



Physico-Chemical and Electrical Properties of Epoxy Ethyl Esters of Various Vegetable Oils as Bio-Transformer Oils

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Abstract

Chemically modified vegetable oils are biodegradable and eco-friendly particularly in comparison to petroleum transformer lubricant and insulating oils. These advantages motivate us to investigate the use of soybean, sunflower and cook waste vegetable oils as suitable transformer oil alternatives. It is crucial to compare its physicochemical and electrical properties to those of transformer mineral oil to the American Standard Technical Methods (ASTM) specification to confirm its appropriateness. In This Study soybean, sunflower and cook waste oils undergo a two-step chemical modification by transesterification reaction with ethyl alcohol and potassium hydroxide as catalyst at 60 °C followed by epoxidation reaction with hydrogen peroxide and glacial acetic acid in amberlite IR – 120 resins. The physicochemical and electrical properties of synthesized bio-transformer oils were examined without the presence of tert-butyl hydroquinone (TBHQ) as antioxidant and after applying oxidation conditions with the addition of TBHQ using approved methods. The chemical parameters that are measured include acid value, water content and oxidation stability. The physical characteristics that were tested were density, dynamic viscosity at 40 °C and flash point, breakdown voltage is the electrical property that was measured. Most of the data showed that the different characteristics properties of the ethyl ester of various vegetable oils meet the standard ASTM values after the addition of 2 grams of TBHQ antioxidant. Epoxidation of ethyl vegetable oil an improvement in the physico-chemical and electrical properties occurred with and without TBHQ antioxidant, Consequently, it can be used as a substitute for traditional transformer oil because it complies with most ASTM standard requirements.

Keywords: Bio-transformer oil, Ethyl epoxy, Waste cooking oils, Transformer oil, Antioxidant

1. Introduction

The ongoing pursuit of sustainable economic development today necessitates the wise use of resources and energy, including spending money on renewable re-sources and environmentally friendly practices. There has been a lot of focus on the development of alternative fluids, particularly vegetable insulating oils made from renewable resources [1]. The most popular insulating liquid for transformer applications is mineral oil, about which a substantial body of information has been amassed over time. Other oils are being considered for use as transformer insulating fluids due to improved environmental, safety, performance, and economic factors [2]

Since the development of transformers containing oil in the late 1880s, vegetable oils or esters have been utilized as dielectric fluids. The first natural esters were discovered to be incompatible with free breathing apparatus due to their oxidation characteristics, and mineral oils eventually took their place [3]. Bio-transformer oils are seen as more environmentally friendly than mineral oils because they are entirely bio-degradable, non-toxic, and PCB (polychlorinated bi-phenyl) free, which makes leak protection and subsequent disposal easier. Vegetable oils are also much safer than mineral oils due to their higher flash and fire points (larger than 300 °C), earning them the designation of Less-Flammable Dielectric Liquid [4]. Vegetable oils (VOs) are mostly composed of a triglyceride of long-chain

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unsaturated fatty acids. Most of the double bonds in the chains of fatty acids are unconjugated [5]. At lower temperatures, they exhibit poor thermo-oxidative stability, poor bio-resistance, poor hydrolytic stability, and poor fluidity. Consequently, they cannot be used as biodiesel-based stocks or additives directly [6]. The end consequence is the production of an insoluble deposit in vegetable oils, which raises the acidity, viscosity, corrosion, and volatility of the oil [7].

A low-quality feedstock must first undergo trans-esterification, which involves converting the free fatty acids (FFAs) in the feedstock into esters using an acid catalyst. This creates a combination of fatty acid alkyl esters and triglycerides. For the most part, short-chain alcohols like methanol or ethanol are utilized as the base and either potassium or sodium hydroxide is employed as the catalyst when producing biodiesel. Although either base can be used to produce methyl ester, potassium-hydroxide is discovered to be more suited for the manufacture of ethyl ester biodiesel, [8] to produce bio transformer oil, the esters from the second stage are epoxidized using hydrogen peroxide [9,10]. The epoxidation of its olefinic properties is one of the most crucial phases in creating a bio transformer oil (base stock and/or additive) from vegetable oils. Free fatty acids, esters, and vegetable oils can be epoxidized either in-situ or ex-situ in the presence of peracids by changing the following reaction parameters: reactant molar ratio, temperature, solvent type, presence, or absence of a catalyst (mineral acids or ion exchange resins), stirring rate, type of peroxyacid (peracetic, performic, or *m*-chloro perbenzoic acid), mode and rate of H₂O₂ [11].

In a transformer, mineral oil has been employed as the dielectric medium. Vegetable oils do, however, have costs, usage duration, and oxidation stability restrictions [12]. The examined vegetable oils exhibited a significant potential for oxidation. Tert-butyl hydroquinone (TBHQ), an antioxidant, was added to the ethyl ester and epoxy ethyl ester to lessen oxidation, improving the oxidation stability of bio transformer oils [13,14]. In contrast to direct vegetable oils or aged vegetable oils used as fuels in some adapted diesel engines, bio-transformer oil is a refined fuel that is easily used in diesel-engine vehicles. [15].

The aim of this study was to investigate the physicochemical and electrical properties of epoxy ethyl esters derived from various vegetable oils as potential bio-transformer oils. The vegetable oils studied included soybean oil, sunflower oil, and waste cooking oils. The properties of these bio-transformer oils were compared to those of mineral

oil, following the American Standard Technical Methods (ASTM) specification, to determine their suitability as transformer oil alternatives.

2. Materials and Methods

2.1. Materials

Oils: Two vegetable oils (soybean and sunflower oils) were purchased from the open market in Aswan Governorate, Egypt. Whereas the waste cooking oil was collected from homes, oils were filtered to get rid of the impurities. It should be mentioned that these vegetable oils were employed for two major reasons: either they are readily available (waste cooking, soybean, and sunflower oils), or they have a high potential for application in our location due to their ability to withstand harsh conditions.

Chemicals: Ethyl alcohol (99%), anhydrous potassium hydroxide (97.5%), anhydrous magnesium sulphate, tert-butyl hydroquinone (TBHQ) (97%), glacial acetic acid (95%), sodium bicarbonate (99%) were used. Amberlite IR-120 resin, hydrogen peroxide H₂O₂ 30 %, sodium bicarbonate NaHCO₃(99%).

2.2. Methods

2.2.1. Trans esterification of vegetable oil to ethyl esters

In a 125 ml Erlenmeyer flask fitted with stirring hot plate, 1 g of anhydrous KOH was mixed with 20 ml of pure ethanol. 100 gm of VO in 250 ml conical flask was heated to 60 °C then the potassium ethoxide added to the VO on stirring followed by few drops of glacial acetic acid which it is used as medium for complete the separation. The reaction time was 1 h. The content of the flask was transferred to a separating funnel and rest for 30 min. The upper layer is the ethyl ester, which was washed 3 times with warm distilled water, then dried using anhydrous magnesium sulphate and filtrated. then placed in rotary evaporator under reduced pressure to remove the excess ethanol. and was neutralized by sodium bicarbonate to remove excess amount of acetic acid [16].

2.2.2. Epoxidation of ethyl ester vegetable oil to epoxy ethyl ester vegetable oil

Acetic acid (7 g) was placed in a 125 Erlenmeyer flask followed by the addition of amberlite IR-120 (16 wt%). The mixture was then stirred continuously and followed by the addition of 1.5 M of hydrogen peroxide per mole of ethylenic unsaturation (According to mole calculation and the iodine value of the ethyl ester of vegetable oils) to the mixture to produce peracetic acid (PAA). Ethyl ester of vegetable oil (100 g) was placed in a three-necked flask and was heated to 70 °C followed by the addition of the PAA mixture gradually and slowly

due to the exothermic medium. This was allowed to react at 70 °C for 7 h with continuous stirring. (Aliquots were taking out every 1 h for FTIR analysis to determine the maximum reaction time at 70 °C). The sample was then purified with 5% NaHCO₃ to neutralize the remnant acid present and filtrated to remove sodium bicarbonate. The sample was dried over anhydrous magnesium sulphate. and then filtrated to remove anhydrous magnesium sulphate, the amberlite IR 120 can be washed and reused for a new Epoxidation reaction [17].

2.3. Characterization

2.3.1. Gas chromatography

The composition of the ethyl ester was analysed with GC, the analysis was carried out using Hewlett Packard Gas Chromatography apparatus (Model G1512A Autosampler Control Module - 7673C Tower for the 6890 GC - 7673C Tra) The column utilised had the following specifications: 0.25 mm ID, 0.25 mm thickness, and 30 m length. It was a Thermo- Scientific Trace GOLD TG-5MS Column. For most Gas Chromatography applications, this Thermo Scientific Trace GOLD TG-5MS column, which has a 5% diphenyl/95% dimethyl polysiloxane composition, has low-polarity. This phase has a maximum operating temperature of 350 °C and provides very little bleed. The oven's temperature was first maintained at 160 °C for 2 minutes, then increased to 180 °C at 2 °C/min and maintained for 2 minutes, before being steadily raised to 250 °C at 10 °C/min and maintained for 2 minutes. The temperatures of the injector, transfer, and source were 250°C, 260°C, and 240°C, respectively. Helium served as the carrier gas, and the scan took 24 minutes [18].

2.3.2. Fourier Transform Infrared (FT-IR) Spectrometry

The FTIR spectra was carried out using Cary 630 FTIR Spectrometer. The IR light used in ATR sampling passes through a crystal, was completely internally reflected at least once at the crystal-sample interface, and then was directed to an FTIR detector. A portion of the IR light enters the sample during internal reflection, where it might be absorbed. The evanescent wave is the part of the light that penetrates the sample. The difference in refractive indices between the sample and the ATR crystal determines the depth of the evanescent wave's penetration into the sample. A drop of the sample was placed on the spectrometer measurement then cell. The sample was scanned with infrared radiation through frequency of KBr 7,000 to 350 cm⁻¹ to obtain the spectrum. The amount of radiation absorbed by the sample was plotted as a function of the wave number of the absorbed radiation by a detector. Each spike (ab-sorption bands) in the IR

spectrum represents absorption of energy. The functional groups of the epoxy ethyl ester of soybean, sunflower and cook waste samples were identified [19].

The polyester obtained will be divided to 4 parts with different weights of TBHQ antioxidant which are: (0 weight [un inhibited oils] - 0.4 gm [trace inhibited oils] – 2 gm [full inhibited oils] – 3 gm [saturated inhibited oils]), while epoxy alkyl ester vegetable oils will be divided to 2 parts with and without TBHQ antioxidant [0–2 gm]. This applied to the critical characteristics tests according to ASTM methods and the results were compared with international standard specifications ASTM.

It is imperative to measure the crucial traits after ap-plying oxidation of the synthesized oils in presence of TBHQ antioxidant to evaluate the improvement that will be achieved after the addition of TBHQ antioxidant. Conditions of the oxidations is After reaching the required temperature (70 °C), the sample began to oxidise in an open-air cup in the oven. The experiment was terminated after 4 hours by rapidly chilling the sample and keeping it at room temperature for subsequent analysis. To the addition of TBHQ antioxidant, the appropriate amount of antioxidant was given to 100 ml of sample, which was then completely dis-solved by ultrasonic for 15 minutes [67].

2.3.3. Characterization of Physical, Chemical and Electrical Properties of Synthesized Vegetable Oils

2.3.3.1. Density

The primary factor affecting the quantity of mass injected is density. Density information is crucial for many unit processes in the manufacture of biodiesel. The rotational viscometry principle is used by Brookfield viscometers; it states that the torque needed to rotate an object in a fluid, such as a spindle, reveals the fluid's viscosity, The viscous drag of the test fluid against the spindle is measured by applying torque through a calibrated spring to a disc or bob spindle that is sub-merged in the fluid [20].

2.3.3.2. Dynamic Viscosity

ASTM D7042 mandates the application of a rotating method. The metal spindle type S0₂ is attached to the viscometer, and 12 ml of sample is placed at the bottom. The maximum level of the sample was higher than the spindle marks as recommended. The spindle rotated in the sample at a fixed RPM, and the torque needed to rotate the spindle as well as the viscosity was measured [21].

2.3.3.3. Flash Point

Transformer oil's flash point is the temperature at which the oil will ignite. Using the Pensky Martens equipment, a brass test cup is filled with a test specimen and covered with a lid, through which an ignition source may be intermittently injected, the

capacity to tolerate arcing fire dangers during operation is indicated. Depending on the material being examined, the sample is heated and swirled at specific rates. The creation of an equilibrium between the liquid and the air volume is made possible by this. At regular intervals, the ignition source is directed into the cup while the stirring is simultaneously stopped. The test is over when a flash is seen spreading throughout the interior in the cup. The corresponding temperature is the liquid's flash point [22].

2.3.3.4. Water Content

Karl Fisher reagent was used in this method to titrate oil with solvent to an electrometric end point. Bunsen is an analytical technique and the underlying principle. Iodine and sulphur dioxide react in an aqueous media, and the process is changed to estimate the water content. a non-aqueous system with an excessive amount of sulphur dioxide [23].

2.3.3.5. Acidity

To determine the amount of KOH required to neutralize the acid in 1 g of oil, 10- 12 gm of oil and 100 ml of isopropyl in presence of 10 – 12 drops of Phenol Ph as indicator and titrated with 0.1 N potassium hydroxide [24].

2.3.3.6. Oxidation Stability (Rancimat Method)

This test method evaluates the oxidation stability of oil using an oxygen-pressured vessel in the presence of water and copper catalyst at 110 °C. The tested oil, water, and copper catalyst coil are contained in a covered glass container and were added to a vessel equipped with a pressure gauge, the vessel was charged with oxygen to gauge pressure, and the results were recorded [25].

2.3.3.7. Breakdown voltage

An electric volt is raised by 2 kv between two electrodes and immersed in the tested sample, a spark appears as the volt of breakdown [26].

2.4. Statistical analysis

By using MINITAB (Ver. 2021), the ANOVA statistical analysis two ways factor was performed to expect the effect of two factors on the physico-chemical and electrical properties of Ethyl and epoxy ethyl of (Soybean, Sunflower, and Cook Waste) vegetable oils.

3. Results and Discussion

It is noticeable from first chemical modification of various vegetable oils (transesterification) that acetic acid was necessary to be used as a catalyst to complete the reaction, which leads to the separation of the compound into two layers, one biodiesel layer and the other is glycerol, and according to previous studies, in this case the studied vegetable oils considered to be low quality. Since studied vegetable oils (soybean and sunflower) cannot be used as foodstuff and can therefore be regarded as waste, it is evident from the chemical treatment that the current study regarded as recycling of these oils rather than disposed of [29].

3.1. Spectrometry Identification

3.1.1. Gas Chromatography (GC) of the Synthesized Esters

The fatty acid composition of biodiesel made from soybean, sunflower and cook waste oil and the results are shown in Table (1). A computerised integrator determined the relative percentage of fatty acid esters from total ion chromatography. It is noted that chemical modification of previous vegetable oil shared the same chemical composition in terms of the percentage and retention time during the 1st chemical modification (transesterification), and it was illustrated by Table (1) that these oils contain a large percentage mixed poly unsaturated fatty acids represented in Linoleic acid (C18:2) which is unsaturated oils, and this explains the high iodine value of those oils even after the first chemical treatment, may account for sunflower biodiesel's lower oxidative stability compared to soybean and cook waste biodiesel with lower ethyl linoleate concentrations. As a result, FAEE analysis is essential to determine the approximate concentration of antioxidants and their requirement.[30] This outcome is consistent with research done by Mohammed A. Zayed et al., Ana Carolina et al and George Anastopoul et al, who produced biodiesel from used soybean, sunflower and cook waste oils, Their FAEE analysis revealed that the main fatty acids in these bio-diesels were linoleic acid and oleic acid. [30, 31, 32] Consequently, as ethyl linoleate is the primary FAEE obtained, it may affect some properties of soybean, sunflower, and cook waste biodiesel.

Table (1): Fatty acid profile of alkyl ester vegetable bio transformer oils.

Fatty acids	Soybean oil	Sunflower oil	Waste cooking oil
Palmitic acid (C16:0)	8.31	7.12	7.32
Palmitoleic acid (C16:1)	4.34	2.76	4.85
Palmitic acid (C16:0)	2.94	3.80	2.88
Stearic acid (C18:0)	16.99	23.38	17.71
Oleic acid (C18:1n9c)	7.34	7.40	9.61
Oleic acid (C18:1n6c)	35.32	38.57	34.16
Linoleic acid(C18:2n 6c)	16.69	12.88	20.13
Linoleic acid (C18:2n 6t)	4.42	2.22	1.84
α , Linolenic acid (C18:3n3)	2.02	0.74	1.10
γ , Linolenic acid (C18:3n6)	0.22	0.36	0.17
Arachidic acid (C20:0)	1.39	0.75	0.25

The FT-IR spectra of the products of second chemical modification (epoxidation) for epoxy ethyl ester of (soybean, sunflower and cook waste) vegetable oils samples are shown in Figures (1-a, b and c) the conjugated double bond of ethyl linoleate is a reactive component of the molecular structure and is more vulnerable to oxidation [39-40]. This may account for sunflower biodiesel's lower oxidative stability compared to soybean and cook waste biodiesel with lower ethyl linoleate concentrations. As a result, FAEE analysis is essential to determine the approximate concentration of antioxidants and their requirement. While some of the peaks in the

3.1.2 Fourier Transform Infrared (FT-IR) Spectrometry of Epoxy Ethyl ester: epoxy samples are common, the other are distinctive to each sample and are known as characteristic peaks. These peaks were used as the samples' unique fingerprints. 2930.7 cm^{-1} and 2855.6 cm^{-1} which indicates the presence of the C–H stretch, while the peak at 1740 cm^{-1} are an assignment for C=O stretch, The transmittance signals C-O-C stretching from the oxirane vibration appears at around 1245 cm^{-1} , and the peaks around 824.7 and 848.9 cm^{-1} are the fingerprint The most representative signal reveals the oxirane group in the epoxidized ethyl ester, The appearance of a large band around at 3423.7 , 3434.5 ,

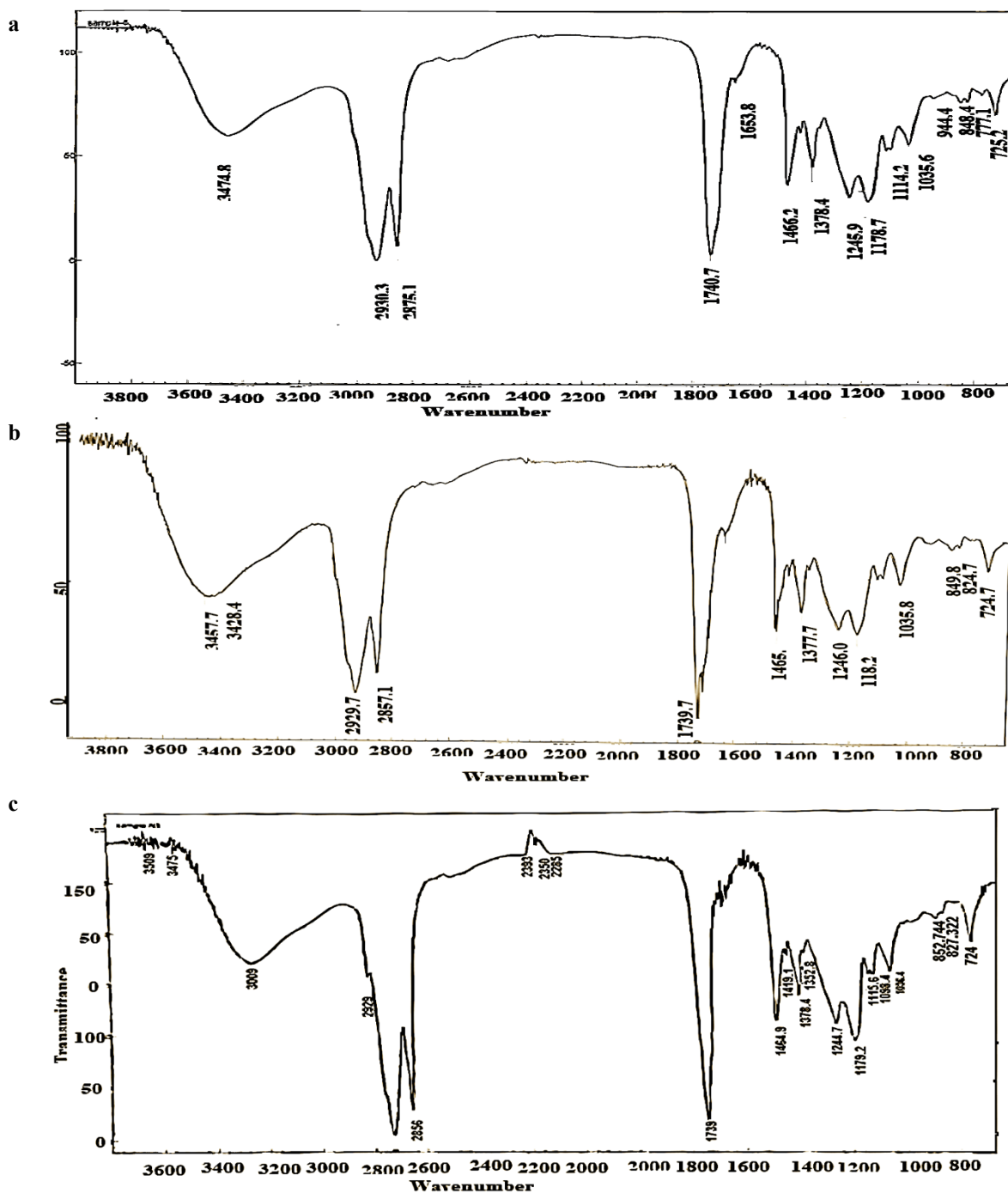


Figure (1): FTIR of epoxy ethyl esters from soybean, sunflower and waste cooking oils.

3459.5, 3456.1, 3464.3, 3473.9 and 3474.8 cm⁻¹ are attributed to OH stretching, which suggests the

occurrence of side reactions of the epoxy groups. [27, 28]

3.2. Physical, chemical, and electrical characteristics of synthesized ethyl ester without and with different weights of TBHQ antioxidant.

Different characteristics were measured for ethyl ester vegetable oils with the following different

weights of TBHQ antioxidant (0 weight [uninhibited oils] - 0.4 gm [trace inhibited oils] - 2 gm [full inhibited oils] - 3 gm [saturated inhibited oils]), the results illustrated by **Table (2)**.

Table (2): Critical characteristics of ethyl ester vegetable oils with different weights of TBHQ antioxidant

Tests	Soybean Ethyl Ester				Sunflower Ethyl Ester				Cook Waste Ethyl Ester				ASTM
	0	0.4	2	3	0	0.4	2	3	0	0.4	2	3	
Density	1.18	1.1	0.9	1.35	1.102	1.102	0.85	1.45	2.012	2.012	1.1	1.65	$\leq .91 \text{ g/cm}^3$
Dynamic viscosity at 40°C	13.33	10.5	10.0	12.5	17.5	12.3	8.0	13.4	17.9	15.2	10.5	15.4	$\leq 0.358\text{-}15.8 \text{ mPa}$
Flash Point	134.6	138.7	145.6	140.7	175.3	180.6	181.7	179.9	180.8	190.7	195.4	185.7	$\geq 135 \text{ }^\circ\text{C}$
Water Content	120	100	62	95	85	50.5	28.1	79	96	75.2	28.2	85	$\leq 500 \text{ mg/kg}^{-1}$
Acid Value	0.08	0.07	0.06	0.075	0.09	0.087	0.07	0.085	0.2	0.15	0.10	0.17	Max 0.5 mg/KOH
Oxidation Stability	4.5	5.05	5.2	4.8	3.9	4.07	4.6	3.8	3.8	4.05	4.8	4.1	$\geq 3 \text{ h}$
Break Down Voltage	11.8	15.6	22.2	18.7	18.3	22.8	30.2	25.5	11.4	17.2	22.4	17.4	25-40kV

3.2.1. Density

The density values of several ethyl ester vegetable oils are higher than the ASTM standards. While the addition of 0.4 grammes of TBHQ doesn't affect the density values of the synthesised ethyl ester vegetable oil, the addition of 2 grammes of TBHQ antioxidant decreases the density values in all the synthesised ethyl ester vegetable oil, which means that the addition of 2 grammes of TBHQ causes the density values of the ethyl ester of soybean, sunflower, and cook waste to be close to the standard value of ASTM,. On the other hand, the density values increase when 3 grammes of TBHQ are added. [34]

3.2.2. Dynamic Viscosity

The level of unsaturation is yet another element that influences the bio-transformer 's viscosity. One double bond will enhance viscosity, whereas two or more double bonds will cause the lubricant's viscosity to drop [69]. Except for soybean vegetable oil's ethyl ester, all ethyl ester vegetable oils' dynamic viscosity ratings are higher than the conventional ASTM values. Additionally, the use of TBHQ results in a decrease in the synthetic ethyl ester vegetable oil's viscosity values, making the bio transformer easily fluid in the engine turbines and wires. The ASTM standard values list all the viscosity values. Maximum viscosity decrement values are noticed at 2 gm of TBHQ content The viscosity values for all the synthetic ethyl ester vegetable oils increase with the addition of 3 grammes of TBHQ. This could be because the two hydroxyl groups in TBHQ's molecular structure make it more likely to create hydrogen bonds with FAEs, which would increase the viscosity (resistance to flow).[41] The mentioned results were a consequence of FAEE polymerization and its subsequent byproducts, which have higher viscosity values than their precursors. In this regard,

and the sample's stability had a definite bearing on maintaining this feature during storage or under extreme oxidising conditions. Second, the addition of TBHQ resulted in a favourable outcome. [33]

3.2.3. Flash Point

Flash point values of the various ethyl ester vegetable oil are in the standard flash point values of ASTM and higher than the minimum limit except for ethyl ester of soybean vegetable oil which is slightly less than ASTM values also it is less than the flash point that was measured by Akanksha Kanitkar et al 2011 which was 135.5 at 60° C [34]. The addition of 0.4 grams and 2 grams of TBHQ make an increment in the flash point values for all synthesized ethyl ester vegetable oils, but the maximum increment occurs in the case of addition 2 grams of TBHQ, while in the presence of 3 grams TBHQ, the flash point values for all vegetable oil starts to decrease but still higher than the lower limit.

3.2.4. Water Content

Water content values of the synthesized ethyl ester of vegetable oil is in the standard values of the water content for ASTM , and it was found that water content values of sunflower and cook waste ethyl ester lessen than of sunflower and cook waste methyl ester 154 , 376 mg/ kg⁻¹ reported at George Anasto poulos [70] , but after the addition of TBHQ with the amounts 0.4 and 2 grams , the water content values starts to de-crease . However, the addition of 3 grams of TBHQ made an increment in the water content but still in the standard water content values of ASTM. [19, 61]

3.2.5. Acid Value

More poly unsaturation double bonds in the structure of fatty acid ethyl esters make them more susceptible to oxidation, which results in the production of

primary products such hydroperoxides. Under ideal circumstances, most of these primary products disintegrate and produce secondary oxidation products. [45]. Propanol, hexanal, and other alcohols and aldehydes are frequently the byproducts of secondary oxidation. According to Kamal-Eldin and Pokorny [46] and Dridi et al. [47], secondary products are highly reactive and quickly oxidise into low molecular organic acids such formic acid, acetic acid, propionic acid, caproic acid, etc. The acid value rises as a result. According to Ezeanyanoso et al. [48], an important factor in the secondary oxidation process of long-term bio-diesel storage is the acid value.

Before the addition of TBHQ the acidity values of the synthesized ethyl ester of vegetable oil didn't exceed the standard values of acidity values for ASTM. Especially for soybean ethyl ester in which its acid value was less than of the acid value of Akanksha Kanitkar et al and James Pullen and Khizer Saeed [35, 42] which was 0.4 but for sunflower oil it was greater than that was reported in H. M. Wilhelm which was 0.04 and for cook waste oil it was less than the acid value which reported in Magín Lapuerta et al 2008 which was 0.27 mg/KOH [43, 44]. The addition of 0.4 gm of TBHQ make a slightly decrement in acidity values of the synthesized ethyl ester vegetable oil, while the addition of 2 grams of TBHQ effect on the acidity values in which it makes notified decrements for all the vegetable oils, in contrast the presence of 3 grams of TBHQ make an increment in the acidity values, but it doesn't exceed the available values of ASTM [45, 49].

3.2.6. Oxidation Stability

Oxidation stability values of all ethyl ester without antioxidant exceed the minimum limit of the standard ASTM values little a bit. However, the results described are typical for biodiesel samples created by other authors, exhibiting a similar behaviour, namely high flash points and low oxidative stabilities (from 2 to 6 h, depending on the raw material) [36, 37] Addition of 0.4 and 2 grams of TBHQ make an increment in the oxidation stability values for all synthesized vegetable oils, that's higher than the oxidation of soybean bean ethyl ester obtained by Anderson K. Domingos et al [38] which reported that the oxidation stability of ethyl soybean while the addition of 3 grams TBHQ decreases the oxidation

stability values for the ethyl ester of the vegetable oil. That's enhancement in oxidation stability It might be because this antioxidant has two hydroxyl groups that can be used to neutralise free radicals in FAEEs in its chemical structure. Previous studies have discovered comparable effectiveness [12]

3.2.7. Break down voltage:

Break down voltage values of all ethyl ester vegetable oil didn't meet the standard ASTM values, The addition of 0.4 and 2 grams of TBHQ causes an increment in the break down voltage values for all the synthesized vegetable oils, the best value was for ethyl ester of sunflower in which are in the standard values of ASTM in which are in the standard values of ASTM, and the ethyl ester of cook waste and soybean are close to the minimum limits of ASTM, but in the addition of 3 grams of TBHQ the break down voltage values starts to decrease for all the synthesized ethyl ester vegetable oils. the break down voltage values of the synthesized soybean and cook waste oil with TBHQ are slightly similar, but does not match the standard ASTM values, but can be used in low – to – medium voltage transformers whose minimum dielectric break down voltage is within 20 – 39 kv. According to a previous study [50], the presence of antioxidants causes an increment break down of vegetable oils. This outcome could be attributed to mono-aromatic compounds' improved ability to absorb the gas from vegetable oils [51- 52]. Another factor is that antioxidants of the aromatic kind cause more streamer branching, which raises the break down voltage [52].

3.3. Physical, chemical, and electrical characteristics of synthesized epoxy ethyl ester without and with 2 wt % of TBHQ antioxidant

Distinctive characteristics were measured for epoxy ethyl ester vegetable oils without and with 2wt % of TBHQ antioxidant, the results illustrated by **Table (3):**

Table (3). Physical , Chemical and Electrical properties of Epoxy Vegetable oils without and with TBHQ antioxidant

Tests	Soybean Epoxy		Sunflower Epoxy		Cook Waste Epoxy		ASTM
	0	2	0	2	0	2	
Density	1.207	0.897	1.198	0.884	1.962	0.986	≤ .91 g/cm ³
Dynamic viscosity at 40 °C	20.94	15.67	20.84	14.95	24.13	16.7	≤ 0.358-15.8 mPa
Flash Point	229.0	235.7	230.5	236.5	223.4	227.4	≥ 135 °C
Water Content	55.3	40.9	54.8	40.2	56.4	45.2	≤ 500 mg/kg ⁻¹
Acid Value	0.1	0.08	0.3	0.2	0.7	0.5	Max 0.5 mg/KOH
Oxidation Stability	5.8	5.9	5.9	6.01	4.5	4.7	≥ 3 h
Break Down Voltage	27.8	35.2	30.7	37.2	24.8	28.7	25-40kV

3.3.1. Density

Cook waste oil exhibits the highest increase in density from ethyl to epoxy during the epoxidation of ethyl ester of (soybean, sunflower, and cook waste) oils without the addition of TBHQ antioxidant. On the other hand, it is well known that the addition of TBHQ antioxidant causes a decrease in density values of ethyl vegetable oils. The same phenomenon also occurs in epoxy ethyl vegetable oils for (soybean, sunflower and cook waste) by the addition of 2 gm of TBHQ antioxidant. the increment in density values by epoxidation reaction agreed with Kongyai, Chainarong et al [56]

3.3.2. Dynamic Viscosity

It was noticed that epoxy ethyl ester of various vegetable oils without TBHQ antioxidant exceed the limited values of ASTM for dynamic viscosity, and by the addition of 2 gram of TBHQ antioxidant dynamic viscosity values started to decrease for all epoxy ethyl vegetable oil except for cook waste which didn't meet the standard ASTM values.

The results obtained were in accordance with Sapawe et al.'s and Pranav Prasannakumar et al [53, 71] investigation on pure super palm olein with TBHQ. Low molecular weight and chemical structure of TBHQ antioxidant are responsible for reduction in dynamic viscosity of synthesised soybean, sunflower, and cook waste generated alkoxide [54]. Additionally, Belitz et al. [55] noted that several interactions, such as oxidation adducts with the unsaturated lipids, may change the fatty acid composition throughout processing and treatment with additives, impacting variations in viscosity.

3.3.3. Flash Point

All epoxy ethyl ester of vegetable oils without TBHQ antioxidant are greater than the minimum the values of ASTM, which mean it meet the possible limit. By the addition of 2 gram of TBHQ

antioxidant flash point values had a slight increment makes it remain within the permissible standard limits. It is noticed that the epoxidation increased the flash point of the modified oils, this is because it contained more saturated ethyl ester than unaltered biodiesel did. [57, 58]. Epoxy ethyl vegetable oil with and without 2 % wt. of TBHQ antioxidant was shown to have a higher flash point than palm kernel epoxy alkyl ester with 148° C [63]. And higher than the flash point of mineral transformer fluid 152° C [62]

3.3.4. Water Content

All epoxy ethyl ester of vegetable oils without TBHQ antioxidant achieve the specified proportions of ASTM and it is lower than of the water content of ethyl ester vegetable oil before epoxidation, in the presence of 2 gram of TBHQ antioxidant water content values had a slight decrement and still check the permissible standard limits. Although the water content values of epoxy vegetable oil with and without TBHQ antioxidant were greater than reported by Paul et al. [65] for epoxidized waste cooking oil methyl ester, they were lower than those reported for bio-transformer fluids made from coconut and palm oil by Aimi and Hussin.[66]

3.3.5. Acid Value

Epoxy Ethyl ester of cook waste oil shows the highest value of acidity among the 3 epoxy ethyl vegetable oils, and it exceed the standard value of ASTM. Also epoxy ethyl ester of sunflower has a high value of acidity and it is greater than of soybean oil, but both remain within the standard ASTM limits for acidity. It is noticed that the epoxy ethyl ester of (soybean, sunflower and cook waste) vegetable oils without TBHQ antioxidant has a highest acidity values than for ethyl ester (soybean, sunflower and cook waste) vegetable oils without TBHQ, and this is

due to the excess usage of acetic acid for formation the peracetic acid, that's leads to arise in the acidity values. Additionally, it was noticed that the acid values of the epoxy cook waste vegetable oil with and without TBHQ antioxidant were higher than 0.142 and 0.59 mg/KOH respectively, reported for purified calabash seed oil used as bio-transformer fluids and epoxidized methyl ester of Parkia biglobosa seed oil, reported by Oyelaran et al. [60] and Ikuoria et al. [64]. greater than the published acid values of 0.20 mg/KOH by Paul et al for epoxidized waste cooking oil methyl ester and 0.09 by Adhvaryu and Erhan [65]. For epoxidized soybean oil, respectively. However, compared to the acid value of 1.08 mg/KOH reported for epoxidized castor oil fatty acid methyl ester, the acid values of epoxy soybean and sunflower with and without TBHQ antioxidant were found to be lower [5].

3.3.6. Oxidation Stability

The oxidation stability values of the three synthesized epoxy Ethyl Esters are greater than the available standard of ASTM. The oxidation stability values of the epoxy ethyl ester of (soybean, sunflower and cook waste) oils with TBHQ antioxidant are within the standard limits of ASTM. The oxidation stability values of soybean and sunflower oils are slightly close. The lowest oxidation stability values were for epoxy ethyl cook waste oil.[33]

3.3.7. Break Down Voltage

Epoxy ethyl of (soybean and sunflower) oils exceed the minimum values of ASTM for break down voltage, while epoxy ethyl of cook waste oil was less the minimum ASTM values. The addition of 2 grams of TBHQ made all epoxy ethyl vegetable oil exceed the minimum standard value and be suitable to be used as bio-transformer oil. The breakdown voltage was observed to have changed (increased) after the modification of the ethyl ester vegetable oils; the epoxy sample had a higher break down voltage value. The increment in the break down voltage, resulting from the modification of the ethyl

ester vegetable oils, can be attributed to the acid catalysed esterification and base catalysed transesterification processes used to obtain the ethyl ester [59]. While higher than purified calabash seed oil transformer fluid (24 KV), the breakdown voltage of epoxy ethyl vegetable oil with and without 2 wt. of TBHQ antioxidant is comparable [60]. The different triglyceride nature of the various vegetable oils, because of their variable polar natures, was said to be the cause of this variance in the break down voltage of and other oils. Along with other studies in the literature, this difference in the break down voltage of epoxy ethyl vegetable oil without and with 2 % wt. of TBHQ antioxidant sample may be attributed to various modification process pathways and the reagents used [61].

3.4. Statistical Analysis of Chemical Modification for Vegetable Oils and The Presence of TBHQ Antioxidant

By using mini-tab 2021 (Anova statistical analysis two ways factor), We can expect the effect of two factors on the physico-chemical and electrical properties of Ethyl and epoxy ethyl of (Soybean, Sunflower, and Cook Waste) vegetable oils. These factors include: the type of chemical modification and the effect of the presence of antioxidants or not. In which there are 6 chemically modified vegetable oils were studied and they are: 1- ethyl soybean, 2- epoxy soybean, 3- ethyl sunflower, 4- epoxy sunflower, 5- ethyl cook waste and 6- ethyl cook waste, and there are two cases of addition of TBHQ antioxidant which are: without and with 2 % wt. of TBHQ antioxidant.

3.4.1. Dynamic Viscosity

The Results in **Table (4)** showed that the P-value of the 6 chemically modified vegetable oils is = 0.0000 (< 0.05), with F-Value =30.06, while the P-value of the chemical modified vegetable oil with and without TBHQ antioxidant is = 0.000 (< 0.05), with F-Value =186.73 which indicate that the addition of TBHQ antioxidant caused significant differences in the dynamic viscosity values more than the effect of the chemical modification.

Table (4). Analysis of Variance of Dynamic Viscosity values

Source	DF	Adj SS	Adj MS	F-Value	P-Value
effect	5	401.57	80.314	30.06	0.000
level	1	498.82	498.824	186.73	0.000
Error	41	109.53	2.671		
Lack-of-Fit	5	74.95	14.990	15.61	0.000
Pure Error	36	34.58	0.960		
Total	47	978.72			

In **Figure (2a)** the mean of the dynamic viscosity of ethyl soybean (1), ethyl sunflower (3) and ethyl

cook waste (5) are= (12.33, 13.99 and 14.201 mPa) consequently, had a decrement in mean dynamic viscosity values, However the values of

ethyl soybean (1) exceed the limited minimum mean values of dynamic viscosity for various chemically modified vegetable oils, the mean of the dynamic viscosity value of epoxy soybean (2), epoxy sunflower (4) and epoxy cook waste (6) are = (18.30, 17.90 and 20.415) in sequence, had an increment in the mean dynamic viscosity values, in which the mean of dynamic viscosity values of epoxy cook waste (6) exceed the limited maximum mean values of dynamic viscosity for various chemically modified vegetable oils, that means the mean dynamic viscosity value of the various ethyl vegetable oils are less than of the mean dynamic viscosity values of various epoxy vegetable oils [68,72].

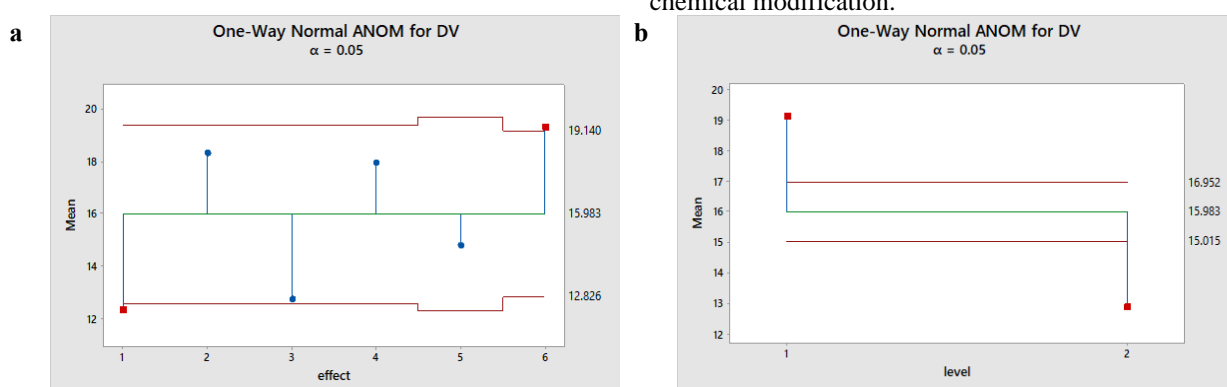


Figure (2a, b). The Mean of the dynamic viscosity of different chemical modified vegetable oils (a), without and with TBHQ antioxidant (b).

3.4.2. Flash Point

The Results in **Table (5)** showed that the P-value of the 6 chemically modified vegetable oils is = 0.0000 (< 0.05), with F-Value =224.50, while the P-value of the chemical modified vegetable oil with and without TBHQ antioxidant is = 0.027 (< 0.05), with

F-Value =5.30 which indicate that the addition of TBHQ anti-oxidant caused significant differences in the flash point values but less than the effect of the chemical modification.

Table (5). Analysis of Variance of Flash Point values

Source	DF	Adj SS	Adj MS	F-Value	P-Value
effect	5	57064.5	11412.9	224.50	0.000
level	1	269.3	269.3	5.30	0.027
Error	41	2084.3	50.8		
Lack-of-Fit	5	1008.9	201.8	6.75	0.000
Pure Error	36	1075.4	29.9		
Total	47	59634.6			

In **Figure (3a)** the mean of the flash point of ethyl soybean (1), ethyl sunflower (3) and ethyl cook waste (5) are 140.05, 178.5 and 188.1 °C, consequently are the lowest mean flash point values among the chemically modified vegetable oils, However the values of various ethyl vegetable oils exceed the limited minimum mean values of flash point for various chemically modified vegetable

oils, the mean of the flash point value of epoxy soybean (2), epoxy sunflower (4) and epoxy cook waste (6) are = (232.35, 233.5 and 230.68 °C) in sequence, are the highest mean flash point values, in which the mean of flash point values of various epoxy vegetable oils exceed the limited maximum mean values of flash point for various chemically modified vegetable oils, that means the mean flash

point value of the various ethyl vegetable oils are less than of the mean flash point values of various epoxy vegetable oils.

In **Figure (3b)** the mean of flash point values without TBHQ antioxidant (1) in various chemically modified vegetable oils is = 197.35°C, and the mean of flash point values with TBHQ antioxidant (2) in various

chemically modified vegetable oils is = 203.91 °C , that means the addition of 2 grams of TBHQ in all chemical modified vegetable oils cause a significant increment in the mean flash point value . but all the mean flash point values of all chemically modified vegetable oil without and with TBHQ antioxidant are in the available general mean flash point values.

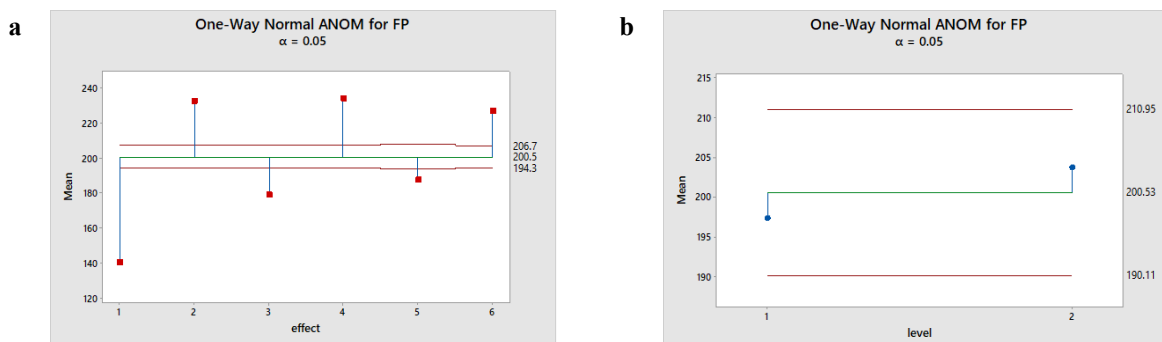


Figure (3a, b). The mean of the flash point value of different chemical modified vegetable oils (a), without and with TBHQ antioxidant (b).

3.4.3. Water Content

The Results in **Table (6)** showed that the P-value of the 6 chemically modified vegetable oils is = 0.003 (< 0.05), with F-Value =4.33 , while the P-value of the chemical modified vegetable oil with and without TBHQ antioxidant is = 0.000 (< 0.05), with

F-Value = 42.75 which indicate that the addition of TBHQ antioxidant caused significant differences in the water content values more than the effect of the chemical modification .

Table (6). Analysis of Variance of water content values

Source	DF	Adj SS	Adj MS	F-Value	P-Value
effect	5	11743	2348.6	4.33	0.003
level	1	16628	16628.4	42.75	0.000
Error	41	22777	542.3		
Lack-of-Fit	5	74.95	17.238	15.70	0.000
Total	47	38580			

In **Figure (4a)** the mean of the water content of epoxy soybean (2) , ethyl sunflower (3) , epoxy sun-flower (4) and epoxy cook waste (6) are= (48.07, 56.675 , 47.74 and 50.95 mg/kg⁻¹) consequently locate below the mean water content values for the chemically modified vegetable oils and do not exceed the limited minimum mean values of water content for various chemically modified vegetable oils , the mean of the water content value of ethyl soybean (1) , ethyl cook waste (5) = (91 and 62.1 mg/kg⁻¹) in sequence , locate above the mean water content values for the chemically modified vegetable oils , that mean that the transesterification modification causes a decrement in the mean water content values for the

chemically modified vegetable oils more than epoxidation modification except in the mean water content value epoxy sun-flower which decreased.

In **Figure (4b)** the mean of water content values without TBHQ antioxidant (1) in various chemically modified vegetable oils is= 77.99 mg/kg⁻¹ and the mean of water content values with TBHQ antioxidant (2) in various chemically modified vegetable oils is = 40.76 mg/kg⁻¹, that means the addition of 2 grams of TBHQ in all chemical modified vegetable oils cause a significant decrement in the mean water content value . But all the mean water content values of all chemically modified vegetable oil without and with TBHQ antioxidant exceed the available general mean water content values.

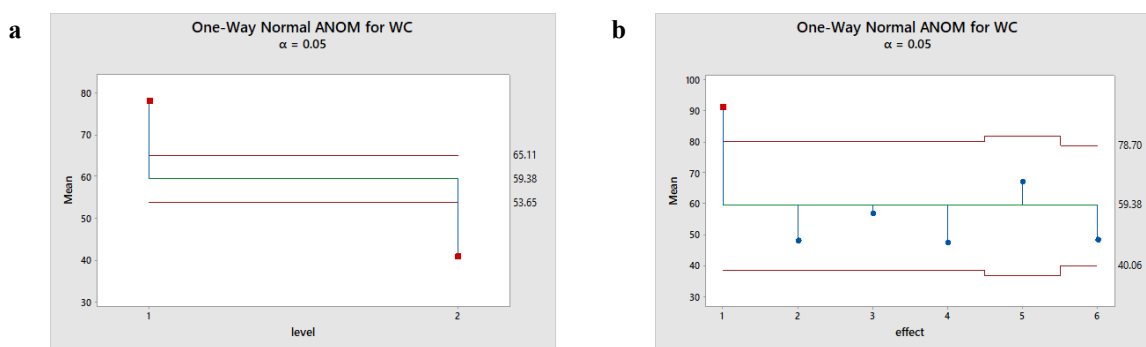


Figure (4a, b). The mean of the water content value of different chemical modified vegetable oils (a), without and with TBHQ antioxidant (b).

3.4.4. Acid Value

The Results in **Table (7)** showed that the P-value of the 6 chemically modified vegetable oils is = 0.000 (< 0.05), with F-Value = 18.90, while the P-value of the chemical modified vegetable oil with and without TBHQ antioxidant is = 0.212 (< 0.05), with

F-Value = 1.60 which indicate that the addition of TBHQ antioxidant caused non-significant differences in the acid values in comparison with the effect of the chemical modification. The decreased acid value suggests that the chemically modified oils will last longer [76].

Table (7) Analysis of Variance of Acid Values

Source	DF	Adj SS	Adj MS	F-Value	P-Value
effect	5	1.4490	0.28981	18.90	0.000
level	1	0.07053	0.07053	1.60	0.212
Error	42	0.6439	0.01533		
Lack-of-Fit	5	84.95	17.238	19.70	0.000
Pure Error	33	95.58	0.892		
Total	47	2.0929			

In **Figure (5a)** the mean of the acid values of ethyl soybean (1), epoxy soybean (2), ethyl sunflower (3), and ethyl cook waste (5) are = (0.07, 0.08, 0.08 and 0.14 mg/KOH) consequently locate below the mean acid values for the chemically modified vegetable oils but ethyl soybean (1), epoxy soybean (2), ethyl sunflower (3) exceed the limited minimum mean values of acidity for various chemically modified vegetable oils, the mean of the acidity value of epoxy sun-flower (4), epoxy cook waste (6) = (0.25 and 0.46 mg/KOH) in sequence, locate above the mean acid values for the chemically modified vegetable oils, however the mean of acid values of epoxy cook waste (6) exceed the limited maximum mean values of acidity for various chemically modified vegetable oils, that means that the transesterification modification causes a decrement in the mean acidity

values for the chemically modified vegetable oils more than epoxidation modification.

In **Figure (5b)** the mean of acidity values without TBHQ antioxidant (1) in various chemically modified vegetable oils is = 0.24 mg/KOH and the mean of acidity values with TBHQ antioxidant (2) in various chemically modified vegetable oils is = 0.16 mg/KOH, that means the addition of 2 grams of TBHQ in all chemical modified vegetable oils cause a significant decrement in the mean acidity value. But all the mean acid values of all chemically modified vegetable oil without and with TBHQ antioxidant are in the available general mean acidity values.

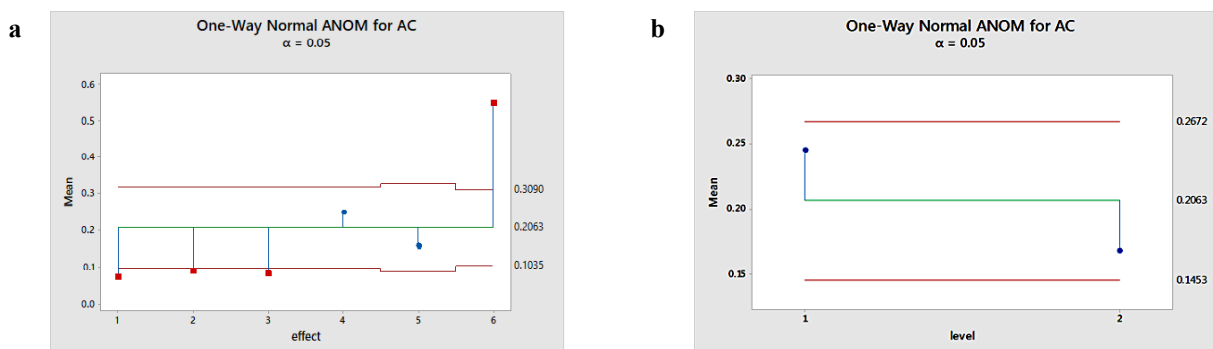


Figure (5a, b). The mean of the acidity value of different chemical modified vegetable oils (a), without and with TBHQ antioxidant (b).

3.4.5. Break Down Voltage

The Results in **Table (8)** showed that the P-value of the 6 chemically modified vegetable oils is = 0.000 (< 0.05), with F-Value = 95.08, while the P-value of the chemical modified vegetable oil with and without

TBHQ antioxidant is = 0.000 (< 0.05), with F-Value = 188.06 which indicate that the effect of the chemical modification caused a significant differences in the break down voltage values more than the addition of TBHQ antioxidant

Table (8) Analysis of Variance of Break Down Voltage Values

Source	DF	Adj SS	Adj MS	F-Value	P-Value
effect	5	1979.21	395.842	95.08	0.000
level	1	782.96	782.961	188.06	0.000
Lack-of-Fit	5	122.39	24.478	18.24	0.000
Total	47	3012.66			

In **Figure (6a)** the mean of the break down voltage Values of ethyl soybean (1), ethyl sunflower (3), and ethyl cook waste (5) are = (17, 24.37 and 16.9 kV) consequently locate below the mean break down voltage values for the chemically modified vegetable oils and the mean break down voltage of ethyl soybean (1) and ethyl cook waste (5) exceed the limited minimum mean values of breakdown voltage for various chemically modified vegetable oils, the mean of the break down voltage values of epoxy soybean (2), epoxy sunflower (4) and epoxy cook waste (6) = (31.5, 33.93 and 26.75 kV) in sequence, locate above the mean break down voltage values for the chemically modified vegetable oils, however the mean of break down voltage values of epoxy soybean (2), epoxy sunflower (4) exceed the limited maximum mean values of break down

voltage for various chemically modified vegetable oils. that means that the mean breaks down voltage values of transesterification modification are lowest than the mean breaks down voltage values of epoxidation modification.

In **Figure (6b)** the mean of break down voltage values without TBHQ antioxidant (1) in various chemically modified vegetable oils is = 20.83kV, and the mean of break down voltage values with TBHQ antioxidant (2) in various chemically modified vegetable oils is = 29.31 kV, that means the addition of 2 grams of TBHQ in all chemical modified vegetable oils cause a significant increment in the mean break down voltage. And all the mean break down voltage values of all chemically modified vegetable oil without and with TBHQ antioxidant exceed the available general mean break down voltage values.

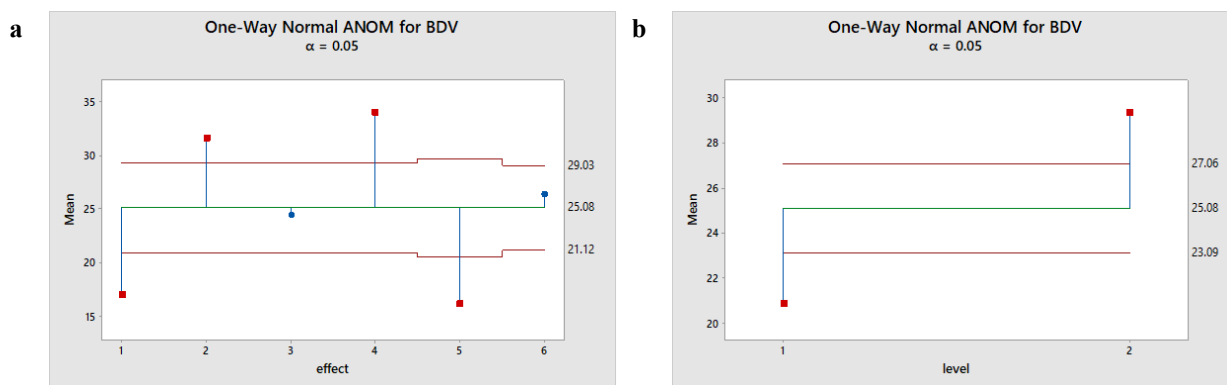


Figure (6a, b) The mean of the break down voltage value of different chemical modified vegetable oils (a), without and with TBHQ antioxidant (b).

4. Conclusion

The following were the main outcomes of this study:

- The examined vegetable oil was regarded as being of low quality, yet the bio-transformer agreed with ASTM standards. Therefore, this research may be considered as a recycling of non-edible or waste vegetable oils. Because mineral oil is less recyclable than other types of oil, it has a lower rate of outflow during operation and causes more environmental pollution as a result.
- The quality characteristics of epoxy biodiesel samples were maintained at 2% wt of TBHQ antioxidant. Antioxidants may alter the properties of biodiesel, which should be considered to ensure that the finished product complies with the standard (especially when the qualities of the biodiesel are close to the limits set by the standard).
- Chemical modifications effect on the critical characteristics especially epoxidation process, but not as the effect of the addition of TBHQ antioxidant.
- Because they are wastes that require rigorous treatment, soybean and sunflower seemed like interesting substrates and the addition of TBHQ enhanced their marketability.
- Due to its superior biodegradability property, high flash point, and high solubility, epoxy ethyl soybean, sunflower, and cook waste oil has earned a reputation as an alternative material for trans-former oil. According to the experimental findings, cook waste oil, sunflower, and soybean epoxy with 2 % wt TBHQ antioxidant also have good breakdown strengths. Utility costs could be reduced by using ethyl epoxy soybean oil as bio-transformer oil because it will make remediation and cleanup procedures simpler. However, locations where there is spillage or leakage benefit most from the actual savings.

This is true for utilities in environmentally sensitive areas where accidents or leakage are known to endanger marine life.

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