectric properties, essential for transformer performance. Furthermore, integrating machine learning and artificial intelligence in antioxidant development and monitoring presents a transformative opportunity. This review provides insights into the role of antioxidants in natural ester-filled power equipment, supporting their broader adoption and contributing to a more sustainable energy future.

Keywords: transformer; insulating liquids; natural esters; oxidation stability; antioxidants

2.2 Introduction

Plant-extracted oils, often referred to as natural ester liquids, have found multiple applications within power equipment in the electrical industry, with a particular emphasis on high-voltage transformers. Natural esters have emerged as a highly attractive option in electrical insulation owing to their biodegradability, eco-friendliness, and enhanced fire safety characteristics [3, 11]. Additionally, vegetable oils possess hydrophilic characteristics and can safeguard solid insulators, such as cellulose, from deterioration, a feature that sets them apart from mineral oils [12, 13]. This moisture-attracting ability can be ascribed to their polar nature and the presence of hydroxyl groups, which readily enable the formation of water–oil emulsions [14-18]. Furthermore, natural ester-based insulating liquids have dielectric strength and dielectric permittivity higher than that of mineral oil [19, 20]. The significant dielectric permittivity of natural esters is a crucial factor that, when combined with cellulose paper, ensures better distribution of electrical stress, effectively reducing partial discharges within the insulation system [21, 22]. Figure 1 summarizes the qualities of natural esters as excellent insulating liquids for transformer insulation [23].

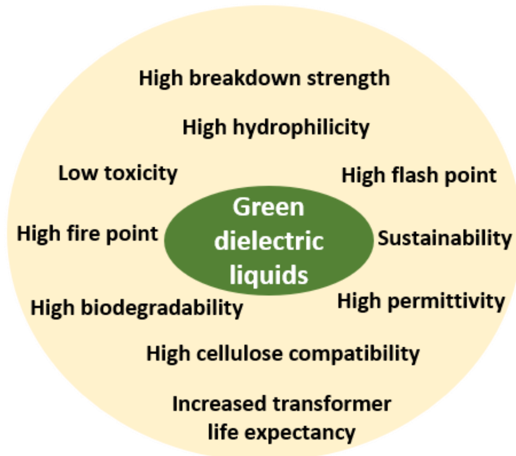
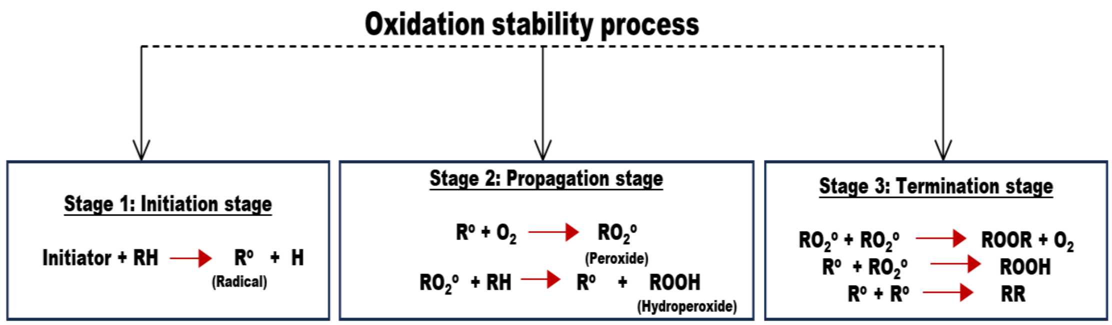


Figure 1:Qualities of natural esters as an insulating liquid.

Natural esters, derived from plants, comprise a complex mixture of fatty acids that fundamentally define their properties. It is worth noting that the timing of planting can exert an influence on the characteristics of the oil extracted from the seeds [24]. During the cold test, it was observed that oils extracted from seeds grown in the dry season crystallize rapidly. This rapid crystallization can be attributed to the high content of saturated fatty acids produced in response to dry stress conditions, indicating that the planting time also has a significant influence on the oil's properties [25]. The fatty acids can be categorized into three groups: saturated, monounsaturated, and polyunsaturated [26]. The green insulating liquids used in electrical appliances are derived from several plant seeds like soybean, rapeseed, canola, and sunflower [27-32]. A significant majority of these oils are characterized by a prevalence of mono or polyunsaturated fatty acids. Oils rich in long-chain unsaturated fatty acids are favored for their reliable performance in subzero climates. Nevertheless, the susceptibility of these oils to oxidation raises concerns that cannot be neglected, particularly when transitioning from monounsaturated to polyunsaturated compositions [33, 34]. This is because the oxidation of vegetable-based insulating oils generates several unwanted products, which are detrimental to the lifespan of transformers [8, 9, 15, 35]. Among the products generated during the oxidation reaction of vegetable-based insulating oils are moisture, alkane, ketones, alcohols, and aldehydes [15, 36].

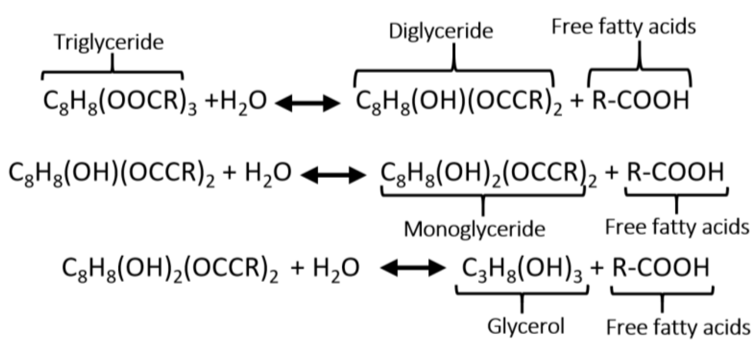
It is worth noting that not only does the oxidation process produce acids, but hydrolysis also plays a significant role in elevating the acidity of natural esters [7, 37]. Short-chain fatty acids can be more susceptible to hydrolysis, in part due to the steric hindrance phenomenon, along with other factors such as chain length and saturation level [37]. There are three major stages in both oxidation and hydrolysis of natural esters. Figure 2a,b show the progressive oxidation reaction and the reversible hydrolysis reaction, respectively [1].

Acids are core chemical markers that are used for monitoring the degradation of both oil and insulating paper [38]. Unlike low molecular weight acids (LMAs), the acids generated by natural esters are high molecular weight acids (HMAs), which are hardly soluble in the oil with low impact on the insulating system of the transformer, especially the paper [39, 40]. Nevertheless, the accumulation of the acids generated could affect the dielectric properties of both the oil and the paper insulation. Moreover, these high molecular weight acids can increase the viscosity of the oil, impeding its heat dissipation capabilities and potentially affecting its insulation performance and efficiency. While aging is influenced by time and various physical conditions, such as temperature, the introduction of antioxidants can help reduce the degradation process of the oil. Numerous antioxidants are documented in the literature, categorized into donors and acceptors. The donors provide hydrogen, whereas acceptors trap free radicals to create stable compounds [35]. Furthermore, the introduction of antioxidants into the base liquid positively influences specific dielectric properties of natural esters, such as the AC breakdown voltage [11, 32]. However, the loading percentage is a crucial consideration when incorporating antioxidants into natural esters following the regulation by the CIGRE working group [41]. Excessive loading of antioxidants in the base sample (>0.3 wt.%) can potentially elevate critical oil parameters, such as conductivity and dielectric loss, which may adversely affect the insulating quality of transformer oil.



(a)

Figure 2: Oxidation process in natural ester insulating liquid



(b)

Figure 2: (b) Hydrolysis process in natural ester insulating liquid.

This review study aims to scrutinize the improvement of oxidation stability in natural esters. It reports on the efficacy of antioxidants utilized in recent studies. Additionally, it investigates the effects of antioxidants on physical properties and dielectric properties and examines their environmental impact. Improving the oxidation stability of natural ester insulating liquids is key to their broader adoption in transformer insulation. This transition will eliminate the use of environmentally harmful mineral-based insulating oils, reducing environmental pollution, lowering the carbon footprint of transformers, and supporting clean and renewable energy initiatives.

2.3 Oxidation Mechanism in Natural Esters

The degradation of natural esters via the oxidation process is initiated due to primary factors such as oxygen, heat, light, and potential impurities [35]. When natural esters are exposed to air at higher temperatures, oxygen molecules undergo hemolysis, generating free radicals within the oil. Additionally, an electrical insight into how radicals are formed in petroleum-based insulating liquids is explicitly reported in reference [42]. A free radical is defined as any molecular species that contains an unpaired electron in an atomic orbital capable of independent existence. Free radicals may also result from hydrogen detachment at the weak bond of the α carbon and hydrogen. The presence of copper windings is also among the factors that catalyze the process of oxidation. These radicals are highly reactive due to unpaired electrons, which react with oxygen, forming peroxide free radicals [43]. A laboratory testing technique by UV-vis spectroscopy techniques is proposed in [35] to assess the relative concentration of free radicals in insulating oil. Instability prompts their reaction with unsaturated bond sites in fatty acid chains, producing hydroperoxides and further radicals. This perpetuates a continuous chain reaction known as the propagation stage of oxidation [9]. The chain reaction is hindered in two distinct ways. Firstly, an antioxidant, a radical scavenger, is introduced, halting the chain reaction. These antioxidants act as donors by contributing hydrogen or acceptors by absorbing free radicals within the system. Secondly, natural inhibition occurs when two free radicals unite. The former process preserves oil properties unchanged, whereas the latter notably alters oil characteristics by elevating viscosity and acidity and exhibiting a distinct color change associated with oxidation byproducts like ketones [37]. Furthermore, increased viscosity poses a significant detriment to the transformer's functionality, impacting oil circulation and subsequently compromising the cooling system. Hence, the incorporation of inhibitors into the base oil is crucial when contemplating the use of natural esters as a dielectric liquid.

Over time, diverse inhibiting materials have been used to improve the oxidation stability of natural esters for academic and industrial applications. They are classified as either natural or artificial inhibitors based on their sources. Indeed, despite their importance, reports suggest that the incorporation of inhibitors could affect the biodegradability of these liquids, notably through their biological oxygen demand, especially in the case of chemically synthesized inhibitors [7].

2.3.1 Effect of Oxidation on Transformer Useful Life and Sustainability

The lifespan of a transformer is tied to the integrity of its oil–paper insulation system [44, 45]. Any contamination in the insulating liquids significantly impacts the overall stability of the transformer, posing a threat to its functionality. Contaminants, notably moisture and particulate matter, escalate the risk of electrical faults and impede proper heat dissipation within the transformer. The effect of oxidative reaction on both oil and paper are, therefore, discussed as follows.

2.3.1.1 Impact of Oxidation Reaction on Oil Properties

The oxidative degradation of natural ester insulating liquids is closely linked to their chemical structure, particularly the presence of carbon–carbon double bonds (C=C). These unsaturated sites, unlike mineral oils, render natural esters more susceptible to oxidation [46]. The extent of oxidation stability largely depends on the degree of unsaturation in the feedstock used for producing the esters. Esters derived from saturated, monounsaturated, di-unsaturated, and tri-unsaturated fatty acids exhibit oxidation stability ratios of approximately 1:10:100:200, respectively, meaning tri-unsaturated esters are the most prone to oxidation [1]. The oxidation process typically initiates at the allylic position, the carbon atom adjacent to a double bond, where hydrogen abstraction leads to the formation of free radicals. These radicals undergo a chain reaction involving oxygen, resulting in hydroperoxides, which eventually break down into a variety of secondary oxidation products. A significant consequence of oxidation in natural esters is the increase in oil viscosity [9], primarily due to oligomerization, where radical recombination leads to the formation of larger molecular structures [46]. This viscosity increase negatively affects the heat transfer efficiency of the transformer, as there is an inverse relationship between dynamic viscosity and the heat transfer coefficient [47-49]. Prolonged oxidation and viscosity buildup can lead to local overheating, impairing transformer performance and potentially triggering thermal failure. Additionally, when the viscosity rises beyond 35% of its original value, the reclamation of natural esters becomes technically and economically unfeasible [50], emphasizing the critical need for early detection and mitigation of oxidation processes.

2.3.1.2 Impact of Liquid Oxidation on Insulating Paper

The degradation of natural esters due to oxidation significantly impacts the properties of the insulating paper, leading to a cascade of effects that jeopardize the transformer's performance and longevity. As oxidation byproducts, carboxylic acids, and water accumulate, they interact with the solid insulation (typically impregnated cellulose paper), resulting in further degradation [45]. While natural esters tend to generate high molecular weight acids with lower absorption rates by paper compared to mineral oils [46], the combined presence of acidity and moisture remains detrimental to paper insulation. One of the most severe impacts is acid hydrolysis, a chemical process where the acidic oxidation byproducts degrade the cellulose fibers in the paper [1]. During this reaction, acidic compounds dissociate in the presence of water, forming hydronium ions (H_3O^+) that can donate protons to the cellulose chains. This proton transfer induces a chain scission process, breaking down the cellulose structure, which weakens the paper's mechanical properties and insulation effectiveness [39, 51, 52]. Furthermore, acid-catalyzed hydrolysis is self-perpetuating; for every linkage cleaved in the cellulose, one molecule of water is consumed and three water molecules are released, creating an auto-catalytic effect. This process accelerates the degradation of paper insulation, as each cycle of hydrolysis leads to more breakdown of the cellulose chains. In addition to acid hydrolysis, hydrolysis degradation reactions, which occur simultaneously with oxidation reactions in natural esters, can also lead to the formation of long-chain free fatty acids (FFAs) and diacetyl glycerol (DAG) [46]. These byproducts, which result from the hydrolysis of triglycerides in the natural esters, can further impact the dielectric properties of the paper insulation. When these products recombine with cellulose through transesterification, they alter the electrical characteristics of the paper, particularly its ability to resist electrical stress. Moreover, hydroxy radicals generated during the oxidation process, especially from the decomposition of hydrogen peroxide, can catalyze the oxidation of cellulose itself, generating carbon dioxide and water [1]. This process weakens the dielectric strength and reduces its ability to perform as an effective insulator under high voltage conditions. Therefore, while the oxidation of natural esters is a primary concern for the oil's performance, the resulting byproducts, moisture and acids, further deteriorate the solid insulation system. This compounded effect ultimately compromises both the liquid and solid components of the transformer insulation system, making it essential to monitor and mitigate oxidation processes to safeguard transformer integrity, enhance sustainability, and extend the operational lifespan.

2.4 Antioxidants Classification

The primary function of antioxidants is to avert the activation and proliferation of oxidation mechanisms [43]. The antioxidants currently utilized for the enhancement of natural ester performance in transformer insulation systems fall into two distinct categories: natural and synthetic antioxidants. Natural antioxidants primarily originate from plant-based materials, often extracted from fruits, herbs, and plant seeds [53]. Conversely, synthetic antioxidants are synthetic compounds typically created in laboratory settings, devoid of natural occurrence in plants or any organic sources. While both types demonstrate efficacy in their respective roles, each holds specific advantages. Natural antioxidants align with environmentally conscious initiatives, being readily biodegradable when applied in transformer systems. However, the consistency and stability of natural antioxidants might pose challenges due to environmental influences. On the other hand, synthetic antioxidants offer predictable performance and stability, yet their usage may necessitate rigorous testing to ensure regulatory compliance and environmental compatibility. It is also important to know that the functionality of the antioxidants depends on the fatty acid source and the degree of oil unsaturation. This could be the reason for having a high percentage improvement in the enhancement of cotton seed biodiesel relative to that of palm biodiesel when an antioxidant like butylated hydroxytoluene (BHT) was considered [54].

2.4.1. Natural Antioxidant

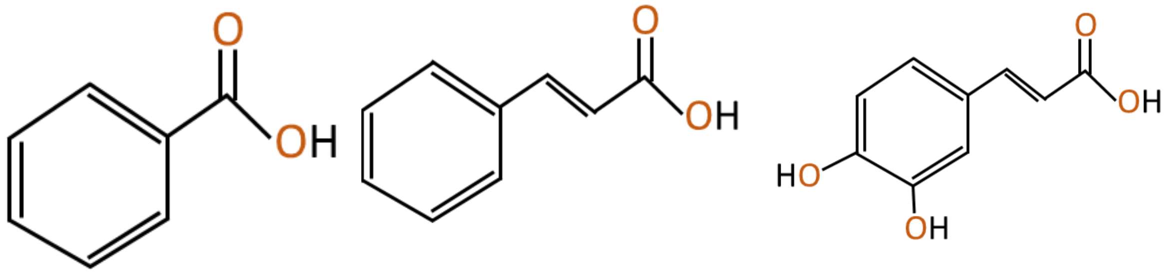
The significance of natural antioxidants extends beyond their role in the food and pharmaceutical industries, finding application in the improvement of transformer insulating fluids. Derived from various plant sources like seeds and leaves, these natural antioxidants not only align with environmental regulations but also contribute to the eco-friendly nature of the industry [55]. For instance, tocopherol is sourced from soybean oil, ascorbic acid from citrus fruits, polyphenols from grapes and tea leaves, and carotenoids from the lycopene found in tomatoes [56, 57]. Throughout plant routine metabolic processes, secondary metabolites emerge from various plant components such as the roots, stems, seeds, leaves, and nuts [58]. Unlike primary metabolites, which drive the plant's photosynthesis, respiration, and growth, secondary metabolites encompass a diverse range of phytochemicals abundantly present in plants. These include phenolics, tocopherols, flavonoids, lignans, peptides, and more [59]. A comprehensive list of natural antioxidants is presented in Table 1.

Table 1: A comprehensive list of natural antioxidants.

Sn	Antioxidants	Chemical Formula	Source	Reference
1	Quercetin	$C_{15}H_{10}O_7$	Apples, onions and berries	[60]
2	Cardanol, epoxy cardanol	$C_{15}H_{27}OH$	Cashew nut shell liquid	[61]
3	Rosemary	$C_{18}H_{16}O_8$	Rosmarinus species	[62]
4	Gallic acid, caffeic acid and ferulic acid	$C_7H_6O_5$, $C_9H_8O_4$, $C_{10}H_{10}O_4$	Macerated barley waste and Moringa Oleifera leaves	[63, 64]
5	Camphor	$C_{10}H_{16}O$	Camphor plant	[54]
6	Limonene	$C_{10}H_{16}$	Lemon and orange	[54]
7	Citric acid (anhydrous)	$C_6H_8O_7$	Citrus fruits	[65, 66]
8	L-Ascorbic acid	$C_6H_8O_6$	Citrus fruits	[67, 68]
9	α-tocopherol	$C_{31}H_52O_3$	Vegetable oils, fruits	[69]
10	Carotenoids	$C40H_{56}$	Fruits, vegetables	[70]
11	Lignin	-	Forestry residue	[71, 72]

2.4.1.1. Phenolics

Phenolic compounds are mostly hydrogen donors or metallic chelators and it is a group of diverse secondary metabolites having over 8000 compounds [73]. They are mostly found in the roots, leaves, and fruits of a plant. The phenolics are classified into two different components which are the simple and complex phenolics. Benzoic acids, cinnamic acids, and caffeic acids are examples of simple phenolics, while tannins and flavonoids are examples of complex phenolics. The chemical structure with the IUPAC nomenclature of some simple phenolics can be seen in Figure 3.



Benzoic acid.

3-phenylprop-2-enoicacid cinnamic acids.

3-(3,4-Dihydroxyphenyl)2-propenoicacid (caffeic acid)

Figure 3: Example of simple phenolics

2.4.1.2. Flavonoids

Flavonoids, classified as polyphenolic compounds, exhibit potent antioxidant properties [73]. Distributed throughout various parts of plants, these compounds play a significant role in medicinal applications by defending against diseases induced by oxidative stress. They achieve this by modulating enzymatic activities and interacting with specific receptors. Higher plant tissues consist of various types of flavonoids, including flavanols, flavanones, isoflavones, chalcones, and flavones [59].

2.4.1.3. Ascorbic Acid

Ascorbic acid, also known as vitamin C, serves as a potent antioxidant with radical-scavenging capabilities. Being water-soluble, it is present in all parts of plants [59]. This antioxidant functions as a reducing agent, hindering the oxidation process by contributing electrons (reducing equivalents) in chemical reactions. It demonstrates effectiveness against radicals such as O_2^- (superoxide), H_2O_2 (hydrogen peroxide), OH (hydroxyl), and $1O_2$ (singlet oxygen) [74, 75]. Upon complete reduction, it transforms into a radical known as monodehydroascorbate, which acts as a scavenger in chemical reactions by interacting with radicals. Most importantly, monodehydroascorbate not only scavenges radicals but also terminates radical chain reactions, preventing the continuous propagation of radical reactions and thereby exerting control over the oxidation process. Within lipids, tocopherol, also recognized as vitamin E, serves to reduce free radicals. However, this reduction process results in the formation of a tocopheroxyl radical. The presence of ascorbic acid plays a role in reducing the tocopheroxyl radicals generated during this reaction. The structural formula of ascorbic acid is presented in Figure 4. It is important to know that this antioxidant is sensitive to some environmental conditions like temperature and light, in which temperature is considered the dominating factor that determines the stability of ascorbic acid. When a material containing ascorbic acid antioxidant is exposed to a temperature range above 100 °C for two hours, ascorbic antioxidant degradation occurs, which generates oxidation products like furfural, 2-furoic acid, 3-hydroxy-2-pyrone, and an unknown compound [75]. Applying this antioxidant in transformer insulation systems may pose challenges.

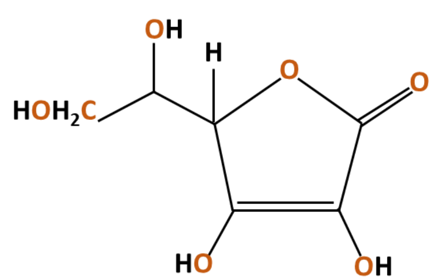


Figure 4: Ascorbic acid (vitamin C).

Moreover, the thermal degradation of the antioxidant produces by-products resembling those found in cellulose-based insulating materials in transformers. The oxidation product resulting from the antioxidant when the transformer operates at high temperatures during energization could be misconstrued as cellulose degradation during routine maintenance. Moreover, ascorbate is primarily derived from citrus fruits, melons, broccoli, tomatoes, and cabbage. Therefore, careful attention should be paid to the agricultural sector to avoid food scarcity and also prevent greenhouse gas emissions during large-scale cultivation when planning to adopt this antioxidant for enhancing oxidation stability in transformer-insulating oil.

2.4.2 Synthetic Antioxidants

The special attributes of synthetic antioxidants are the ability to withstand several conditions and a prolonged shelf life. They are considered superior to natural antioxidants due to their stability in products with prolonged storage times and consistent performance and effectiveness, as well as their high resistance to temperature degradation. In the context of enhancing transformer insulating liquids, several synthetic antioxidants have been explored and their effects documented. These include tert-butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and lauryl tert butyl hydroquinone [10, 32, 76, 77]. Table 2 gives a comprehensive list of synthetic antioxidants.

Table 2: Common synthetic antioxidants.

Sn	Antioxidants	Chemical Formula	Source	Reference
1	N,N′-disec-butyl-p-phenylenediamine	$C_{22}H_38N_2$	Reaction of p-phenylenediamine with sec-butyl alcohol	[78, 79]
2	Tert-butylhydroquinone	$C_{10}H_{14}O_2$	Petroleum	[80, 81]
3	Propyl gallate (PG)	$C_{10}H_{12}O_5$	Esterification of gallic acid	[82, 83]
4	Butylated hydroxy toluene	$C_{15}H_24O$	Petroleum	[84]
5	1,2,3-trihydroxybenzene (Pyrogallol)	$C_6H_6O_3$	Hydrolysis of gallotannins or oxidation of gallic acid	[84]
6	Butylated hydroxyl anisole	$C_{11}H_{16}O_2$	Reaction of p-methoxyphenol and isobutylene	[85]

2.4.3 Antioxidant Activity Assessment

Understanding the activity of antioxidants used in enhancing the oxidation stability of natural esters is crucial when it comes to the selection of appropriate antioxidants. In a controlled system, the rate and amplitude of oxidant formation should be neutralized by antioxidants. However, in natural systems, there is often an imbalance between pro-oxidants and antioxidants, leading to oxidative stress. An increase in reactive oxygen species (ROS) in natural ester insulating liquids accelerates the aging of these liquids, which can be detrimental to transformer life [86]. The common reactive oxygen species during the degradation of natural esters include peroxyl radicals, hydroxyl radicals, and alkoxyl radicals. An example of a non-free radical species is hydrogen peroxide. This imbalance may be attributed to the activity and effectiveness of the antioxidants themselves. Additionally, the activity of antioxidants depends on several factors, such as their chemical structure, which directly influences their intrinsic reactivity to free radicals and other ROS.

The enhancement of oxidation stability in natural ester insulating liquids can be fundamentally influenced by molecular-level interactions between antioxidant molecules and the fatty acid chains present in the oil matrix. These interactions are essential in interrupting the autoxidation chain reactions, which are typically initiated by the attack of free radicals on unsaturated fatty acids. Due to the presence of double bonds, particularly at the allylic positions, unsaturated fatty acids are especially susceptible to radical-induced degradation [46]. The effectiveness of antioxidants in scavenging these radicals is determined by several structural attributes, including aromaticity, polarity, steric configuration, and the presence of functional groups [87].

Among these structural features, aromaticity plays a particularly crucial role in radical scavenging efficiency. Many synthetic antioxidants, such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), and hindered phenolic compounds like Irganox 1076 and Irganox L57, contain aromatic rings bearing phenolic hydroxyl groups [88, 89]. These molecular structures facilitate resonance stabilization of the antioxidant radical that forms after hydrogen donation. Specifically, when a phenolic antioxidant donates a hydrogen atom to a lipid peroxyl radical (ROO•), it forms a phenoxyl radical, which is subsequently stabilized by delocalization of the unpaired electron across the aromatic ring. This stabilization reduces the reactivity of the resulting radical, thereby hindering the propagation phase of the oxidative chain reaction [89]. Furthermore, the efficiency of these antioxidants is strongly influenced by the nature and positioning of substituent groups on the aromatic ring. Bulky alkyl substituents, such as tert-butyl or octadecyl groups, positioned at the ortho or para locations, enhance radical stability through steric hindrance and electronic effects, making such antioxidants particularly effective under elevated thermal conditions commonly encountered in transformer operation. Additionally, the presence of electron-donating groups like –OH or –OCH3 further increases the antioxidant's hydrogen-donating capacity, whereas electron-withdrawing groups may diminish the compound's radical-quenching potential [89, 90]. Polarity and solubility also play critical roles in determining antioxidant performance, particularly in relation to their compatibility with the ester matrix [91, 92]. Polar antioxidants tend to associate more closely with ester functional groups and may preferentially localize in polar domains of the insulating fluid, such as at oil–paper interfaces or in regions rich in polar degradation byproducts. In contrast, non-polar antioxidants disperse more uniformly throughout the bulk oil, providing widespread oxidative protection. Consequently, the solubility and dispersion behavior of antioxidants significantly influence their spatial availability for effective radical scavenging [93-95].

The distribution and concentration of the antioxidants in the base liquid are also critical for their activity. Furthermore, the kinetics of the reaction, including the thermodynamics and the ability of antioxidants to react, play a significant role in determining their effectiveness [96].The methods for determining antioxidant activity based on techniques are categorized into spectrometry, electrochemical assays, and chromatography [86, 97].

Spectrometry-based assays: This includes several methods for evaluating antioxidant capacity. The ORAC (oxygen radical absorbance capacity) assay operates on the principle of an antioxidant's reaction with peroxyl radicals, which are induced by 2,2′-azobis-2-amidino-propane (AAPH). The efficacy of the antioxidant is determined by observing the loss of fluorescence of fluorescein. The HORAC (hydroxyl radical averting capacity) assay measures the antioxidant's ability to quench hydroxyl radicals generated by a cobalt (II)-based Fenton-like system, with the outcome also determined by the loss of fluorescein fluorescence. Similarly, the TRAP (total radical-trapping antioxidant parameter) assay evaluates the antioxidant's capacity to scavenge luminol-derived radicals from AAPH decomposition, with chemiluminescence quenching serving as the determinant. Other spectrometric methods include CUPRAC (cupric ion reducing antioxidant capacity), FRAP (ferric reducing antioxidant power), PFRAP (potassium ferricyanide reduction antioxidant power), and DPPH (2,2-diphenyl-1-picrylhydrazyl), all of which involve colorimetric determinations based on the reduction of specific compounds by antioxidants [86].

Electrochemical techniques: These offer another approach to analyzing antioxidant activity. Voltammetry is a technique based on the reduction or oxidation of a compound at the working electrode's surface when an appropriate potential is applied, with the assay's effectiveness measured by the cathodic or anodic peak current. Another technique is amperometry, which involves setting the working electrode's potential at a fixed value relative to a reference electrode, with the current produced by the oxidation or reduction of the electroactive analyte serving as the measure. Biamperometry, another electrochemical technique, assesses antioxidant activity by measuring the current passing between two identical working electrodes that are subjected to a slight potential difference and submerged in a solution containing the sample and a reversible redox couple [86].

Chromatography techniques: These include gas chromatography (GC) and high-performance liquid chromatography (HPLC). In gas chromatography, the separation of compounds in a mixture is achieved by their distribution between a liquid stationary phase and a gas mobile phase, with the results detected through flame ionization or thermal conductivity detection.

High-performance liquid chromatography, on the other hand, involves the separation of compounds by their partitioning between a solid stationary phase and a liquid mobile phase under conditions of high flow rate and pressure. The separated compounds are detected using various methods, including UV-Vis detection, fluorometric detection, mass spectrometry, or electrochemical detection [86]. Determination of antioxidant activity can be categorized into two different types: hydrogen atom transfer (HAT) and single electron transfer (SET).

2.4.3.1 The Hydrogen Atom Transfer (HAT) Reaction Method

The efficiency of antioxidants can be determined by measuring the ability of antioxidants to remove a free radical through the donation of a hydrogen atom. In this process, the donating ability of antioxidants is determined by monitoring hydrogen atom transfer from the phenol to the peroxyl radical. It is, therefore, important for the antioxidant, the hydrogen donor, to react faster than the molecules being protected [98]. Several tests are available to evaluate the hydrogen atom transfer capability of a donor antioxidant. Among these are the oxygen radical absorption capacity (ORAC) and the total peroxyl radical trapping antioxidant parameter (TRAP) [99].

ORAC Test: The ORAC test assesses antioxidant efficiency by measuring how well antioxidants can inhibit the oxidation initiated by peroxyl radicals. The peroxyl used in this assay is generated from azo-compounds such as lipophilic α,α-azobisizobutyronitrile (AIBN), 2,2′-azobis (2-amidinopropane) hydrochloride (ABAP), 2,2′ azobis(2,4 dimethylvaleronitrile) (AMVN), and the hydrophilic 2,2′-azobis(2-amidinopropane) dihydrochloride (AAPH) [86]. The generated peroxyl radicals react with a fluorescent sample, resulting in a reduction in fluorescence. The data are then analyzed using the area-under-the-curve method, comparing results both in the presence and absence of the antioxidant.

TRAP Test: This test is performed by measuring the ability of the antioxidants to inhibit the reaction between the target molecules and the peroxyl radicals. The oxygen absorption rate is a significant factor in determining the efficiency of antioxidants in this method. When peroxyl radicals react with the target molecules, there is always an oxygen consumption; however, a retardation in the consumption time, i.e., the period in which the antioxidants reduce the reaction between the peroxyl and the target molecules, signifies the efficiency of the antioxidants. In this assay, the trap value is always expressed as the induction period following the time in which the antioxidant effectively delays the oxidation reaction.

2.4.3.2 The Single Electron Transfer (SET) Test

In this test, the reduction of metallic ions, carbonyl groups, and free radicals by the antioxidant through the transfer of electrons shows the ability of antioxidants as an oxidation inhibitor. The single electron transfer method depends on the pH value since reactivity in single electron transfer is based on the deprotonation and ionization potential of the reactive functional group [100]. Unlike the hydrogen atom transfer techniques that use peroxyl radicals when measuring antioxidant activity, this method uses fluorescent or colored samples. Examples of tests under this category are the ferric reduction of antioxidant power (FRAP) and the cupric antioxidant capacity (CUPRAC).

2.5 Natural Esters–Antioxidant Preparation

The preparation of natural insulating liquids with antioxidants can be seen in Figure 5. It is important to know that the preparation method could affect the percentage of oxidation stability enhancement. In some cases where the antioxidant is not soluble in natural ester, pre-dissolving the antioxidant in a suitable solvent is paramount as it ensures homogeneity and ready interaction between the antioxidant and the oil molecules. The solvent used in the pre-dissolving process can be removed through the process of distillation. The most commonly used polar solvent for dissolving antioxidants is ethanol which can be easily separated from the oil using a distillation process. Among the factors to be considered during the sample preparation for oxidation stability enhancement of natural esters are moisture content, the stirring time, and the temperature of the reaction.

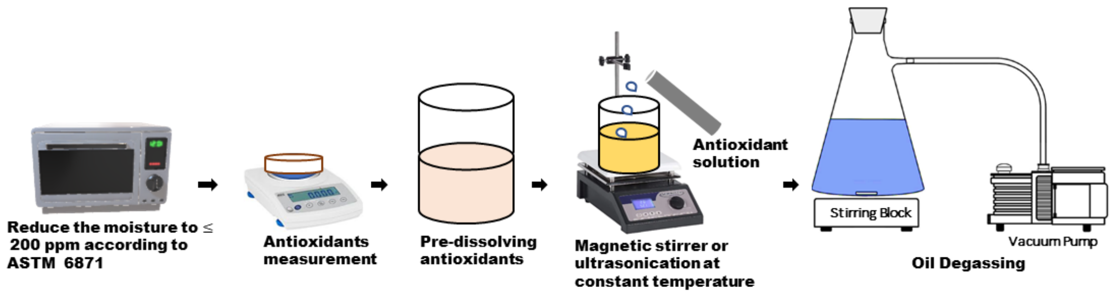


Figure 5: Natural ester antioxidant preparation stages.

2.5.1 Moisture Content

The presence of high moisture concentration in natural esters can lead to a chemical process known as hydrolysis, as presented in Figure 2b. Moisture presence causes triglycerides to break down into their simplest forms, glycerol and fatty acids. The resulting fatty acids from hydrolysis are more susceptible to oxidation compared to the stable triglycerides, impacting the quality of insulating liquids. Therefore, it is crucial to minimize the moisture content of the base liquid during sample preparation. The American Society for Testing and Materials (ASTM) 6871 specifies that the moisture content of natural esters should be equal to or less than 200 ppm [101, 102], which is a safety range to prevent the transformers from metal corrosion and prevent the insulators from degradation. In addition, it is important to know that when considering natural esters dominated by short-chain fatty acids, especially C8/C10, a very low concentration of moisture is required as the short-chain fatty acids are susceptible to hydrolysis [37].

2.5.2 Stirring Time and Temperature

Ensuring an optimal stirring duration is crucial in the preparation of natural esters and antioxidants. Adequate stirring time promotes uniform dispersion of antioxidant molecules, enabling a smooth integration with oil molecules. Insufficient distribution of antioxidants may result in localized areas with low concentrations, adversely affecting the desired properties of the oil. The reaction temperature is another critical factor in sample preparation. Various antioxidants exhibit distinct solubility temperatures in oil. It is imperative to carefully select and maintain an optimum temperature to prevent heat-induced degradation of the oil while ensuring the effective incorporation of antioxidants.

Several multiparameter optimization methods are available in the literature that have been used for natural ester–antioxidant preparation [10, 77, 101]. These methods can be used to optimize the stirring time and the temperature of the reaction during natural ester oxidation stability enhancement.

2.6 Antioxidant Mechanism in Insulating Liquids

Antioxidants operate according to their inherent properties. Their mechanism can be complex and varies based on the type of antioxidant and the condition under which they operate. Primarily, antioxidants protect the integrity of oils by scavenging free radicals, such as hydroperoxyl and alkyl radicals, as illustrated in Figure 2a [103]. An antioxidant can act either as a donor or an acceptor [35]. Donor antioxidants work by donating a hydrogen atom to free radicals, effectively neutralizing their harmful effects. Acceptor antioxidants, which are known as the chain breakers, stop the reaction by reacting with the free radicals. The classification of some of the common antioxidants is shown in Table 3, and the equation describing the scavenging activity of both the donor and the acceptor is presented in Figure

6. In operational transformers at elevated temperatures, the dissolved oxygen content in the oil increases, which can raise the concentration of metal ions due to the presence of transformer windings [104]. Antioxidants, particularly metal chelators, bind to these metal ions, inhibiting their catalytic activity and preventing the decomposition of hydroperoxides even under high-temperature conditions [105, 106]. At elevated temperatures, the activation energy of the oil decreases, increasing the likelihood of oxidative reactions. However, antioxidants mitigate this by raising the activation energy required for radical chain reactions, thereby slowing down the oil's degradation. Despite their benefits, the effectiveness of antioxidants is highly dependent on the transformer's operating temperature. Higher temperatures often compromise their stability and efficiency. Consequently, further research is crucial to develop antioxidants with enhanced thermal stability and effectiveness for high-temperature applications, such as in transformer oils.

Donor

$$R^* + AH \longrightarrow RH + A^*$$
$$ROO^* + AH \longrightarrow RH + A^*$$

Acceptor

$$R^* + A^* \longrightarrow RA$$
$$ROO^* + A^* \longrightarrow ROOA$$

Figure 6: Activity of antioxidants (donor and acceptor are represented in red and the (*) is for the radicals).

Table 3: Antioxidant classification according to behavior[107].

Antioxidants		
Donor	**Acceptor**	**Acceptor/Donor**
Vitamin C (Ascorbic Acid)	Superoxide Dismutase (SOD)	Glutathione
Vitamin E (Tocopherol)	Catalase	Trolox
Butylated Hydroxytoluene (BHT)		
Butylated Hydroxyanisole (BHA)		
THBQ		
N,N′-disec-butyl-p-phenylenediamine		

2.7 Natural Esters' Oxidation Stability Assessment

The oxidation assessment of natural esters is still a point of concern as there is no established or approved method for evaluating the oxidation stability of natural esters [108]. Due to variations in the fatty acid composition of natural esters, which pose variations in oxidation stability, establishing a method of oxidation stability assessment may be a challenge. The variation in the fatty acids composition of natural esters is a result of different plant sources as presented in Table 4 [26, 109-111]. However, there are some proposed methodologies for the assessment of the oxidation stability of natural esters. It is important to note that some standards, which are primarily used to assess the stability of mineral-based insulating oils, may not be directly applicable to natural esters due to significant differences in their chemical compositions. IEC 61125 originally focused on methods for evaluating the oxidation stability of mineral oils [112]. However, recognizing the distinct chemical and physical properties of natural esters, IEC 62770 was introduced to specifically address the oxidation stability of these oils [113]. IEC 62770 is now the standard for natural esters, providing a more accurate and relevant assessment tailored to their unique characteristics [114]. Additionally, ASTM D2112 [115] and ASTM D2440 [116]were designed to assess the oxidation stability of mineral oils [108]. While some studies have used these methods for natural esters, modifications to the testing conditions, such as oxidation time and reagents, have been necessary [26, 117]. Due to the polar nature and fatty acid composition of natural esters, their behavior during oxidation differs from that of mineral oils, making these tests less applicable or less accurate for evaluating the oxidation stability of natural esters.

i. The IEC 62770 suggested that oxidation stability of natural esters could be performed at 120 °C, 48 hours of heating time [15, 108]. It is to be mentioned that an investigation is still ongoing on the oxidation assessment of natural esters, which is to be reported in the near future.

ii. RBOT: Oxidation assessment of natural esters can be determined using the rotating bomb oxidation test (RBOT). The natural ester sample is aged in a pressurized vessel at 120 °C in the presence of oxygen following the ASTM 2272 [118]. The completion of the test is indicated by the reduction in pressure within the vessel and the measurement of the corresponding time interval in minutes. The oxidation assessment value for mineral insulating liquids is 300 min, whereas for natural esters, it is less than 40 min [15, 119]. A table comparing the oxidation induction time of different types of esters is presented in [120]. Table 5 shows the oxidation induction time of natural esters and other insulating liquids. Although the RBOT is an in-depth test for determining the oxidation stability of the insulating liquids, comparing the thermo–oxidative stability of different liquids when considering this method might be a challenge [119].

iii. The turbine oil oxidation stability test (TOST): This approach efficiently assesses the oxidative stability of oils and has proven effective in evaluating the oxidation stability of natural ester insulating oils for transformer applications [37]. A schematic diagram illustrating the sequential stages of the turbine oil oxidation stability test (TOST) following ASTM D-943-04a [121] is depicted in Figure 7. As depicted in Figure 7, samples are taken every 168 h, and testing ceases upon reaching an acid value of 2.0 mgKOH/g. The oxidation lifetime of the liquid samples is calculated using the expression given in Equation (1).

$$Oxidation\ lifetime\ (H) = A + \left[\frac{2.0 - C}{D - C}\right] \times (B - A) \qquad (1)$$

where A represents the duration in test hours when the acid number was last recorded below 2.0; B represents the duration in test hours when the acid number was recorded above 2.0; C represents the acid number at A hours; and D represents the acid number at B hours [37].

iv. Differential Scanning Calorimetry (DSC): DSC is a widely used technique for evaluating the oxidation stability of natural ester insulating liquids. During oxidation, oxygen reacts with the fatty acid chains in vegetable oils, leading to the generation of heat due to the energy released from the breaking and formation of chemical bonds. At the propagation stage of the oxidation process, the formation of lipid hydroperoxides is typically accompanied by heat release, which can be detected as an exothermic signal. Based on this principle, the oxidation induction time (OIT), defined according to ASTM E1858, is determined from the onset of the exothermic oxidation reaction and serves as a relative indicator of the oil's oxidative stability [10]. An extended OIT implies improved oxidation resistance, especially when antioxidants are introduced, as their radical scavenging effect delays the onset of oxidation and increases the measured induction time.

Table 4: Percentage composition of oil fatty acids from different plants**.**

	Fatty Acid	**Chemical Structure**	**Palm Kernel Oil**	**Coconut Oil**	**Canola Oil**	**Soybean Oil**	**Cotton Seed Oil**	**Neem Oil**	**Sun flower Oil**	**Rapeseed Oil**	**Safflower Oil**
Oxidation stability decreases downward	Caprylic acid C8:0	s	3.30	9.16	-	-	-	-		-	-
	Capric acid C10:0	s	3.40	6.44	-	-	-	-		-	-
	Lauric acid C12:0	s	48.20	45.57	-	-	-	-		-	-
	Myristic acid C14:0	s	16.20	16.65	0.07	0.08	1.00	-		-	-
	Palmitic acid C16:0	s	8.40	8.21	1.29	14.04	23.70	18.10	7.00	4.00	7.00
	Stearic acid C18:0	s	2.50	3.42	2.40	4.07	3.40	18.10	5.00	2.00	2.00
	Palmitoleic acid C16:1	mus	-	-	0.29	0.09	0.60		-	-	-
	Oleic acid C18:1	mus	15.40	6.27	64.40	23.27	19.40	44.50	19.00	56.00	13.00
	Erucic acid C22:1	mus	-	-	0.50	-	-	-		-	-
	Linoleic acid	pus	2.30	1.40	17.40	52.18	53.20	18.30	68.00	22.00	78.00

	C18:2										
	Linolenic acid C18:3	pus	-	-	9.60	5.63	0.50	0.20	1.00	10.00	-

Symbols: s = saturated; mus = monounsaturated; pus = polyunsaturated

Table 5: RBOT Test results of different insulating liquids.

Types of Insulating Liquids	RBOT Test (Minutes)
Silicon fluids	>450
Natural esters	<40
High oleic natural esters	197
Synthetic esters	421
Mineral oils	300

Recent advancements have seen the application of pressure differential scanning calorimetry (PDSC) and thermogravimetric analysis-differential scanning calorimetry (TGA-DSC) in assessing the oxidation stability of natural esters, with promising results reported in the literature [35, 122, 123]. These techniques are also instrumental in analyzing thermal degradation behavior, where TGA monitors changes in the sample's mass due to evaporation, decomposition, or oxidation, while DSC simultaneously captures thermal events such as exothermic and endothermic transitions [10, 35, 37, 77, 101]. However, there are significant analytical challenges associated with DSC and TGA measurements, especially when analyzing complex systems that contain antioxidants. One critical issue is the overlapping of exothermic peaks, which arises from the simultaneous occurrence of oxidation of the base ester and degradation of antioxidant molecules. Antioxidants, particularly phenolic types, may thermally degrade within a temperature range close to that of ester oxidation, producing their own exothermic signals. This overlap can result in broad or indistinct thermal peaks, making it difficult to differentiate between the thermal contributions of the base oil and the additives. Consequently, accurate determination of OIT and interpretation of oxidative behavior become less straightforward.

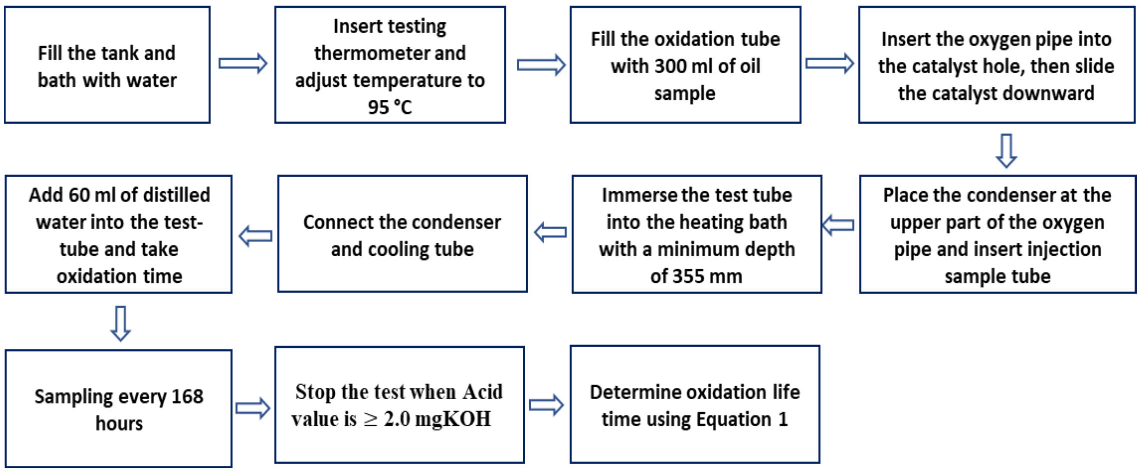


Figure 7: Procedure for turbine oil oxidation stability test.

Similarly, in TGA analysis, mass loss associated with antioxidant volatilization or decomposition may overlap with the degradation of the ester matrix, leading to ambiguous multi-stage weight loss profiles. These challenges indicate the need for careful data interpretation and, in some cases, the use of complementary analytical techniques, such as Fourier transform infrared spectroscopy (FTIR) or gas chromatography-mass spectrometry (GC-MS), to validate the identity of degradation products and assign thermal events more precisely. Furthermore, modulated DSC or isothermal DSC protocols can help improve resolution and separate overlapping thermal signals. Thus, while DSC and TGA remain powerful tools for assessing oxidation stability and thermal behavior, their limitations in complex systems must be acknowledged and addressed through a more comprehensive analytical approach.

2.8 Antioxidants and Effects on Some Imperative Properties of Natural Ester-Based Insulating Liquids

In this section, the effect of antioxidants on some fundamental properties of natural ester insulating liquid is investigated. Among the parameters considered are the dielectric strength, fire properties, and viscosity.

2.8.1. AC Breakdown Voltage of Natural Esters Containing Antioxidants

Improving the oxidation stability of insulating liquids, particularly natural esters, requires careful consideration of how antioxidants impact the electrical properties of the oil. Tables 6 and 7 provide a summary of the impact of various commonly used natural and synthetic antioxidants on the AC breakdown voltage of natural esters. Table 6 illustrates the influence of composite antioxidants determined through experimental design, while Table 7 showcases the effect of individual antioxidants on the AC breakdown voltage of various natural esters. The tables demonstrate that incorporating antioxidants into the base liquids leads to an increase in the breakdown voltage. This enhancement can be attributed to the monoaromatic nature of the antioxidants, which have been found to enhance gas-absorbing behavior when natural esters are exposed to electrical stresses [32, 124].

Table 6: Influence of composite antioxidants on the AC breakdown voltage of natural esters**.** [32, 125].

Antioxidants	Ratio of Antioxidants	Soybean Oil(% Increment)	Pongamia Pinnata Oil	Sunflower Oil (% Increment)	Rice Bran Oil (% Increment)	Corn Oil (% Increment)	Rapeseed Oil (% Increment)
α-Tocopherol + CA	1.0:1.0	+40.0	-	+44.0	+23.0	+50.0	-
	0.5:0.5	+37.0	-	+59.0	0	+47.0	-
α-Tocopherol + BHT	2.5:2.5	-	+60	-	-	-	+63.0
	1.25:1.25	-	+41	-	-	-	+53.0
BHA + BHT	2.5:2.5	-	+88	-	-	-	+53.0
	1.25:1.25	-	+50	-	-	-	+59.0
BHT+ (citric acid) CA	1.0:1.0	+48.0		+32	−3.0	+53.0	
	0.5:0.5	+44.0		+12	+15.0	+34.0	
PG (1 mg) + CA (1 mg) + α-Tocopherol(1mg)	500 mL of the composite antioxidants in 500 mL of oil (90 °C)	-	-	+20	-	-	-
PG (1 mg) + CA (1 mg) + α-Tocopherol (1 mg)	1000 mL of the composite antioxidants in 500 mL of oil (90 °C)	+19.2	-	-	-	-	-
PG (1 mg) + CA (1 mg) + α-Tocopherol (1 mg)	500 mL of the composite antioxidants in 500 mL of oil (90 °C)	-	-	-	−12.0	-	-

Table 7: Effect of standalone antioxidants on the AC breakdown voltage of natural esters.[76, 85, 126].

Base oil	Antioxidants	Ratio of Antioxidants	Percentage Increment
25% Olive oil and 75% of Rice bran oil	BHT	0.25%	+46.6
75% Olive oil and 25% of Soya bean oil	BHT	1.00%	+52.54
50% Olive oil and 50% of Sunflower	BHT	1.00%	+48.50
25% Olive oil and 75% of Corn oil	BHT	1.00%	+48.50
75% Olive oil and 25% of Rice bran oil	BHA	1.00%	+62.50
50% Olive oil and 50% of Soya bean oil	BHA	1.00%	57.14
25% Olive oil and 75% of Sunflower	BHA	1.00%	+40.63
50% Olive oil and 50% of Corn oil	BHA	1.00%	+51.61
Vegetable oil	DBPC	9 g in 1108 mL of oil	+27.58
Vegetable oil	BHA	9 g in 1108 mL of oil	+48.27
Vegetable oil	TBHQ	9 g in 1108 mL of oil	+51.72
Honge oil	GA	0.50%	+12.14
Neem oil	GA	0.50%	+11.63
Mustard oil	GA	0.25%	+25.00
Punna oil	GA	0.50%	+20.56
Castor oil	GA	0.25%	+51.61
Sunflower oil	AA	1.00 g	+24.00
Soya bean oil	AA	1.00 g, 5.00 g	+56.00, +96.00
Corn oil	PG	1.00 g, 5.00 g	+72.00, +72.00

2.8.2. Ignition Properties of Natural Esters Containing Antioxidants

Effective asset protection in any industry is of great importance, especially in the electrical sector, where assets are expensive and interconnected. The application of high ignition point liquids in oil-filled transformers significantly protects the asset and prevents downtime, financial implications, and safety of the personnel and the environment. Natural esters are known to have higher flash and fire point temperatures relative to mineral oil and synthetic esters [5]; however, understanding the effect of antioxidants on the fire property of the base liquids is paramount. Table 8 gives a summary of recent investigations reported on the effect of antioxidants on the ignition and combustion properties of natural esters. It can be observed from Table 8 that the addition of antioxidants to natural esters generally increases both the flash point and fire point, albeit with some exceptions. This improvement can be attributed to antioxidants' ability to curtail the thermal decomposition of natural esters, thus impeding the release of flammable gases at lower temperatures. However, when introducing new antioxidants to enhance natural ester-insulating liquids, careful consideration of the loading concentration is crucial. Studies have demonstrated that at elevated concentrations of antioxidants, both the flash point and fire point begin to decline. This decrease might be attributed to the formation of higher ignition combinations within the oil [64].

Table 8: Effect of antioxidants on flash and fire points of natural esters [76, 85, 125].

Base Oil	Antioxidants	Ratio of Antioxidants	Flash Point Percentage Increment	Fire Point Percentage Increment
Sunflower	PG (1 mg) + CA (1 mg) + α-Tocopherol (1 mg)	500 ppm in 500 mL	+8.70	+8.00
Soybean	BHT (1 mg) + CA (1 mg) + α-Tocopherol (1 mg)	500 ppm in 500 mL	−3.70	−9.67
Rice bran	BHT (1 mg) + CA (1 mg) + α-Tocopherol (1 mg)	500 ppm in 500 mL	+8.00	+7.14
25% Olive oil and 75% of Rice bran oil	BHT	0.25%	+8.57	+3.66
50% Olive oil and 50% of Sunflower	BHT	0.50%	+5.26	+3.33
75% Olive oil and 25% of Corn oil	BHA	1.00%	+1.66	+1.94
75% Olive oil and 25% of Sunflower oil	BHA	1.00%	+2.75	+4.33
Honge oil	BHT	0.75%	+3.36	+5.81
Neem oil	BHT	0.75%	+6.94	+13.80
Mustard oil	BHT	0.5%	+7.27	+10
Punna oil	BHT	0.75%	+12.14	+8.20
Castor oil	BHT	0.75%	+6.43	+9.66
Neem oil	GA	0.5%	+8.33	+9.43
Mustard oil	GA	0.25%	+7.96	+11.00
Punna oil	GA	0.50%	+6.43	+4.26
Castor oil	GA	0.50%	+13.57	+14.48
Corn oil	PG	5.00g	+7.00	+6.00
Sunflower	AA	5.00g	+8.00	+19.00
Sunflower	α-Tocopherol + CA	1:1	+12.00	+11.00
Sunflower	BHT + CA	0.5:0.5	0	+11.00

2.8.3. Effect of Antioxidants on Cooling Properties of Natural Esters

In transformer insulation systems, dielectric liquids play a crucial role in facilitating cooling and dissipating heat. The cooling efficiency of these insulating liquids depends directly on their viscosity [127]. Consequently, investigating the impact of antioxidants on the viscosity of these base liquids is paramount. Table 9 presents the effect of various antioxidants on the viscosity of natural ester insulating liquids. Antioxidants exhibit diverse behaviors regarding the viscosity of the base liquid. While some antioxidants decrease viscosity, others increase it. References [85, 125] highlight the irregular nature of the effect of antioxidant loading on base liquid viscosity. Thus, it can be inferred that the behavior of antioxidants in base liquids is contingent upon the chemical composition of the antioxidants and their interaction with the base liquid. In situations where antioxidants reduce the viscosity of the base liquids, they may be categorized as solvents or dispersants. These antioxidants work by breaking molecular bonds, thereby reducing the attractive forces between oil molecules and, ultimately, decreasing viscosity [76]. Conversely, if antioxidants increase the viscosity of the base liquid, they may have formed chemical bonds with the oil molecules, leading to an elevated viscosity.

Table 9: Influence of antioxidants on the viscosity of natural ester insulating liquids[64, 76].

Base liquids	**Antioxidants**	**Ratio of Antioxidants**	**Percentage Increment/Decrement at Room Temperature**
Sunflower oil	PG	1.00 g	−15.00
	AA	1.00 g	−8.00
	BHT + CA	0.5:0.5	−17.00
	α-Tocopherol + CA	0.5:0.5	−17.00
Corn oil	PG	1.00 g	−19.00
	α-Tocopherol + CA	0.5:0.5	−22.00
	BHT + CA	0.5:0.5	−7.00
	AA	5.00 g	−7.00
Castor oil	BHT	0.25%	+35.12
	BHA	0.25%	+40.13
	GA	0.25%	+35.12
Punna oil	BHT	0.25%	−20.12
	BHA	1.00%	−32.22
	GA	0.50%	−14.48
Mustard oil	BHT	1.00%	+21.81
	BHA	0.25%	−10.93
	GA	1.00%	+9.82
Neem oil	BHT	0.50%	+35.95
	BHA	0.25%	−21.61
	GA	0.25%	+0.79
Honge oil	BHT	1.00%	−14.55
	BHA	1.00%	+8.95
	GA	1.00%	+6.71

It is worth noting that the concentration of antioxidants added to the base liquid can also impact viscosity [64]. Additionally, whether antioxidants increase or decrease viscosity, these scenarios may not necessarily negatively affect the oxidation enhancement of the base liquids. Increased viscosity could impede oxygen diffusion processes, slowing down the rate of oxidation. Conversely, decreased viscosity may facilitate better dispersion of antioxidant molecules throughout the base liquid, potentially enhancing antioxidant effectiveness.

Low-viscosity liquids are preferred for efficient cooling in transformers, as supported by established literature regarding their favorable Reynolds number and heat transfer coefficient [8, 128]. However, during transformer operation, various factors like thermal, electrical, and environmental contribute to the deterioration of insulating liquids. Specifically, the oxidation of natural esters leads to the formation of polymeric materials, which, in turn, increases the viscosity of the insulating liquids. This rise in viscosity is attributed to the higher molecular weight of the polymeric materials generated during the oxidation process. The relationship between viscosity and the average molecular weight of the aged liquid is described by the following expression in Equation (2) [48].

$$[\mu] = K\bar{M}^{\propto} \tag{2}$$

where μ is the viscosity of the liquid, M is the molecular weight, and K and α are constants that depend on solvent and temperature [129].

Incorporating antioxidants into natural esters during transformer operation is crucial for maintaining efficient cooling. Antioxidants, whether donors or acceptors interrupt the oxidation process before it reaches the termination stage, where harmful polymeric materials are formed. By preventing this progression, antioxidants help preserve the integrity of the insulating oil and protect against thermal breakdown, consequently enhancing the reliability and longevity of the transformers.

2.8.4. Effect of Antioxidants on the Dielectric Dissipation Factor of Natural Esters

The dielectric dissipation factor is a crucial parameter for assessing the quality of insulating liquids. It is influenced by factors such as ionic conduction and dipolar interaction when materials are subjected to alternating electric fields [130]. During the aging process of natural esters, particularly when transformers are in operation at high temperatures, aging byproducts such as moisture, polymeric materials, acids, and ketones gradually form. These byproducts lead to an increase in the dielectric loss of the insulating liquids. At low frequencies, it is possible to monitor charge transport within the liquids, a means of identifying the presence of foreign materials in the liquid. As aging progresses, the accumulation of byproducts enhances ionic conduction and interfacial polarization, consequently increasing the dielectric loss of the insulating liquids. When the imaginary part of the dielectric response exhibits a slope of -1, it indicates that the loss process is dominated by DC conduction. Furthermore, a dielectric loss exceeding 1 is detrimental to the transformer’s operational lifespan due to the associated dielectric heating. This heating can adversely affect both the dielectric and mechanical properties of the cellulose insulation material within the transformer by reducing its degree of polymerization.

The increase in dielectric loss of natural esters during transformer operation can be minimized by the addition of antioxidants since it prevents or reduces the formation of thermo-oxidation byproducts. The early influence of antioxidants on unaged natural esters is also important as it gives the compatibility of the antioxidants with the liquids. When antioxidants are introduced into natural esters, understanding ionic conduction and dipolar interaction due to the alignment and reorientation of molecular dipoles within the insulating material in response to the electric field is crucial.

The impact of butylated hydroxytoluene (BHT) antioxidants was studied in [131], employing mineral oil, sunflower oil, and rapeseed oil at concentrations of 0.25 wt.%, 0.3 wt.%, and 0.35 wt.%. It was observed that the dielectric dissipation factor of both uninhibited and inhibited oils remained unchanged. In reference [132], the effect of antioxidants, including propyl gallate (PG), citric acid (CA), tert-butyl hydroquinone (BTHQ), and butylated hydroxyanisole (BTHX) on rapeseed oil was examined. At 30 °C, no notable changes in the dissipation factor value were detected across all prepared samples. However, with rising temperatures, an increase in the dielectric dissipation factor was observed, particularly in samples with higher concentrations of antioxidants, which exhibited the highest values. For samples containing 1 wt.% of PG, BTHQ, CA, and BTHX at 90 °C, the dielectric loss of the oil increased by 126.4%, 71.42%, 335.71%, and 128.57%, respectively. This implies that an increase in temperature increases the disorderliness in both oil and antioxidant molecules, leading to an increase in dielectric loss. Among the antioxidants considered, BTHQ demonstrated the least percentage increment in dielectric loss, indicating its superior stability even at elevated temperatures. The rise in dielectric dissipation factor values may be ascribed to heightened molecular mobility within the oil, facilitating easier interaction between oil molecules and antioxidant molecules.

It is, therefore, important to optimize the loading of antioxidants that can improve the oxidation stability of natural esters without compromising the dielectric loss.

2.8.5. Antioxidant Monitoring in Online Transformers

Over the operational life of a transformer, the concentration of antioxidants in insulating oils gradually decreases due to the aging process and the ongoing reaction with free radicals. These antioxidants are crucial for maintaining the stability and effectiveness of the insulating liquid by preventing the formation of harmful byproducts that can lead to deterioration. Monitoring the depletion of antioxidants is, therefore, essential for assessing the health and longevity of the insulating system. A reduction in antioxidant levels can indicate increased oxidative stress and impending failure, making it critical for transformer owners to track these changes over time. Various analytical techniques can be employed to monitor the concentration of antioxidants in insulating oils, each with its unique advantages and applications.

Analytical measurements like high-performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR) spectroscopy are highly sensitive techniques that can be employed in antioxidant monitoring [133, 134].

i. High-Performance Liquid Chromatography (HPLC):

High-performance liquid chromatography (HPLC) is a powerful analytical technique widely used for the identification, quantification, and resolution of compounds [135]. This liquid chromatography method has significant applications across various fields, including research, manufacturing, biomonitoring of pollutants, and pharmaceuticals. The basic principle of HPLC involves injecting a small amount of liquid sample into a flowing stream of liquid, known as the mobile phase [135, 136]. As this mobile phase moves through a column packed with particles of the stationary phase, the mixture separates into its components based on their degree of retention within the column. The retention of each component is determined by its partitioning between the liquid mobile phase and the stationary phase, allowing for effective separation and analysis [135]. In the context of monitoring antioxidants, natural ester insulating oil is passed through a stationary phase, where the antioxidants are separated based on their interactions with the stationary phase. Detectors, such as UV-Vis, are then used to identify and quantify the antioxidant components. HPLC is particularly useful for tracking the concentration of antioxidants and determining the remaining quantity over a specific aging period. The advantages of this analytical technique include its high sensitivity, precision, and capability to analyze a wide range of antioxidants, making it an ideal tool for this purpose [137].

ii. Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatography-mass spectrometry (GC-MS) is also a powerful technique used for the separation and identification of compounds. It involves the vaporization of samples, followed by the separation of components based on their volatility using gas chromatography [138]. The separated components are then further identified and quantified using mass spectrometry. When applied to insulating liquids containing antioxidants, mass spectrometry provides detailed molecular information about the quantity of antioxidants present [139]. Among the numerous advantages of GC-MS are high sensitivity, the ability to provide structural information about antioxidants and the capability to identify an unknown compound in an insulating liquid.

iii. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy is widely used in material synthesis and characterization, particularly for the identification of functional groups in various materials

[128]. This technique measures the absorption of infrared radiation by samples at different wavelengths. Since each antioxidant, whether synthetic or natural, possesses a unique infrared spectrum, FTIR can be employed to identify and quantify their presence in natural ester insulating liquids [140, 141]. Additionally, FTIR is valuable for monitoring the rate of degradation of these liquids in real-time [9, 117, 140]. Furthermore, FTIR is a non-destructive and fast measurement capable of analyzing the quality of both liquid and solid insulators in transformers. It can be used to monitor the early degradation of insulating materials [132].

iv. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR can be used in understanding the degradation of natural ester insulating liquids [142, 143]. It involves the interaction of nuclear spins with an external magnetic field. This interaction causes the nuclei to resonate at specific frequencies, depending on their chemical environment. The resulting NMR spectra provide detailed information about the molecular structure of antioxidants [144, 145]. NMR spectroscopy is not destructive and provides detailed molecular information by detecting the interaction between antioxidants and oil molecules.

2.8.6. Machine Learning and Artificial Intelligence in Oxidation and Antioxidant Monitoring

The introduction of machine learning (ML) and artificial intelligence (AI) is revolutionizing materials research in the new industrial era. These advanced approaches are increasingly being applied in transformer monitoring and condition assessment, with a particular focus on transformer insulation systems [146]. Unlike traditional methods of detecting, diagnosing, and predicting the condition of transformer insulation, ML offers a more cost-effective and efficient technique for transformer health monitoring [147]. The practical applications of ML and AI in transformer oxidative assessment are given as follows.

i. Predictive Models for Oxidation Stability

A key application of ML is the development of predictive models that can forecast the oxidation stability of natural ester insulating liquids. Popular ML models such as adaptive boosting (AdaBoost), random forest (RF), k-nearest neighbor (kNN), artificial neural networks (ANNs), and support vector machines (SVMs) have demonstrated utility in the area of predictive analysis on transformers [148]. These models analyze the chemical composition of insulating liquids alongside key operating conditions like temperature, moisture content, and ambient environment to provide accurate predictions about oxidation behavior and stability.

ii. Integration with Molecular Dynamics

By integrating ML with molecular dynamics simulations, researchers can model the interactions between antioxidant molecules and natural ester insulating liquids at the atomic level. This enables the prediction and optimization of novel antioxidant additives tailored for specific operating conditions. Such approaches have the potential to accelerate research and reduce costs by minimizing the need for extensive laboratory testing [130].

iii. Real-Time Monitoring of Antioxidants

AI-powered systems can play a critical role in the real-time monitoring of antioxidant depletion during transformer operation. Smart sensors embedded in transformers can continuously track antioxidant levels and other parameters, feeding data into AI algorithms for analysis. This allows operators to maximize operational stability, reduce the frequency of offline testing, and prevent rapid degradation of insulating liquids [149]. For example, the application of convolutional neural networks (CNNs) has been applied for analyzing infrared spectroscopic data, enabling precise monitoring of antioxidant levels [150, 151].

iv. Fault Detection and Maintenance Optimization:

ML algorithms, when combined with data from transformer sensors, can identify patterns that indicate early signs of oil degradation or antioxidant depletion. Predictive maintenance strategies powered by AI can, thus, reduce downtime and extend transformer lifespan.

The integration of machine learning (ML) and artificial intelligence (AI) into antioxidant monitoring is still in its early stages, but several promising future directions are emerging. Embedding transformers with the Internet of Things (IoT)-)-enabled sensors and integrating them with AI systems could create a comprehensive, real-time monitoring network capable of automatically adjusting antioxidant levels or recommending corrective measures to maintain optimal insulation performance. Digital twin technology, which involves creating virtual replicas of physical systems, could be extended to include the dynamics of antioxidant behavior in transformer oil. These virtual models would simulate real-time transformer operations, providing predictive insights into antioxidant performance and enabling the timely mitigation of risks. Additionally, the future of transformer operation may involve fully autonomous systems where AI not only monitors antioxidant levels but also manages their replenishment or formulation adjustments in real-time, ensuring optimal performance. However, despite these promising applications, several challenges must be addressed. These include collecting high-quality and representative data from transformers across varying operational conditions, ensuring a sufficient volume of data to train robust ML models, and validating predictive models across diverse transformer systems and insulation types. Addressing these challenges is crucial for fully realizing the potential of ML and AI in oxidation stability and antioxidant monitoring.

2.9 Antioxidants and Other Additives in Insulating Liquids

Natural ester insulating liquids are often formulated with several functional additives, including antioxidants, pour point depressants, metal deactivators (passivators), anti-foaming agents, and viscosity modifiers. The total concentration of these additives is typically limited to no more than 5% to maintain optimal performance and chemical compatibility. It is, therefore, essential to understand the interactions between antioxidants and other additives, as these interactions can significantly impact the oxidation stability and overall performance of the insulating liquid [15]. Among these additives, metal passivators play a crucial role in protecting both the oil and metallic components within the transformer. These compounds form a chemical varnish on the surface of copper, creating an impermeable barrier between the metal and the surrounding oil or insulating cellulose. This dual action prevents the catalytic degradation of oil by copper ions and also protects the copper from chemical attack by the oil. A widely used example of a metal passivator is Irgamet 39™, a benzotriazole-based copper passivator commonly recommended for transformer applications [152]. Studies have shown a strong synergistic relationship between antioxidants and metal passivators [153-156]. Metal deactivators help reduce the catalytic initiation of oxidation reactions, thereby decreasing the oxidative load on antioxidants and enhancing their efficacy. This complementary action contributes to improved long-term oxidation stability of the insulating liquid. Although antioxidants and pour point depressants serve distinct functional roles, recent reports [13,14] have highlighted potential synergistic effects when antioxidants are grafted onto pour point depressants. Such formulations not only improve oxidation resistance but also enhance the low-temperature flow properties of the insulating liquid. However, it is important to note that polar additives such as pour point depressants and viscosity modifiers can influence the solubility, dispersion, and reactivity of antioxidants, particularly in complex multi-component ester systems. These interactions may impact the diffusion and mobility of antioxidant molecules, thereby affecting their radical scavenging performance. Furthermore, potential antagonistic effects must be considered. Certain surfactant-like additives, for instance, may encapsulate antioxidant molecules, reducing their availability to interact with oxidative radicals and diminishing their overall effectiveness. Therefore, understanding and optimizing the compatibility and combined behavior of antioxidants with other functional additives is critical for enhancing the oxidative stability, dielectric performance, and long-term sustainability of natural ester insulating liquids used in transformers.

2.10 Environmental Impact of Antioxidants Used in Natural Ester Oxidation Stability Enhancement

Having an environmental understanding of the effect of antioxidant addition to natural ester insulating liquids is paramount. The chemical composition and biodegradability of antioxidants could pose environmental challenges in the case of accidental release, such as leakage, spills, or during antioxidant refilling to natural ester in service [140]. Natural antioxidants, which are mainly derived from plants, may not pose any significant challenge to the environment since they are non-toxic and readily biodegradable. However, the application of these antioxidants in transformer application is limited due to their poor stability at high temperatures. Synthetic antioxidants, on the other hand, are chemically synthesized, and proper understanding of their interaction with the environment is crucial. The wide application of synthetic antioxidants has exposed the environment (air, soil, and water) to pollution. It was recently reported that synthetic phenolic antioxidants and some of their by-products are found in humans (tissue, serum, urine, breast milk) and the environment [157, 158]. Some are found in mollusks and shrimps [159].

Toxicity studies have revealed that some synthetic antioxidants can be carcinogenic and also cause endocrine disruption effects [160, 161]. Some of the secondary products from synthetic antioxidants during degradation are more dangerous and can cause DNA damage at low concentrations [162]. These secondary products are often from DNA adducts, where electrophilic reactants generated during degradation covalently bind to nucleophilic sites on DNA. This process disrupts the normal structure and function of DNA, leading to mutations if the damage is not properly repaired [163]. The mechanism involves the metabolic activation of these secondary products into a reactive intermediate, which then interacts with the DNA base. For example, the oxygen and nitrogen atoms in DNA bases serve as nucleophilic targets for the electrophilic intermediates forming stable adducts. The adducts can mispair during DNA replication or create structural distortion that blocks replication entirely. If not addressed by DNA repair systems, the resulting damage can contribute to carcinogenesis [164]. While data on the toxicology of some synthetic antioxidants, such as BHT, are limited, studies have shown that sub-lethal doses (0.1–60 μM) of BHT significantly impact zebrafish embryos. Specifically, heart rate was reduced by 25–30%, and doses above 0.1 μM led to increased movement both in terms of distance traveled and speed. Furthermore, exposure to 0.01 μM BHT resulted in increased expression of the dopamine transporter gene. It was also reported in reference [165] concerning zebrafish that the effective concentration (EC50) was 1.375 mg/L, causing cardiotoxicity and teratogenic effects and potentially causing developmental defects in aquatic organisms. These suggest that BHT not only causes acute toxicity but also interferes with the dopamine system in aquatic organisms [166, 167].

Although synthetic antioxidants have been observed to biodegrade rapidly in soil and aquatic environments, with over 95% of some antioxidants degrading within 24 days [162], it is still important to exercise caution to prevent exposure. Synthetic antioxidants have the potential to cause significant health damage if proper precautions are not taken. Therefore, it remains crucial to handle and dispose of synthetic antioxidants responsibly to minimize the risk of adverse health effects and environmental contamination.

2.10.1. Antioxidant-Related Contamination Mitigation Strategy

The adoption of antioxidants to enhance the oxidation stability of natural esters has been crucial in the power industry. This enhancement has prolonged the usability and lifespan of natural esters in liquid-filled transformers, leading to a reduced reliance on mineral-based alternatives [168]. Consequently, this mitigation strategy helps prevent environmental damage caused by hydrocarbon spillage. However, proper handling of natural esters containing antioxidants is needed to prevent environmental and human exposure to these compounds and their by-products, particularly synthetic antioxidants. There are several ways to mitigate environmental contamination.

i. It is of utmost importance to understand the environmental effect of specific antioxidants that are being considered in natural ester enhancement by conducting thorough environmental impact assessments before use. This could involve assessing the toxicity of both the antioxidants and their secondary products in the ecosystem.
ii. Effective handling and storage of natural esters containing antioxidants is important regardless of the toxicity of the antioxidants used. This helps prevent spills or leaks of the liquids by ensuring that the containers are securely sealed, labeled, and stored appropriately.
iii. In the event of accidental oil spills or leaks, it is important to have effective means of oil detection and excellent cleaning measures in place to prevent the release of

antioxidant-containing natural esters. Installing sensors or oil detection alarms in transformer units enables swift response to oil leakages. Furthermore, regular transformer maintenance and monitoring are vital for detecting wear, corrosion, and damage, allowing a prompt intervention to prevent oil leakage or spills.

iv. When insulating oil reaches the end of its life, it is essential to ensure proper disposal in accordance with recommended regulations and guidelines for used oil disposal. Additionally, if the used oils are being considered for recycling, such as conversion into lubricants and biodiesel, it is important to take proper precautions, especially for workers, by providing reliable personal protective equipment.

2.10.2. Oxidation Stability Enhancement of Natural Esters for Sustainable Energy

Electricity is fundamental to modern life, powering essential services across medical, security, industrial, and social sectors. Even brief power interruptions can have severe consequences, including loss of life, security breaches, and significant financial losses for both private and governmental entities. Ensuring a reliable and sustainable power supply is, therefore, a critical necessity. As global electricity demand rises with population growth, power equipment, particularly transformers, is increasingly burdened. The longevity and reliability of transformers are directly tied to the quality of their insulating materials.

In alignment with the United Nations' Sustainable Development Goals, particularly those related to affordable and clean energy, there is a growing shift towards using natural esters as an alternative to traditional mineral insulating oils in transformers. Natural esters are more environmentally friendly, but they have a key drawback, which is low resistance to oxidation, especially at elevated temperatures. This susceptibility to reactive oxygen leads to rapid degradation of the insulating liquids, which in turn compromises transformer reliability and efficiency. This degradation not only diminishes the effectiveness of transformers but also undermines the environmental benefits of using natural esters. In renewable energy applications, such as wind and solar power installations, where sustainability is paramount, the failure of transformers due to poor oxidation stability can result in increased maintenance costs, heightened environmental risks, and reduced overall efficiency. These issues directly conflict with sustainability objectives. Therefore, improving the oxidation stability of natural esters is crucial for enhancing their performance, reliability, and alignment with the goals of sustainable energy. To achieve this, it is essential to thoroughly investigate the compatibility of antioxidants with natural esters and optimize their use in transformer insulation. The benefits of antioxidants in enhancing the oxidation stability of natural esters are as follows.

i. Inhibition of Oxidation Reactions: Antioxidants play a critical role in interrupting the oxidation chain reaction within natural esters. By neutralizing free radicals, which are highly reactive species responsible for initiating and propagating oxidation, antioxidants help prevent the degradation of the insulating liquid.

i. Thermal Stability and Extended Transformer Lifespan: Antioxidants significantly enhance the thermal stability of transformer oils, allowing natural esters to function effectively at high temperatures without experiencing pronounced degradation or thermal aging of insulating components. This improvement in thermo–oxidative stability enables transformers to handle higher and fluctuating loads without compromising efficiency, which is vital for ensuring reliable and sustainable energy.

ii. Increased Compatibility with Existing Transformer Designs: By enhancing the oxidation stability of natural esters, antioxidants also improve their compatibility with existing transformer designs. This increased compatibility supports the broader adoption of natural esters as a replacement for mineral oils, promoting a shift towards more sustainable and environmentally friendly insulating liquids. To achieve sustainable, reliable, and efficient electricity generation and distribution, it is essential to focus on enhancing the oxidation stability of natural esters. The introduction of antioxidants extends the life and performance of transformers and also aligns with the global sustainability goals, making it a key strategy for the future of energy.

2.10.3. Economic Importance of Antioxidants in Natural Ester Enhancement

The application of antioxidants in oxidation stability enhancement of natural esters offers numerous benefits to transformers, including prolonging transformer lifespan and reducing maintenance and replacement frequency, thus saving costs for utilities and operators [169]. The addition of antioxidants to natural esters prevents the degradation of the liquids, which consequently reduces the probability of downtime and associated maintenance expenses, thereby improving operational efficiency and productivity [170]. Furthermore, transformers insulated with natural esters containing antioxidants may achieve improved energy efficiency, resulting in long-term cost savings through reduced energy consumption and enhanced system performance.

2.11 Challenges and Outlook

Despite the proven technical and economic benefits of incorporating antioxidants into natural ester insulating liquids, several challenges persist. The application of antioxidants for enhancing the performance of natural esters remains an evolving area of research, particularly regarding the use of multiple antioxidants, as recommended by CIGRE [171]. One of the key considerations is the variability in fatty acid composition among different natural esters, which directly influences antioxidant behavior and efficacy. Antioxidants may demonstrate varying degrees of effectiveness depending on whether the base liquid is rich in saturated, monounsaturated, or polyunsaturated fatty acids. Generally, antioxidant performance tends to be more pronounced in esters with a higher degree of unsaturation. Consequently, the selection of appropriate antioxidants must be tailored to the specific characteristics of each base liquid to achieve optimal enhancement. Environmental sustainability is another critical concern. Certain synthetic antioxidants are known to exhibit persistence in the environment and pose potential ecological toxicity risks. Thus, minimizing the environmental impact of antioxidant-containing insulating liquids is a vital consideration for green transformer technologies. To mitigate environmental concerns, proper disposal and recycling of used insulating liquids are essential. Oil reclamation processes provide a cost-effective and environmentally responsible approach to reduce the ecological footprint of antioxidants and minimize waste generation. Furthermore, achieving a balance between antioxidant efficacy and preserving other essential physicochemical and dielectric properties of the base liquid presents a significant challenge. Antioxidants must be optimized in a way that enhances oxidation stability without adversely affecting other performance parameters of the liquid. Additionally, ongoing research should focus on advancing the chemistry of antioxidant formulations to develop environmentally benign, biodegradable, and low-persistence alternatives that align with sustainability goals.

Looking toward the future, the development of antioxidants for natural ester insulating liquids should focus on several key directions. First (i), the design of next-generation bio-based antioxidants derived from natural sources such as lignin, tocopherols, and polyphenols, which offer high efficiency with minimal environmental impact, should be prioritized. Second (ii), there is a need to develop multifunctional antioxidants that can simultaneously act as radical scavengers, metal passivators, and stabilizers against hydrolytic degradation. Third (iii), exploring synergistic antioxidant systems, where multiple antioxidants or additives are combined to provide broader and more robust oxidative stability across various operating conditions, is essential. Fourth (iv), the application of machine learning and computational chemistry tools to enable predictive modeling and screening of antioxidant performance based on ester composition and aging profiles can significantly accelerate formulation development. Fifth (v), the incorporation of encapsulated or controlled-release antioxidant technologies, which can deliver antioxidant compounds progressively during transformer operation, may offer a promising potential for extending the service life of insulating liquids. Sixth (vi), the formulation of tailor-made antioxidant solutions that are customized for different transformer designs, operating conditions, and geographical locations, particularly in harsh or subpolar climates, should be considered. Finally (vii), a comprehensive evaluation of antioxidant compatibility within complex multi-additive formulations is necessary to prevent potential antagonistic interactions and enhance additive synergy. Therefore, while antioxidants hold immense promise in improving the longevity and performance of natural ester insulating liquids, further research is needed to resolve compatibility issues, optimize formulation strategies, and ensure long-term environmental safety. Advancing antioxidant science through innovative chemistry and sustainable engineering will be central to supporting the global transition toward more reliable and eco-friendly transformer insulation systems.

2.12 Conclusions

The oxidation of natural ester insulating liquids in transformers poses a significant threat to their functionality, ultimately impacting the socioeconomic activities within a society. This degradation, resulting from oxidation, can lead to the breakdown of the transformer system. While natural esters are viewed as promising alternatives to mineral oil, their susceptibility to oxidation presents certain limitations. As a result, they are primarily utilized in sealed transformers. When natural esters undergo oxidation, they undergo a thickening process and may eventually polymerize. This, in turn, adversely affects both the cooling and dielectric activity of the liquids within the transformer. The importance of antioxidants in the enhancement of natural esters used in green transformers cannot be overemphasized. These materials have boosted the long-term stability of the green alternative insulating liquids, consequently promoting carbon net zero. This ultimately extends the lifespan of transformers and decreases maintenance costs. In addition, antioxidants have reportedly increased the properties of natural ester insulating liquids like AC breakdown voltage and fire safety. However, concerns persist regarding the environmental impact and potential toxicity of antioxidants.

Thus, it is imperative to carefully manage the disposal and recycling of natural esters containing antioxidants in accordance with environmental regulations. Furthermore, there is a pressing need for the development of new environmentally friendly antioxidants that exhibit low persistence and high performance at low concentrations. These advancements are crucial not only for improving the oxidation stability of natural ester insulating liquids but also for minimizing associated environmental risks. Overcoming these challenges can pave the way for broader adoption of natural ester-based insulating liquids in transformers, significantly reducing the power sector's carbon footprint. This aligns with the Sustainable Development Goals (SDG 7: Affordable and Clean Energy, and SDG 13: Climate Action), promoting a cleaner, more sustainable energy infrastructure while minimizing the environmental impact of transformer operations.

2.13. Recommendation

The focus on clean and affordable energy is growing rapidly in both industrial and academic sectors, particularly within the power industry. This trend is driven by increasing environmental and social responsibilities. To ensure the widespread adoption of natural esters as insulating liquids in transformers, it is crucial to address the challenges associated with their poor oxidation stability and the aspect of copper dissolution in the liquid. Despite the advancements in technology, the integration of machine learning (ML) and artificial intelligence (AI) with molecular simulation for the development and monitoring of antioxidants remains largely unexplored in the literature. The application of cutting-edge technologies like ML and AI presents a transformative opportunity for the energy sector. These technologies could play an important role in designing novel, more effective antioxidants that significantly enhance the oxidation stability of natural esters. Furthermore, leveraging AI to optimize the concentration of antioxidants in natural ester formulations could lead to substantial improvements in the performance and reliability of transformer insulation systems. This approach would mark a significant advancement in the industry, aligning with the ongoing transition towards more sustainable energy solutions.

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CHAPTER 3

MÉTHODES EXPÉRIMENTALES ET MATÉRIAUX

ENHANCING OXIDATION STABILITY OF NATURAL ESTERS: A MULTI-RESPONSE STATISTICAL ANALYSIS APPROACH

TITRE: Amélioration de la stabilité à l'oxydation des esters naturels : une approche d'analyse statistique multi réponses

JOURNAL : IEEE Transactions

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ÉTAT DE L'ACCEPTATION; En cours de relecture

RÉSUMÉ: L'exploration des esters naturels en tant que liquides isolants écologiques a suscité un intérêt croissant au cours des deux dernières décennies, en raison de leurs qualités remarquables pour les transformateurs de puissance. Toutefois, leur composition chimique, notamment la présence d'acides gras, les rend plus sensibles à l'oxydation que les huiles minérales, ce qui souligne la nécessité d'améliorations. Cette étude examine l'amélioration thermo-oxydative de deux esters naturels, NE1 et NE2, par l'ajout d'antioxydants : le tert-butylhydroquinone (TBHQ) et l'acide citrique (CA).

La recherche a été menée en deux phases. Lors de la première phase, la stabilité à l'oxydation a été évaluée à l'aide d'un plan factoriel complet pour analyser les réponses cibles — facteur de dissipation, acidité et viscosité — selon des méthodes normalisées. Les résultats, analysés par une analyse de la variance (ANOVA), ont permis d'identifier des concentrations optimales d'antioxydants : 0,2 % en masse de TBHQ et de CA pour NE1, et 0,2 % de TBHQ

avec 0,15 % de CA pour NE2. Le TBHQ a principalement influencé la viscosité et l'acidité, tandis que le CA a eu un impact significatif sur le facteur de dissipation.

Lors de la seconde phase, des essais de vieillissement thermique accéléré ont été réalisés afin d'évaluer le comportement des huiles sous contrainte thermique. Les échantillons traités avec des antioxydants ont montré des améliorations notables de la stabilité à l'oxydation, avec une augmentation de la viscosité limitée à 11,45 % pour NE1, contre 20 % pour NE2 après 1500 heures de vieillissement.

Ces résultats mettent en évidence l'importance d'adapter la formulation antioxydante à la structure chimique des esters naturels, en vue de favoriser leur utilisation à grande échelle dans l'isolation des transformateurs.

3.1 Abstract

The exploration of natural esters as green insulating liquids has gained significant attention over the past two decades due to their exceptional qualities for power transformers. However, due to their chemical compositions, the fatty acids make them more susceptible to oxidation compared to mineral oils, highlighting the need for improvements. This study explores the thermo-oxidative enhancement of two natural esters, NE1 and NE2, through the incorporation of tert-butylhydroquinone (TBHQ) and citric acid (CA) antioxidants. The research was conducted in two phases. In the first phase, oxidation stability was evaluated using a full factorial design to analyze the target responses, dissipation factor, acidity, and viscosity through standard methods. The results, assessed through analysis of variance (ANOVA), identified optimal antioxidant concentrations of 0.2 wt.% TBHQ and CA for NE1, and 0.2 wt.% TBHQ with 0.15 wt.% CA for NE2. TBHQ primarily influenced viscosity and

acidity, while CA notably impacted the dissipation factor. In the second phase, accelerated thermal aging tests were conducted to evaluate the performance of the oils under thermal stress. The antioxidant-treated samples demonstrated significant improvements in oxidative stability, with NE1 showing only an 11.45% increase in viscosity, compared to a 20% increase in NE2 after 1500 hours of aging. These results highlight the importance of tailoring antioxidant formulations to the chemical structure of natural esters, supporting their broader application in transformer insulation.

Index Terms—acidity, aging, antioxidants, dissipation factor, natural ester, optimization, viscosity.

3.2 INTRODUCTION

Transformers are the crucial and indispensable components in an electrical power network which exert a significant impact on network reliability. It has been established that the service reliability or life span of power transformers largely depends on the condition of the oil-paper insulation. Oil in a transformer plays a dual role as insulation and as a coolant to expand the transformer's life span [1]. There is a rising interest in plant-based dielectric liquids for liquid-filled transformers due to their eco-friendly nature and advantages over mineral oil, such as fire safety, biodegradability, hydrophilicity and good insulation. However, natural esters face challenges like poor oxidation stability, high viscosity, low impulse breakdown resistance, and gelling after oxidation, largely due to their fatty acid structure [172]. Natural esters from plants contain fatty acids classified as saturated, monounsaturated, or polyunsaturated, with most being mono- or polyunsaturated. Oils high in saturated fatty acids exhibit greater oxidation stability; however, they crystallize easily, leading to poor cold flow properties, as seen in coconut and palm oils [26]. Oils rich in long-chain unsaturated fatty acids perform well in subzero climates due to the bends in their double bond regions, which weaken intermolecular forces compared to saturated fatty acids. However, natural esters with a high concentration of carbon-carbon double bonds, such as soybean and sunflower oil, are more prone to oxidation. Therefore, the susceptibility of natural ester oils to oxidation becomes more pronounced when transitioning from monounsaturated to polyunsaturated compositions [25].

Oxidation stability is a crucial factor for any dielectric liquid, yet it is observed to be poor in the case of natural ester dielectrics, posing a challenge for their general application in power transformers. This stability is particularly critical for maintaining the lifespan and quality of insulation in transformers, especially in free-breathing distribution transformers. During the oxidation process, highly reactive free radicals are produced, initiating chain reactions with other molecules. These interactions generate additional free radicals, ultimately accelerating oil degradation. Among the products generated during the oxidation reaction of vegetable-based insulating oils are moisture, alkane, ketones, alcohols, and aldehydes [9]. Researchers have introduced various technological advancements to overcome the challenges associated with natural ester oils. These include chemical modifications and the addition of additives like nanoparticles and antioxidants which notably improve the oxidative stability of natural esters [173]. Antioxidants are essential compounds that inhibit or slow the oxidation process by disrupting the chain reactions responsible for oil degradation and scavenging free radicals such as hydroperoxyl and alkyl radicals. They are classified as natural which are derived from plant-based materials such as fruits, herbs, and seeds, or synthetic antioxidants, which are laboratory-produced compounds with no natural origin. In addition, antioxidants can be classified as either donors or acceptors. Donor antioxidants neutralize free radicals by donating hydrogen, while acceptor antioxidants (chain breakers) stop oxidation by reacting directly with free radicals [101].

Over time, various antioxidants have been used to improve the oxidative stability of natural esters, with recent studies focusing on antioxidant combinations to enhance effectiveness through synergistic effects. The combination of antioxidants is based on the recommendation provided by CIGRE Working Group D1.30, which emphasizes the importance of improving the oxidation stability of insulating liquids through optimized additive formulations[171]. For example, Ghani et al. demonstrated that adding citric acid and propyl gallate to rapeseed-based oil significantly improved the dielectric strength and oxidative stability of the oil [10]. It was reported that tert-butylhydroquinone (TBHQ) provided better oxidation stability for natural ester oils compared to other antioxidants, such as butylated hydroxytoluene (BHT), butylated hydroxy anisole (BHA), and propyl gallate (PG) [174]. In reference [76], different antioxidant mixtures were investigated on natural ester oxidation stability enhancement and enhancement of other parameters, like AC breakdown voltage, flash, and fire point, was reported. The report in [101] also stated that the addition of 0.25 wt.% propyl gallate and 0.25 wt.% citric acid significantly enhances the oxidation stability of rapeseed oil. Despite advancements in enhancing the oxidation stability of natural esters, challenges persist, and achieving optimal oxidation stability remains a critical area of research.

Unlike conventional one-factor-at-a-time methods that are costly and time-consuming, this study employs Design of Experiments (DOE) to efficiently optimize mixed antioxidants at different levels. DOE is particularly effective for multi-factor experiments, as it identifies optimal design parameters efficiently while minimizing time and resource expenditure [175]. It has been widely applied in manufacturing and other scientific fields due to its ability to efficiently analyze factor interactions and identify optimal conditions while reducing experimental effort. Although there are several techniques like Full Factorial Design, Fractional Factorial Design, Response Surface Methodology (RSM), Taguchi Methodology, and Central Composite Design (CCD) for parameter optimization in DOE application [176], in this work, Full Factorial Design was adopted due to its ability to comprehensively evaluate all possible combinations of antioxidant levels and provide higher accuracy and reliability in identifying optimal conditions. This ensures a complete understanding of both the main effects and interactions between factors, which is crucial for optimizing oxidation stability [177]

As previously mentioned, the fatty acid composition of natural esters affects their oxidation stability, indicating that optimal antioxidant concentrations may vary between saturated and polyunsaturated fatty acid-based oils. To date, no research has systematically optimized antioxidant loading while considering the fatty acid composition of the base oil. Therefore, the central aim of this study is to enhance the performance of two distinct natural ester oils (NE1 and NE2), each characterized by unique fatty acid profiles, through the combined use of tert-butylhydroquinone (TBHQ) and citric acid (CA), as illustrated in Fig.8a-b. The basic properties of natural esters from their respective data sheet and antioxidants used in this work are given in Table 10 and Table 11 respectively [178]. These antioxidants were chosen for their complementary functionalities, TBHQ reduces the susceptibility of esters to oxidation, while citric acid is an effective radical and hydroperoxide scavenger [173]. To examine their combined effects, a full factorial experimental design was employed, allowing for the evaluation of all potential interactions between variables. The experimental responses considered are key indicators for determining oxidation degradation in an insulating liquid.

These include the dissipation factor, acidity, and viscosity, which are used to assess the synergistic effects of the antioxidant combination on natural esters.

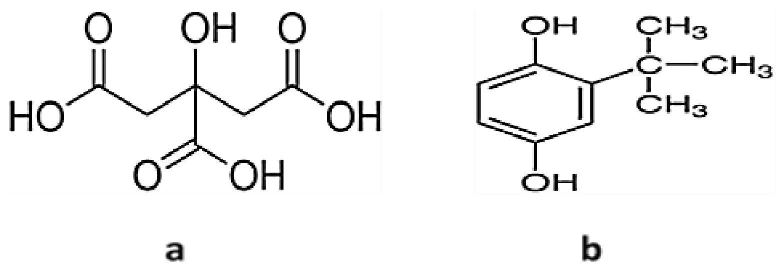


Figure 8: Chemical structure of (a) citric acid and (b) TBHQ.

3.3 Full Factorial Design

The Full Factorial Design (FFD) is an experimental method that systematically examines all possible combinations of factors at different levels to assess both individual and interactive effects. In this study, the factors analyzed were Tert-butylhydroquinone (TBHQ) and Citric Acid (CA), each tested at three concentration levels (0.1, 0.15, and 0.2 wt.%). This resulted in 9 experimental runs ($N = 3^2$), ensuring a thorough evaluation of their influence on oil oxidation stability.

To determine statistical significance, Analysis of Variance (ANOVA) was applied. The F-value, which compares variance between experimental groups to variance within groups, was used to assess the impact of TBHQ and CA. A high F-value, combined with a p-value ≤ 0.05, confirmed that the observed effects were statistically significant, ensuring that the results reflect real trends rather than random variation [19].

3.4 Materials and Methodology

3.4.1. Materials and Sample Preparation

The natural esters insulating oils referred to as NE1 and NE2 in this work are derived from rapeseed and soybean, respectively. The antioxidants used are Tert-butylhydroquinone (TBHQ) and citric acid (CA), and their molecular structures are shown in Fig. 8a-b. The antioxidant concentrations of CA and TBHQ were varied at 0.10, 0.15, and 0.20 wt.% to ensure the total antioxidant content remained within the range recommended by CIGRE [171]. This study used isopropyl alcohol (99.8%) for acid test titration, phenolphthalein as an indicator, ethanol (100%) for oil-antioxidant miscibility, and a copper catalyst.

The samples were prepared following the generated nine runs from the factorial design as given in Tables III and IV. For each oil sample, nine different concentrations of mixed antioxidants were investigated, making 18 samples for the two natural esters. Fig.10 outlines the methodology, from level selection to response analysis. After generating the experimental runs, each natural ester was separately tested with the nine antioxidant combinations. The oil samples were degassed in a vacuum desiccator in the presence of silica gel and dried in a vacuum oven for 72 hours at 70 °C, reducing their moisture concentration to approximately 14 ppm. Due to the insolubility of citric acid in oil, it was initially dissolved in ethanol before being added to the oil along with TBHQ. The mixture was stirred for 30 minutes under controlled conditions to ensure uniform dispersion and residual ethanol was removed by vacuum drying operated at 30 in Hg and 60 °C.

3.4.2 The Oxidation Stability Test

The prepared antioxidant-mixed oil samples were subjected to a thermo-oxidative stability test using the K121XX 6-unit oxidation stability bath, per ASTM D2440 at a constant temperature of 110 °C and oxygen (Extra dry) flow rate of 1 L/hour [179]. A copper catalyst (2.28 g) was introduced into the oil sample to accelerate the oxidation process, simulating the conditions in a transformer. After 48 hours, samples were collected for evaluation.

Figure 9: Oxidation stability set-up

3.4.3 The Aging Test

Thermal aging converts hydrocarbons into polar molecules, reducing unsaturation and increasing viscosity through oxidation, polymerization, and hydrolysis [180]. Accelerated thermal aging was used to simulate the oil's thermal degradation in a shortened timeframe under controlled conditions. Samples were prepared using the antioxidant concentration identified as optimal from the oxidation stability assessment. Both samples without antioxidants (designated NE1 and NE2) and those with antioxidants (designated NE1WA and NE2WA) were aged in open beaker cells at 120 °C according to ASTM D 1934. The aging durations were set at 500, 1000, and 1500 hours.

To evaluate the impact of aging on the insulating fluids, several key properties were analyzed. The total acid number (TAN) was determined following ASTM D974-03 by titrating a 0.1 M KOH solution against 1g of the oil sample, which contained 20 ml of isopropyl alcohol and 2-3 drops of phenolphthalein indicator [181]. Kinematic viscosity was measured at 40°C using a KV3000 viscometer per ASTM D445, with each measurement repeated for consistency [26]. The dielectric loss was measured by a Novocontrol Alpha-A High-Performance Frequency Analyzer at 60 Hz and 25°C, following ASTM D924 [182].

These analyses provided insights into the oxidative stability and dielectric behavior of the aged fluids, offering a comprehensive understanding of the influence of antioxidants on the aging process.

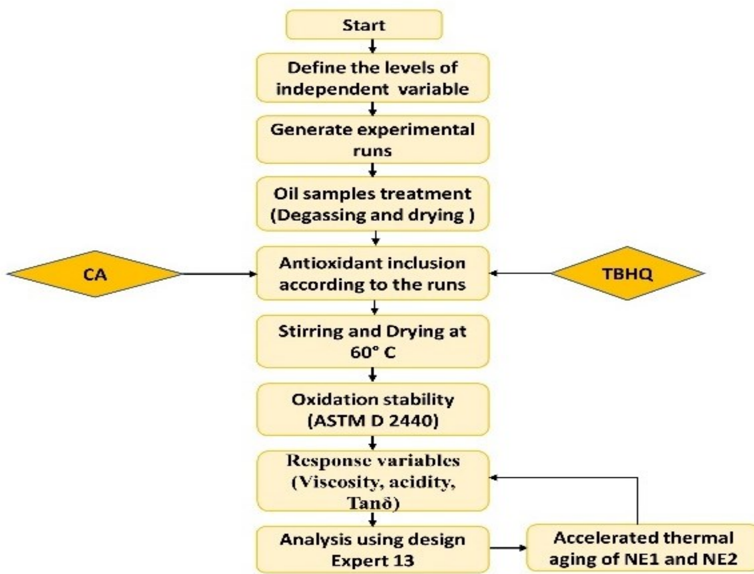


Figure 10: Flowchart of experimental design and analysis

Table 10: Basic Properties of Natural Esters

Properties	NE1	NE2
Fatty acids composition	Dominated with monounsaturated	Dominated with polyunsaturated
Flashpoint (°C)	> 260	> 260
Fire point (°C)	> 350	> 350
Pour point (°C)	-31	-18
Density at 20°C (g/cm^3)	0.92	0.92
Viscosity @ 40 °C (mm^2/sec)	37	32
Appearance	Bright and clear	Bright and clear
Dielectric breakdown (kV) 2.5 mm gap	> 75	> 75
Dissipation factor @ 90 °C	< 0.03	< 0.03

Table 11: Physicochemical Properties of Citric Acid (CA) and Tert-Butylhydroquinone (TBHQ)*[178]*

Physicochemical	Citric acid (anhydrous)	tert-butylhydroquinone
Purity	≥ 99.5 %	97 %
Molecular formula	$C_6H_8O_7$	$C_{10}H_{14}O_2$
Molecular weight	192.12 (g.mol^{-1})	166.22 g/mol
Color	Crystalline white solid	white
Odor	Odorless	Slight aromatic odor
Melting point	153.15 °C Anhydrous	126 -128 °C
Boiling point	175 °C	Decomposes before boiling
Crystal structure	Monoclinic	orthorhombic
Density	1.665 (g.cm^{-3})	1.05g/cm^3
Flash point	Non-flammable	165 °C
Antioxidant function	Chelates metal ions, prevents oxidation	Scavenges free radicals, inhibits lipid oxidation

3.5. RESULTS AND DISCUSSION

3.5.1 Antioxidants Evaluation on Natural Esters

This section examines the impact of antioxidants on the oxidation stability of each natural ester, following the experimental design. Tables 12 and 13 give the experimental outcomes and the performance of the antioxidants in terms of dissipation factor, acidity, and viscosity for NE1 and NE2, respectively, after the oxidation test. Since the goal of the optimization was to achieve the lowest possible values for all responses, the results were analyzed using a "lower is better" approach in the design expert software. The subsequent sections detail both the individual and interactive effects of the antioxidants on each response.

Table 12: Experimental Output for NE1

Runs	Factor 1	Factor 2	Response 1	Response 2	Response 3
	TBHQ (wt.%)	CA (wt. %)	Dissipation factor	Acidity (mgKOH/g)	Viscosity (cSt)
1	0.1	0.15	0.0430	13.549	364.39
2	0.2	0.1	0.0499	9.558	187.75
3	0.2	0.2	0.0368	8.119	182.61
4	0.15	0.15	0.0161	14.132	363.49
5	0.2	0.15	0.0159	7.7498	196.08
6	0.15	0.1	0.0667	10.168	236.51
7	0.15	0.2	0.0151	7.243	171.83
8	0.1	0.2	0.0168	11.351	307.14
9	0.1	0.1	0.0627	15.394	362.59

Table 13: Experimental Output for NE2

Runs	Factor 1	Factor 2	Response 1	Response 2	Response 3
	TBHQ (wt. %)	CA (wt. %)	Dissipation factor	Acidity (mgKOH/g)	Viscosity (cSt)
1	0.1	0.15	0.0190	6.947	291.72
2	0.2	0.1	0.0198	5.839	242.68
3	0.2	0.2	0.0236	5.8166	197.45
4	0.15	0.15	0.0177	6.364	227.44
5	0.2	0.15	0.0183	6.4728	254.44
6	0.15	0.1	0.0153	6.339	269.04
7	0.15	0.2	0.0221	6.8288	287.17
8	0.1	0.2	0.0223	7.1388	374.69
9	0.1	0.1	0.0176	7.3672	367.48

3.5.1.1. Dissipation Factor of NE1 And NE2 After the Oxidation Stability Assessment

Tables 14 and 15 show the ANOVA results for the dissipation factor (DF) of NE1 and NE2 respectively. For NE1, TBHQ has no significant effect (p=0.7707), while CA shows a borderline effect (p=0.0582), with a stronger influence on DF. Similarly, in NE2, TBHQ has no significant impact, but CA significantly affects DF due to its radical scavenging ability, preventing an increase in the DF of the oils [6]. The model's surface plot for NE1, Fig.11a shows that 0.15 wt.% TBHQ and 0.2 wt.% CA yields the best dissipation factor. This matches the experimental values in Table 12 and confirms the model's accuracy. The scatter plot in Fig.11b illustrates a good correlation between predicted and actual values, with points closely aligned to the fit line. For NE2, Fig.12a predicts that 0.15 wt.% TBHQ and 0.1 wt.% CA yields the best dissipation factor, aligning with the experimental values and confirming the model's accuracy and reliability, while the scatter plot in Fig.12b shows a good correlation between predicted and actual values.

Table 14: Dissipation Factor Anova For NE1With R^2= 0.8

Source	Sum of Squares	DF	Mean Square	F-value	p-value
A-TBHQ	0.0001	2	0.0001	0.2781	0.7707
B-CA	0.0026	2	0.0013	6.29	0.0582
Residual	0.0008	4	0.0002		
Cor Total	0.0035	8			

Table 15: Dissipation Factor Anova for NE2with R^2 = 0.91

Source	Sum of Squares	DF	Mean Square	F-value	p-value
A-TBHQ	7.316E-06	2	3.658E-06	2.94	0.1642
B-CA	0.0000	2	0.0000	18.21	0.0098
Residual	4.984E-06	4	1.246E-06		

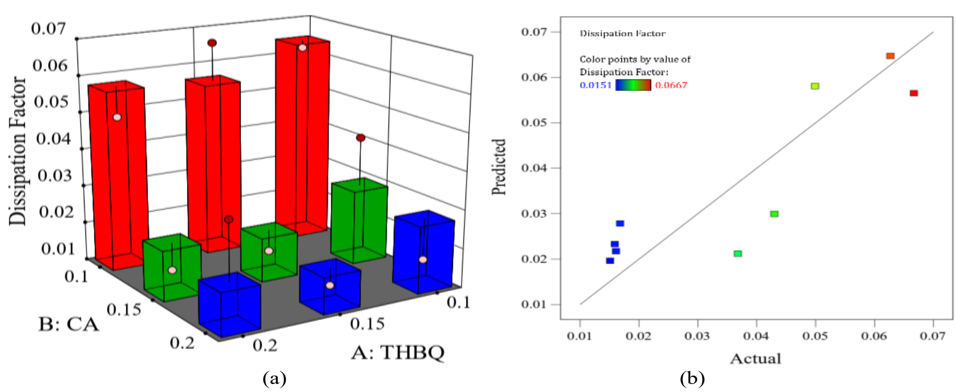


Figure 11: (a) 3D surface plot of DF (b) Correlation between predicted and actual DF for NE1

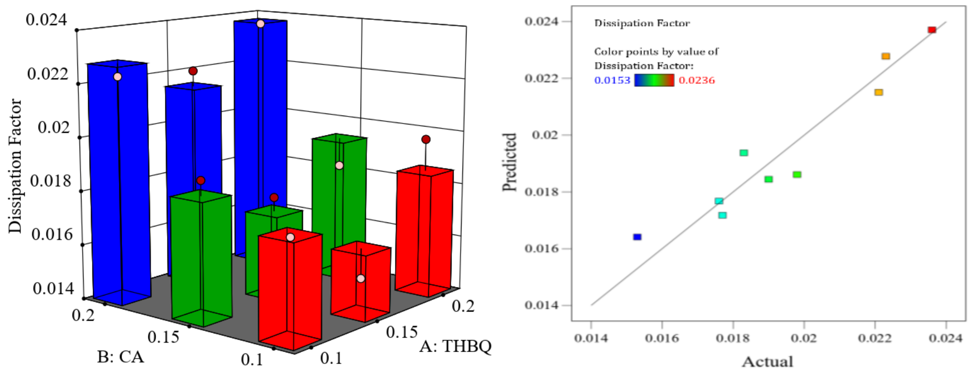


Figure 12: (a) 3D surface plot of DF; (b) Correlation between predicted and actual DF for NE2.

3.5.1.2. Acidity of NE1 and NE2 After the Oxidation Stability Assessment

Table 16 presents the ANOVA results for the acidity. For NE1, neither TBHQ (p=0.1032) nor CA (p=0.2697) significantly affect acidity, as their p-values exceed the 0.05 significance threshold. However, for NE2 in Table 17, TBHQ is statistically significant (p=0.0458), while CA has no significant impact (p=0.9517). In this case, TBHQ is more significant in attaining low acidity. The 3D surface plot for NE1 in Fig. 13a predicts the lowest acidity with 0.2 wt.% TBHQ and CA, but the best experimental result occurs with 0.15 wt.% TBHQ and 0.2 wt.% CA, indicating the model's predictions are accurate despite minor discrepancies. Fig. 13b shows a good correlation between predicted and actual values, indicating the model's accuracy. For NE2, Fig. 14a predicts the lowest acidity at 0.2 wt.% TBHQ and 0.1 wt.% CA, as indicated by the shortest red bar. This is reasonably accurate with the experimental results in Table 13, confirming the model's reliability. The scatter plot in Fig. 14b shows good accuracy for lower to mid-range acidity values, with points closely aligned to the diagonal.

Table 16: Acidity Anova For NE1 With R^2 = 0.80

Source	Sum of Squares	DF	Mean Square	F-value	p-value
A-TBHQ	37.22	2	18.61	4.23	0.1032
B-CA	16.31	2	8.15	1.85	0.2697
Residual	17.62	4	4.41		
Cor Total	71.15	8			

Table 17: Acidity Anova For NE2With R^2= 0.80

Source	Sum of Squares	DF	Mean Square	F-value
A-TBHQ	1.86	2	0.9285	7.35
B-CA	0.0127	2	0.0063	0.0501
Residual	0.5056	4	0.1264	
Cor Total	2.38	8		

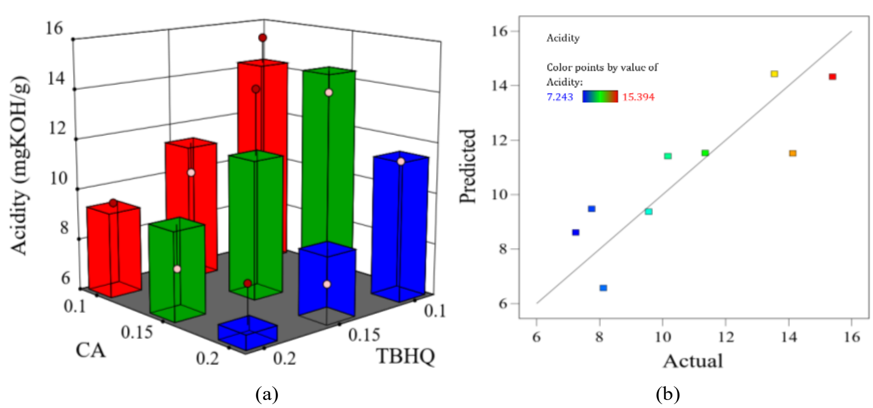
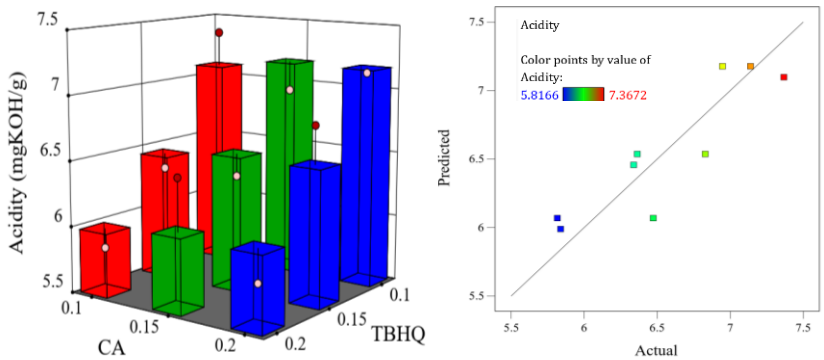


Figure 13: Acidity results for NE1 (a) 3D surface plot and (b) Correlation between predicted and actual Acidity



(a) (b)

Figure 14: Acidity results for NE2 (a) 3D surface plot and (b) Correlation between predicted and actual Acidity

3.5.1.3. Viscosity of NE1 and NE2 After the Oxidation Stability Assessment

Table 18 shows the ANOVA for the viscosity of NE1. TBHQ significantly impacts the oil's viscosity ($p<0.05$), while CA does not. Similarly, for NE2 in Table 19, TBHQ significantly impacts viscosity, but CA does not. For NE1, Fig.15a predicts the best viscosity at 0.2 wt.% TBHQ and CA, but experimental results show the optimal viscosity with 0.15 wt.% TBHQ and 0.2 wt.% CA, confirming that the model is reasonably accurate. Fig. 15b shows a good correlation between predicted and actual values, confirming a good overall model fit. For NE2, Fig. 16a predicts the lowest viscosity at 0.2 wt.% TBHQ and 0.15 wt.% CA as shown by the shortest bar, but the experimental results in Table 13, identify optimal viscosity at 0.2 wt.% TBHQ and 0.2 wt.% CA. This shows the model's reasonable accuracy. Fig. 16b shows points clustered around the fit line, indicating high predictive accuracy with Minor deviations. The viscosity results after the oxidation stability test are closely similar to the findings reported in [183]

Table 18: Viscosity Anova For NE1With $R^2 = 0.83$

Source	Sum of Squares	df	Mean Square	F-value	p-value
A-TBHQ	36633.96	2	18316.98	7.52	0.0441
B-CA	11481.67	2	5740.83	2.36	0.2107
Residual	9742.91	4	2435.73		

Table 19: Viscosity Anova for NE2with $R^2 = 0.80$

Source	Sum of Squares	df	Mean Square	F-value	p-value
A-TBHQ	20632.60	2	10316.30	7.10	0.0483
B-CA	2099.24	2	1049.62	0.7224	0.5397
Residual	5812.23	4	1453.06		
Cor Total	28544.07	8			

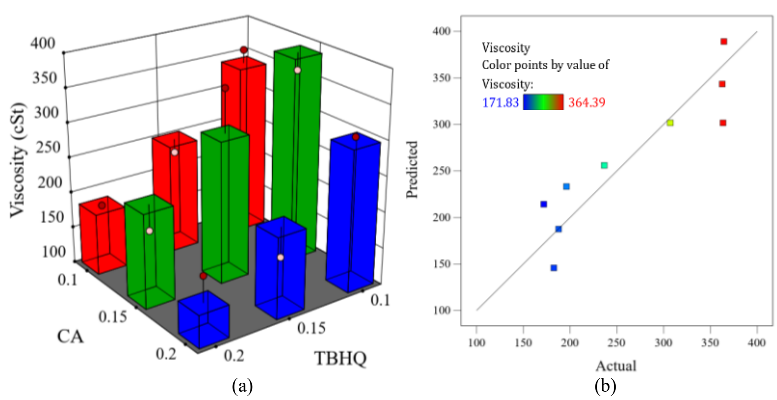


Figure 15: Viscosity results of NE1, (a) 3D surface plot and(b) Correlation between predicted and actual Viscosity

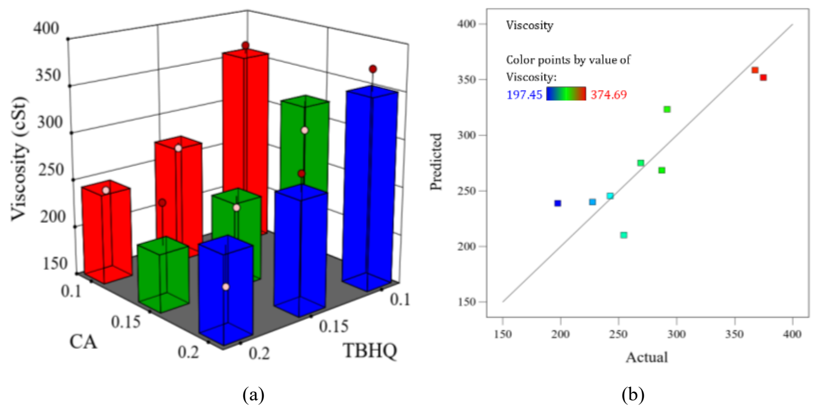


Figure 16: Viscosity results for NE2 (a) 3D surface plot and (b) Correlation between predicted and actual Viscosity

The optimal antioxidant combinations for NE1 and NE2 were determined through the design's numerical optimization after analyzing individual responses across nine categorical factor level combinations, considering dissipation factor, acidity, and viscosity. The best selected solutions, with the highest desirability, are 0.2 wt.% TBHQ + 0.2 wt.% CA for NE1 and 0.2 wt.% TBHQ + 0.15 wt.% CA for NE2, as predicted by the Design Expert.

This implies that achieving stable oxidation resistance in NE1, characterized by low dielectric loss, viscosity, and acidity, requires 0.2 wt.% TBHQ and 0.2 wt.% CA, while NE2 attains similar stability with 0.2 wt.% TBHQ and 0.15 wt.% CA. The optimized concentrations were further evaluated for long-term performance through accelerated thermal aging, with results presented in the next section.

3.5.2. Influence of Antioxidants on Aging of Natural Esters

3.5.2.1. Viscosity

Transformers insulating liquids age over time. Viscosity, which is primarily driven by oxidation, serves as a key indicator of oxidation process. Maintaining a low viscosity is crucial for preserving the cooling efficiency of transformers[9]. Fig. 17 and Fig.118 show the viscosity variations of NE1 and NE2 with and without antioxidants during aging. Both oils initially exhibited similar viscosity behavior following antioxidant addition, with NE1 increasing by 2.19% and NE2 by 1.56%, likely due to the chemical interactions between antioxidants and oil molecules. Antioxidants help preserve oil integrity by slowing oxidation and degradation, reducing viscosity increase, and enhancing long-term stability. The viscosity of NE1 increased by 52.26%, while NE2 increased by 70.51%, indicating a greater oxidative degradation in NE2. Antioxidant-treated oils (NE1WA and NE2WA) in Fig. 19 showed similar viscosity trends, despite base oil differences. This demonstrates that antioxidants consistently slow degradation processes, regardless of the oil type.

At 1500 hours, both antioxidant-treated oils reached nearly identical viscosity values, 42 cSt for NE1WA and 41.97 cSt for NE2WA, as shown in Fig.19. However, the rate of viscosity increases over time differed; NE1WA increased by 11.45%, while NE2WA rose by 20%. This indicates that NE2WA experienced faster degradation despite the final values appearing similar. This suggests that NE2WA undergoes a faster viscosity increase than NE1WA due to its higher content of polyunsaturated fatty acids (PUFAs), which are more prone to oxidation than monounsaturated fatty acids (MUFAs) in NE1WA. While antioxidants slow oxidation, their effectiveness varies with the base oil's fatty acid composition.

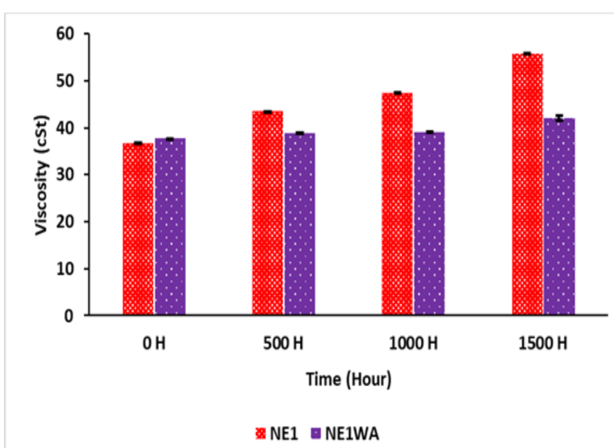


Figure 17: Viscosity of NE1 and NE1WA after aging

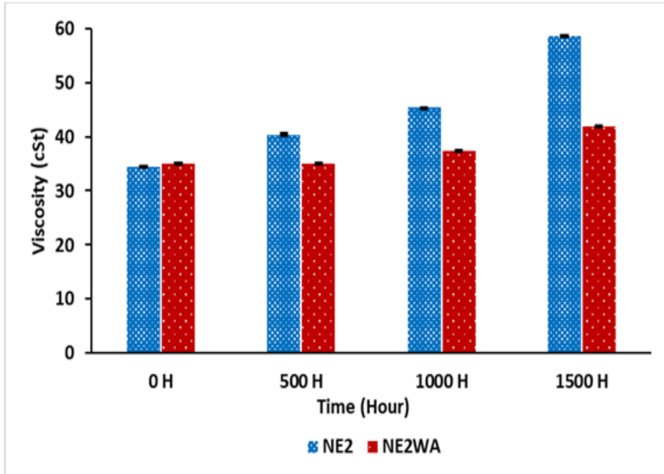


Figure 18: Viscosity of NE2 and NE2WA after aging

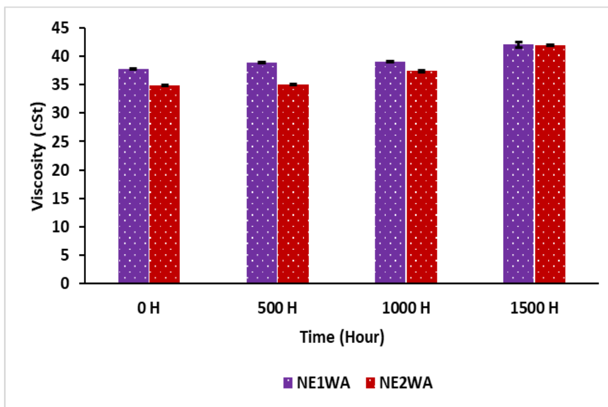


Figure 19: Viscosity of NE1WA and NE2WA after aging

3.5.2.2 Acidity

The addition of antioxidants to the base oils, NE1 and NE2, leads to a slight increase in acidity, as shown in Fig.20 and Fig. 21, respectively. Specifically, the acidity of NE1 increases from 0.04 mgKOH/g to 0.05 mgKOH/g, while NE2 experiences a shift from 0.043 mgKOH/g to 0.054 mgKOH/g. This slight increase in acid values in both oil samples at 0 hours can be attributed to several factors. First, the antioxidants themselves may introduce slightly acidic properties, causing an initial increase in acidity. Additionally, the interaction between antioxidants and pre-existing reactive components in the oil may trigger minor chemical reactions, leading to the formation of acidic by-products [184]. While this initial increase in acidity is noticeable, it does not significantly impact the overall oxidative stability and performance of the oil.

Thermal stress accelerates insulating liquid degradation through oxidation and hydrolysis, breaking down triglycerides into reactive by-products such as carboxylic acids, alcohol, aldehydes, and ketones. These acids can further polymerize into high molecular weight acids (HMAs), increasing acidity and impairing dielectric performance [9]. The effect of thermal aging is evident in Figs. 20 and 21, which show a progressive rise in acidity over time. Similar mechanisms have been reported in prior studies [6, 185, 186]

The rate of acid formation is significantly higher in NE1 and NE2 due to faster degradation without antioxidants. Moreover, NE1 consistently exhibits higher acidity than NE2 at all aging stages, despite being dominated by monounsaturated fatty acids (MUFAs). This phenomenon may be linked to the hydrolysis of short-chain fatty acids in NE1, which undergo degradation more readily due to steric hindrance effects. In contrast, NE2, which contains a higher proportion of long-chain fatty acids, appears to have greater resistance to hydrolytic degradation [122]. The effectiveness of antioxidants in mitigating acid formation is clearly demonstrated in Fig.22, where NE1WA and NE2WA exhibit a significantly slower increase in acidity compared to their non-antioxidant counterparts. This is due to the antioxidants' ability to neutralize free radicals, consequently, preventing the chain reactions responsible for acid formation.

At 1500 hours of aging, NE1WA and NE2WA reach similar acid values of 0.09 mgKOH/g and 0.094 mgKOH/g, respectively, despite differences in fatty acid composition and antioxidant concentration levels. This highlights the importance of optimizing antioxidant concentration for improved performance in natural ester-based insulating liquids.

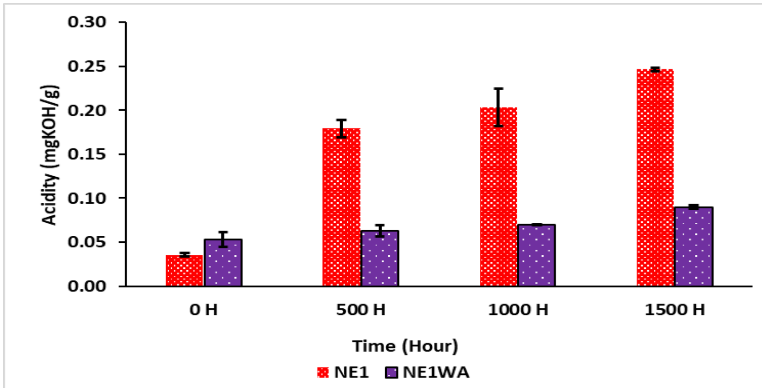


Figure 20: Acidity of NE1 and NE1WA after aging

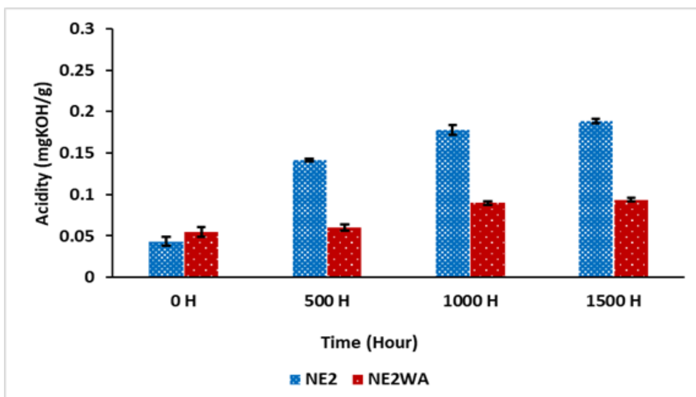


Figure 21: Acidity of NE2 and NE2WA after aging

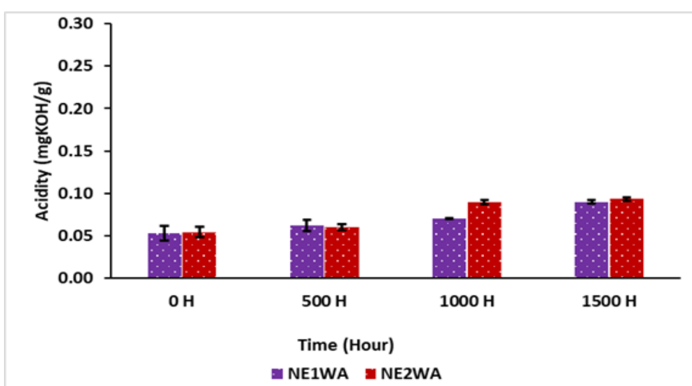


Figure 22: Acidity of NE1WA and NE2WA after aging

At 1500 hours of aging, NE1WA and NE2WA reach similar acid values of 0.09 mgKOH/g and 0.094 mgKOH/g, respectively, despite differences in fatty acid composition and antioxidant concentration levels. This highlights the importance of optimizing antioxidant concentration for improved performance in natural ester-based insulating liquids.

3.5.2.3 Dielectric loss

Dielectric loss in natural esters results from conduction and polarization mechanisms. As aging progresses, the accumulation of polar molecules, moisture, and acids within the oil leads to an increase in dielectric loss. As shown in Fig. 23 and Fig.24, the dielectric loss of the samples without antioxidants increases significantly over time. NE1 exhibited a dielectric loss of 0.025 at 1500 hours, whereas NE2 recorded a value of 0.016 at the same aging duration. Despite this increase, all the dielectric loss values remained within the acceptable limits defined by ASTM D6871-17 [172]. The higher dielectric loss observed in NE1 may be attributed to the dissociation of acids generated from hydrolysis during aging, likely due to the presence of short-chain fatty acids. In contrast, NE2, which predominantly consists of long-chain fatty acids, exhibited relatively lower dielectric loss. This observation aligns with the acidity results discussed in the previous section.

Antioxidant-treated oils, NE1WA and NE2WA, showed reduced degradation rates. Fig. 25 shows NE1WA maintaining lower and more stable dielectric loss than NE2WA. Both exhibited minimal loss, with NE1WA slightly better due to the antioxidants' stabilizing effect on the chemical structure of NE1, which enhances its resistance to thermal and oxidative stresses [25].

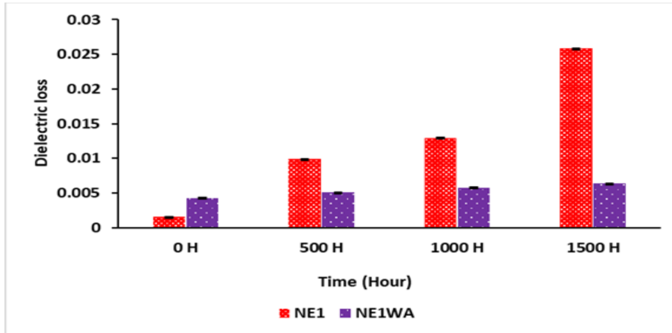


Figure 23: Dielectric loss of NE1 and NE1WA after aging

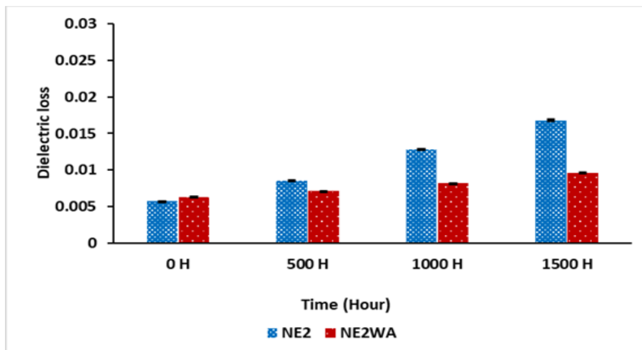


Figure 24: Dielectric loss of NE2 and NE2WA after aging

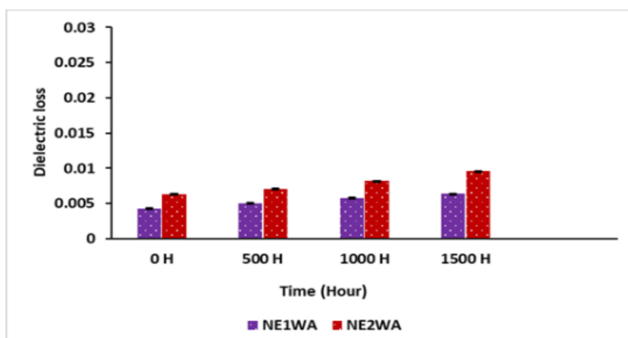


Figure 25: Dielectric loss of NE1WA and NE2WA after aging

3.6 Conclusion

This study comprehensively examined the impact of antioxidant additives on the oxidative and aging performance of two different natural ester insulating liquids through both experimental evaluation and statistical analysis. It took into consideration the performance of antioxidant reactions in different fatty acid compositions, and the conclusions are as follows:

i. Using a full factorial design, this study successfully optimized antioxidant concentrations for the two esters: 0.2 wt.% TBHQ and 0.2 wt.% CA for NE1, and 0.2 wt.% TBHQ and 0.15 wt.% CA for NE2. These formulations effectively enhanced thermo-oxidative stability.

ii. Under 1500 hours of accelerated thermal aging, the antioxidant-treated samples showed marked improvements. NE1WA exhibited only an 11.45% increase in viscosity compared to 20% for NE2WA, alongside lower dielectric losses.

iii. All treated samples complied with the dielectric loss and viscosity limits specified in ASTM D6871-17 and IEEE Std C57.147-2018, confirming their practical relevance. The superior performance of NE1WA is linked to its higher oleic acid content and lower degree of unsaturation, which improves its oxidative resistance.

iv. The findings demonstrate that the effectiveness of an antioxidant is influenced by the molecular structure of the base oil, particularly its fatty acid profile. Therefore, antioxidant concentrations must be tailored to each ester's chemical composition. Further validation in real-world transformer environments is recommended.

3.7 Acknowledgment

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CHAPITRE 4
CONCLUSION GÉNÉRALE ET RECOMMANDATIONS

4.1 CONCLUSION

Cette thèse a permis d'examiner expérimentalement le potentiel des additifs antioxydants pour améliorer la stabilité à l'oxydation des liquides isolants à base d'esters naturels utilisés dans les transformateurs de puissance. À travers un plan expérimental complet et une analyse statistique rigoureuse, les résultats ont montré que l'ajout de combinaisons spécifiques d'antioxydants, telles que l'acide citrique (CA) et le tert-butylhydroquinone (TBHQ), peut améliorer de manière significative les performances thermiques et oxydatives de deux esters naturels distincts.

L'approche par plan factoriel complet a permis d'identifier les concentrations optimales d'antioxydants pour chaque type d'ester, soulignant ainsi l'importance d'adapter le traitement antioxydant à la composition en acides gras de l'huile de base. Cette étude a permis d'optimiser les concentrations des antioxydants comme suit : 0,2 % en masse de TBHQ et 0,2 % de CA pour NE1, et 0,2 % de TBHQ et 0,15 % de CA pour NE2. Ces formulations ont efficacement amélioré la stabilité thermo-oxydative des huiles étudiées.

Les résultats des essais de vieillissement thermique accéléré ont confirmé que les échantillons traités avec des antioxydants présentent une meilleure résistance à l'acidité, de meilleures propriétés diélectriques, et des variations de viscosité mieux contrôlées que les échantillons non traités, tout en conservant leur stabilité thermique pendant le vieillissement. Il est à noter que la formulation à base de NE1 (NE1WA) a montré de meilleures performances que celle à base de NE2 (NE2WA), ce qui souligne l'influence de la structure moléculaire et du degré de saturation en acides gras sur la résistance à l'oxydation.

Ce travail apporte des preuves solides que l'intégration soigneuse de formulations antioxydantes sélectionnées peut réduire efficacement la dégradation oxydative, prolongeant ainsi la durée de vie opérationnelle et la fiabilité des esters naturels dans les applications de transformateurs. Il contribue également à l'enrichissement des connaissances en faveur de la viabilité des fluides isolants écologiques dans les systèmes électriques à haute tension.

Ces améliorations ne sont pas seulement d'ordre technique ; elles s'inscrivent aussi dans une perspective de durabilité, en réduisant la dégradation environnementale et en soutenant la transition mondiale vers des systèmes énergétiques à faibles émissions de carbone. Cependant, malgré ces avancées, une attention particulière doit être portée à la sécurité environnementale et à la gestion des esters traités aux antioxydants. Le développement de nouveaux antioxydants écologiques, à faible persistance et à haute efficacité, demeure une priorité.

4.2. RECOMMANDATIONS

Cette thèse présente l'effet de la combinaison d'antioxydants sur l'acidité, la viscosité et le facteur de dissipation d'un liquide isolant à base d'esters naturels pour application dans les transformateurs. Toutefois, une validation complémentaire dans des conditions réelles d'exploitation est fortement recommandée.

En prolongement de ce travail, les recherches futures devraient explorer d'autres combinaisons d'antioxydants ainsi que les effets synergiques potentiels, notamment en envisageant des hybrides naturels-synthétiques, afin d'identifier des formulations encore plus efficaces. Cela inclut également l'étude d'autres paramètres physicochimiques et diélectriques essentiels, ainsi que la compatibilité des huiles traitées avec les matériaux d'isolation solide.

Par ailleurs, des recherches futures pourraient explorer le potentiel de régénération des esters naturels traités aux antioxydants après vieillissement, afin de comprendre leur comportement à long terme et d'évaluer s'il est possible de restaurer leurs propriétés fonctionnelles par des techniques de régénération physique ou chimique.

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