# Methods used to enhance the physicochemical properties of natural ester insulating oils for transformers: a review

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## **ABSTRACT**

Natural ester insulating oils, derived from vegetable-based feedstocks, are increasingly regarded as sustainable alternatives to conventional mineral oils due to their high fire point, biodegradability, and lower environmental impact. However, their widespread adoption in high-voltage equipment is constrained by their inherent limitations, such as lower oxidation stability, higher viscosity, and poor low-temperature performance. In this review, the three principal enhancement strategies developed to address these shortcomings are examined. The use of antioxidants is analysed for its role improving oxidative resistance and flow characteristics. Transesterification is evaluated as a chemical modification method to alter the molecular structure, thereby enhancing viscosity and thermal stability. Refining and adsorbent treatments are discussed with respect to oil purification and regeneration, emphasising their adsorption efficiency and influence on dielectric performance. A comparative evaluation of these methods highlights their relative effectiveness, scalability, and practical challenges in implementation. This review underscores that no single approach is sufficient, and a combination of different methods is desirable to achieve optimal performance. These insights provide researchers with clear directions for further investigation while offering practitioners a knowledge base to guide the selection and application of enhanced natural ester insulating oils for reliable, long-term transformer operation.

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## 1. INTRODUCTION

Insulating oils are widely used in power equipment for the generation, transmission, and distribution of electrical power [1]. Among the examples of power equipment that use insulating oils are bushings, tap changers, circuit breakers, capacitors, paper-insulated lead cables, and transformers [2], [3]. Insulating oil serves as a dielectric coolant to dissipate heat and improve the efficiency of power transformers, traction transformers, instrument transformers, and even special transformers. Numerous studies have been carried out on insulating liquids, and most of these studies are focused on the use of insulating liquids in distribution transformers [4]. This is because a large number of transformer units are used for distribution compared with those used for generation and transmission. Because distribution transformers are installed in residential

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areas, environmental, safety, and health issues have become a major concern due to the fact that mineral insulating (MI) oils are used as the dielectric liquids in these transformers. In addition, issues on the sustainability of resources and physicochemical properties of MI oils have led scientists and researchers to search for alternative insulating liquids such as silicone oils, synthetic ester oils, mixed liquids, nanofluids, and natural ester insulating (NEI) oils [5]–[9]. NEI oils have gained popularity due to the flammability of MI oils in polychlorinated biphenyls.

Moreover, MI oils were declared as toxic and harmful to the environment by the United States of Health and Human Services in the mid-1970s [2]. NEI oils are basically liquids whose chemical structures are composed of triglycerides. According to the BS EN 62770 (2014) standard, NEI oils for transformers can be divided into two variants: i) unused natural ester or virgin vegetable oil (VVO), mainly composed of triglycerides (where three fatty acids are attached to a glycerol backbone), and ii) low viscosity insulating fluids derived from natural esters (which mainly consist of fatty acid esters or mixtures of triglycerides and fatty acid esters). Fatty acids are categorized into two types: i) saturated fatty acids and ii) unsaturated fatty acids. Saturated fatty acids contain carbon chains without double bonds, whereas unsaturated fatty acids contain carbon chains with one, two, or three double bonds. The unsaturated fatty acids are classified as monounsaturated fatty acids and polyunsaturated (di-unsaturated and tri-unsaturated) fatty acids.

NEI oils are found to be the best candidates to replace MI oils because of their high fire points and flash points, non-toxicity, and good biodegradability. In addition, unlike MI oils, NEI oils do not contain corrosive sulphur, and these oils are hygroscopic fluids with a high level of moisture saturation [10]–[16]. However, NEI oils have poor oxidation stability, higher pour points, low resistance towards lightning impulse, and higher viscosity compared with the standard requirements for insulating oils [17]–[24]. At present, much effort is being made to improve the physicochemical properties of NEI oils. This includes improving the oxidation stability by mixing the NEI oil with antioxidants and reducing the oil viscosity by esterification and adsorbent treatment. These methods are reviewed in more detail in the following sub-sections.

## 2. METHODS USED TO IMPROVE THE PHYSICOCHEMICAL PROPERTIES OF NEI OILS

The general principles, types, and effects of using antioxidants, chemical modification through transesterification, refining, and adsorbent treatment on the properties of NEI oils are reviewed in this section. These methods are developed to improve the properties of NEI oils, making it possible to prolong the expected lifetime of NEI oils. Each method is discussed in more detail as follows.

## 2.1. Antioxidants

For the last 50 years, one of the most popular methods to improve the dielectric or physicochemical properties of NEI oils has been by the addition of additives. These include several chemical products which operate as inhibitors, passivators, electron scavengers, and pour point depressants [2]. Their concentration in the oil may vary significantly depending on the additive, ranging from parts per million to several percent. Several studies have shown that the addition of antioxidants enhances the essential properties of NEI oils, such as oxidation stability and dielectric strength. Antioxidant is defined as a radical and hydrogen peroxide scavenger additive that protects various kinds of materials from free radicals and oxidation. Antioxidants have been used in various applications, including pharmaceutical, food safety, packaging, and lubricants. One of the major drawbacks of NEI oils is their low oxidation stability [25]. Oxidation stability is defined as the time taken for oxidative degradation. In general, even though the oxidation process is gradual, it can be hastened by the presence of metal particles, as well as heat and light [26]. The oxidation process can affect the quality and lifetime of NEI oils.

Numerous studies have been carried out to improve the oxidation stability of NEI oils by the addition of antioxidants. The addition of antioxidants can promote the oxidation stability and slow down the oxidation process of NEI oils [27]–[31]. Antioxidants reduce the amount of free radicals, which can generate oxidation reactions and significantly accelerate corrosion [32]. Since the antioxidants remove free radicals, this will significantly reduce corrosion [33]. The enhancement in the properties (e.g., AC breakdown voltage, viscosity, flash point, fire point, and acidity) of NEI oils by the addition of antioxidant mixtures is also reviewed in this section. In general, phenolic antioxidants are most frequently used in vegetable oils and biodiesels owing to their cost, chemical structure, quality, availability, and performance [34]. The addition of phenolic antioxidants such as butylated-hydroxy-anisole (BHA), butylated-hydroxy-toluene (BHT) (also known as 2,6-di-tert-butyl-pcresol), propyl gallate (PG), tertiary-butyl-hydro-quinone (TBHQ), octyl gallate (OG), dodecyl gallate (DG), pyrogallol (PY), and ethoxyquin (EQ) help promote the oxidation stability of NEI oils [28], [29], [31], [35]. Previous studies pertaining to the properties of NEI oils upon the addition of antioxidant mixtures are summarized in Table 1. It can be seen that the addition of antioxidant mixtures enhances the essential properties of NEI oils for use in power transformers.

						mixtures

	Antioxidant	•			Enhancemen	t ratio (%)		
Ref.	mixture	Oil	Concentration	AC breakdown voltage	Viscosity	Flash point	Fire point	Acidity
[30]	Selenium+	Sunflower oil	0.5 g selenium+	32.2	-98.1	-	-	100.0
	Beta carotene	Mahua oil	0.5 g beta	-25.1	61.5	-6.7	-7.2	-300.0
		Rice bran oil	carotene	-42.9	-22.8	-7.4	-9.9	0.0
		Neem oil		38.8	43.5	-5.2	-4.8	0.0
[31]	BHT+ α-tocopherol	Marula oil	1 g BHT+ 1 g α α- tocopherol	5.3	-7.4 at *RTP	6	3	33.3
[36]	Propyl gallate (PG)+Citric acid (CA)	Rapeseed oil	0.25 wt.% PG+ 0.25 wt.% CA	4.5-6.0	-	-	-	-
[30]	Selenium+TB	Sunflower oil	0.5 g selenium+	4.5	-111.6	-	-	0.0
	HQ	Mahua oil	0.5g TBHQ	-32.0	65.3	3.7	2.8	-200.0
		Rice bran oil		-28.6	-28.1	-14.7	-8.5	-50.0
		Neem oil		25.5	66.7	0.9	-0.8	50.0
[30]	TBHQ+	Sunflower oil	0.5 g TBHQ+	10.2	-13.7	-	-	-1300.0
	Beta carotene	Mahua oil	0.5 g beta	6.2	67.1	1.9	1.4	-300.0
		Rice bran oil	carotene	-28.6	-38.6	-7.4	-5.6	-25.0
		Neem oil		7.5	40.3	5.7	4.4	33.3
[30]	Selenium+	Sunflower oil	0.33 g	-14.7	-112.2	-	-	-700.0
	Beta	Mahua oil	selenium+	15	58.7	-	-	0.0
	carotene+	Rice bran oil	0.33 g beta	-14.3	-33.3	-11.8	-7.0	-50.0
	TBHQ	Neem oil	carotene+0.33 g TBHQ	-8.0	35.2	10.0	9.6	50.0
[37]	Acetic acid (AA)+Citric acid (CA)	<i>Terminalia</i> catappa kernel oil	0.15 wt.% AA+ 0.15 wt.% CA	41.0	11.0	7.8	-	-

<sup>\*</sup>RTP=room temperature

#### 2.2. Transesterification

There are three types of fatty acids, namely, saturated, monounsaturated, and polyunsaturated fatty acids. Each type of fatty acid determines the oil properties (viscosity, acidity, oxidation stability, and electrical properties). Owing to differences in the fatty acid composition, the properties of NEI oils differ from one another. To date, commercial NEI oils based on rapeseed, soybean, castor, sunflower, and palm oils are chemically modified in order to ensure that their properties comply with those set in international standards for oil-immersed power transformers.

The three types of chemical modification methods (transesterification, refining, and treatment with adsorbents) are reviewed in this section. Transesterification is a process of converting triglycerides into diglycerides and then into monoglycerides in the presence of an alkali or acid, producing fatty acid esters and glycerol. Chairul *et al.* [38] conducted transesterification of waste cooking oils with methanol in the presence of an alkali catalyst, potassium hydroxide (KOH), in order to produce transformer insulating oil.

The transesterification process was conducted using the following parameters: i) catalyst concentration: 0.7 wt.%, ii) methanol-to-oil molar ratio: 4:1, iii) reaction time: 48 h, and iv) reaction temperature: 60 °C. The results showed that the color of the oil changed from dark brown to light brown, the acidity reduced from 2.7920 mg KOH/g to 0.2561 mg KOH/g, the kinematic viscosity reduced from 40.84 to 14.19 mm2/s, and the flash point reduced from 269 to 184 °C. Based on the results, the acidity and flash point did not fulfill the requirements stipulated in the IEEE C57.147 standard.

On the other hand, Deraman *et al.* [39] performed transesterification of waste cooking oil with methanol in the presence of an alkali catalyst (NaOH) by mechanical stirring (500 rpm), producing methyl ester. The following settings were used for the transesterification reaction: i) sodium hydroxide (NaOH) catalyst concentration: 0.75 wt.%, and ii) reaction temperature: 60 °C. According to the IEEE C57.147 standard, the acidity of the oil should be less than or equal to 0.06 mg KOH/g. The results showed that the color of the waste cooking oil changed from dark brown to light brown after the transesterification reaction. Sitorus *et al.* [40] produced *Jatropha curcas* methyl ester by transesterification with methanol and KOH.

The reaction parameters used in their work were: i) KOH catalyst concentration: 4.0 wt.%, ii) methanol-to-oil molar ratio: 1:6, iii) reaction time: 4 h, iv) reaction temperature: 63 °C, and v) agitation speed: 400 rpm. The results showed that the acidity reduced from 0.9200-1.5000 mg KOH/g to 0.0708 mg KOH/g, which was slightly higher than the acidity specified in the IEEE C57.147 standard. The physicochemical properties of the *Jatropha curcas* methyl ester complied with the requirements stipulated in the IEEE C57.147 standard, except for the flash point and pour point. The properties of the methyl esters after transesterification discussed in this section are tabulated in Table 2.

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Iable / Pro	nerties of t	hree tyne	s of methy	il ester atter	transesterification
1 auto 2. 1 10	permes or i	m cc $typc$	o or memy	i cotoi aitoi	u ansesterme auton

Property	Waste cooking oil methyl ester (WCOME) [38]	Waste cooking oil methyl ester (WCOME) [39]	Jatropha curcas methyl ester (JMEO) [40]	IEEE C57.147 <sup>TM</sup> 2018 standard
Acidity (mg KOH/g)	0.2561	0.2578	0.0708	≤0.06
Colour, ASTM units	-	-	L0.5	_ ≤1.0
Flash point (°C)	184	-	191	≥275
Kinematic viscosity at 40 °C (mm <sup>2</sup> /s)	14.19	-	10.45	≤50
Density at 25 °C (g/cm <sup>3</sup> )	0.8966	-	0.8960	≤0.96
Pour point (°C)	-28	-	0	≤-10
AC breakdown voltage (kV/mm)	30.0	33.4	87.0	≥20
Water content (mg/kg)	156.40	75.12	64.91	≤200

#### 2.3. Refining

In general, crude vegetable oils extracted from oil seeds have a dark color and contain solid constituents such as proteins and fibers [12]. According to Li et al. [41] and Fernández et al. [4], the refining process consists of three steps: i) alkali refining, ii) bleaching, and iii) deodorization. These oils are treated to obtain a refined, bleached, and deodorized oil, which is the starting material used to develop a candidate fluid. Next, research made by Beltran et al. [42] initiated the use of Jatropha curcas oil as a transformer insulating oil. Jatropha curcas oil is a non-edible oil extracted from the seeds of the Jatropha curcas plant, which is widely found in Mexico. They implemented refining to ensure that the properties of the oil fulfilled the requirements set by international standards for insulating oils. During the refining process, the oil underwent three types of operation: i) acid degumming, ii) chemical neutralization, and iii) bleaching. During acid degumming, the gums were separated from the crude oil by heating the oil with citric acid solution, followed by centrifugation. The process reduced the phospholipids, calcium, magnesium, and iron salt contained in the oil, which improved the oil viscosity, acidity, and fire point by 2, 1, and 1%, respectively. During neutralization, they used NaOH to reduce the free fatty acids in the oil. This process improved the oil viscosity, acidity, and fire point by 2, 90, and 2%, respectively. Finally, they conducted bleaching using bleaching earth and the oil was filtered with a membrane filter to enhance its color and reduce the presence of oxidation by-products and metals. The oil viscosity, acidity, and fire point were improved by 3, 90, and 3%, respectively.

Ghislain et al. [43] initiated the use of palm kernel oil as a transformer insulating oil. Palm kernel oil is an edible oil that is widely available in regions with a tropical climate. The refining of crude palm kernel oil has been applied through neutralizing, washing, and drying processes following a previous study by Boyekong et al. [44]. During the neutralization process, they used a solution of caustic soda and mixed it with crude palm kernel oil for 5 min to neutralize the free fatty acids present in the oil. Finally, the neutralized oil was washed with distilled hot water and filtered to remove the neutralization sludge. This process improved the acidity and viscosity of the oil by 99.6 and 18.7%, respectively. The color appearance of the crude palm kernel oil also changed from yellow to bright yellow. However, the AC breakdown voltage, flash point, and fire point were reduced to 1.2, 25, and 28.4%, respectively. Das et al. [45] investigated the potential of coconut oil as a transformer insulating oil. Matharage et al. [46] conducted refining treatments (neutralizing and bleaching) on virgin coconut oil to produce refined coconut oil. They then compared the refined coconut oil to commercial natural esters and mineral oils. This process improved the acidity, viscosity, and flash point of the oil by 97.7, 11.4, and 32.4%, respectively. However, the refining process significantly reduced the AC breakdown voltage of the refined coconut oil by 41.7%.

Chairul *et al.* [47] proposed a similar method to improve the quality of used vegetable oil (UVO). They selected UVO in their research owing to the lack of studies pertaining to the development of UVOs as transformer insulating oils, as well as the higher acidity of these oils compared with other vegetable oils. They implemented a two-step refining process, alkali refining and bleaching. Alkali refining was performed with NaOH (normality: 2.0 N) to produce neutralized UVO and reduce the amount of free fatty acids present in the oil. The oil acidity was the lowest after the alkali refining process, corresponding to a reduction of 94.83% relative to the acidity of the UVO. Next, they applied a two-cycle bleaching process with fuller's earth adsorbent (total concentration: 20 wt.%), and they filtered the oil with a membrane filter to enhance the color and further reduce the acidity of the oil. After the bleaching process, the color rating of the oil was enhanced to L0.5 while the acidity was reduced to 0.1228 mg KOH/g. However, the acidity was still higher than the value stipulated in the BS EN 62770 standard (0.06 mg KOH/g).

Meanwhile, Wu and Zhang [48] introduced alkali refining with KOH in order to reduce the acidity of crude *Jatropha curcas* oil. They optimized the KOH catalyst concentration and time of the refining process. The following KOH catalyst concentrations were considered in their study: 0.0, 0.1, 0.5, 1.0, 3.0, and 5.0 wt.%. The optimum KOH catalyst concentration and alkali refining time were determined based on the acidity of the oil. The acidity reduced from 9.342 to 0.096 mg KOH/g when the KOH catalyst

concentration was increased from 0.1 to 1.0 wt.%. Next, the crude *Jatropha curcas* oil was treated using 1 wt.% of KOH and stirred at different refining times (5, 10, 20, 30, 60, and 90 min). In general, the acidity of the oil decreased with an increase in the refining time. The acidity reached its minimum value (0.096 mg KOH/g) when the refining time was 30 min, after which the acidity tended to stabilize. The oil acidity was improved by 99%. Even though the oil acidity reduced from 9.342 to 0.096 mg KOH/g, the acidity was still higher than the value set in the BS EN 62770 standard (0.06 mg KOH/g). The properties of the NEI oils after the refining process, discussed in this section, are presented in Table 3. Based on the results, it can be deduced that to improve the properties of NEI oils, it is best to combine a few chemical modification methods, rather than implementing a single method.

Table 3. Physicochemical and electrical properties of NEI oils after three stages of refining

				[42], [43],						
		A .: 1:4.	C-1	AC	Insulati Flash	ing oil pro Fire	operties Kinematic	M-:	D	Pour
Refining	Oil	Acidity (mg	Colour	AC breakdown	point	point	viscosity	Moisture content	Density at 15°C	point
process	Oli	KOH/g)		voltage	(°C)	(°C)	at 40°C	(mg/kg)	$(g/cm^3)$	(°C)
		KOII g)		(kV)	( 0)	( 0)	(mm <sup>2</sup> /s)	(mg/kg)	(g/cm)	( C)
	Jatropha	1.5900	-	-	312	354	33.76	-	0.91	-9
Dagumming	curcas									
Degumming	oil									
	UVO	-	-	-	-	-	-	-	-	-
	Jatropha	0.0100	-	-	328	358	34.01	-	0.91	-9
	curcas									
	oil									
	UVO	0.2825	L2.0	-	-	-	-	-	-	-
	Jatropha	0.0960	-	-	-	-	-	-	-	-
Neutralization	curcas									
1104114112411011	seed oil		~				• • • • •			
	Palm	0.05	Bright	76.3	210	240	29.60	-	-	-
	kernel		yellow							
	oil									
	Coconut oil	-	-	-	-	-	-	-	-	-
		0.0400			220	362	22.47		0.91	0
	Jatropha	0.0400	-	-	330	362	33.47	-	0.91	-9
	<i>curcas</i> oil									
	UVO	0.1228	L0.5							
Bleaching	Palm	0.1226	LU.3	-		_	_	-	_	_
Dicacining	kernel	-	-	-	-	-	-	-	-	-
	oil									
	Coconut	0.0500	_	35	298	_	25.70	_	_	_
	oil	0.0000		23	-20		20.70			

### 2.4. Adsorbents

Abderrazzaq and Hijazi [27] introduced a multi-stage filtration method to enhance the properties of olive oil. The olive oil was processed to pass several tests: AC breakdown voltage, acidity, dissipation factor, moisture content, viscosity, and flash point. Figure 1 shows the three stages involved in the multi-stage filtration method. The method was proven to be successful owing to the number of filtration stages and the use of fuller's earth absorbent. The acidity of the olive oil was reduced by 70-80% after the third filtration stage, indicating the effectiveness of the method.

Chairul *et al.* [47] devised a different method to reduce the acidity of bleached used cooking oil by adding synthetic silicate adsorbent at a concentration of 15 wt.%. The properties of the oil were evaluated according to the BS EN 62770 standard. They found that the addition of synthetic silicate absorbent maintained the color rating at L0.5 and reduced the acidity of the bleached used cooking oil from 0.1228 to 0.0182 mg KOH/g, which fulfilled the acidity requirement (≤0.06 mg KOH/g). However, the flash point of the oil was still lower than the recommended minimum value of 250 °C specified in the BS EN 62770 standard.

Meanwhile, Čejková [49] studied the removal of acidic substances and the improvement of acidity and properties of natural rapeseed oil through the use of adsorbents. The results showed that the rapeseed oil had a higher moisture content and acidity compared with MI oil. They used simple laboratory filtration devices and adsorbents such as fuller's earth and basic lumina, which were activated by heat. The addition of fuller's earth and basic lumina was found to improve the properties of the rapeseed oil, where the acidity reduced from 0.091 to 0.020 mg KOH/g, the moisture content reduced significantly from 87.4 to 44.3 mg/kg, and the dissipation factor enhanced from 0.00477 to 0.00315. However, the AC breakdown voltage of the rapeseed oil reduced from 73.5 to 58.5 kV.

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Sari [50] conducted further treatment on an alkyl ester oil (a derivative product of crude palm oil) by adding activated carbon and silica gel adsorbent to improve the properties of the oil. The addition of the activated carbon and silica gel activated by heat at am oil-to-adsorbent ratio of 5:1 significantly improved the ester oil properties, where the acidity reduced from 0.045 to 0.0315 mg KOH/g, the water content significantly reduced from 1383 to 262.3 mg/kg, the AC breakdown voltage increased from 19.08 to 48.5 kV, the viscosity increased from 2.99 to 2.73 mm2/s, and the color rating improved from 0.9 to 0.8. This method clearly shows that the addition of silica gel and activated carbon as adsorbents, followed by a heating process, is recommended as an adsorbent treatment to obtain the optimal chemical, electrical, and physical properties of the alkyl ester oil.

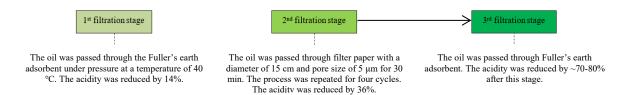


Figure 1. Multi-stage filtration method for olive oil

# 3. CONCLUSION

NEI oils present a viable and sustainable alternative to MI oils in transformer applications, offering significant advantages in terms of fire safety and environmental compatibility. However, their broader adoption is constrained by limitations in oxidation stability, viscosity, and low-temperature performance. In this review, three key enhancement strategies (additives, transesterification, and adsorbent treatments) have been examined, detailing their mechanisms, benefits, and constraints. Additives can effectively improve oxidative resistance and flow characteristics, transesterification enables molecular modification for better thermal and cold-weather performance, and adsorbent treatment supports purification and regeneration. Even though each method demonstrates specific advantages, the integration of multiple methods offers the greatest potential for achieving high-performance insulating fluids that meet operational and regulatory requirements. Continued research is essential to address the long-term ageing behavior of NEI oils, their compatibility with solid insulation, as well as standardized testing procedures. Advancements in these areas will accelerate the transition towards natural esters as a mainstream dielectric fluid, contributing to safer, more reliable, and environmentally responsible power systems.

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## **AUTHOR CONTRIBUTIONS STATEMENT**

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#### CONFLICT OF INTEREST STATEMENT

The authors declare that there are no conflicts of interest that could have influenced the work reported in this paper.

# DATA AVAILABILITY

Data availability is not applicable to this paper as no new data were created or analysed in this study.

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