Chemical and Physical Performance of Kraft Paper Immersed in Natural Ester from Palm Oil Under Accelerated Thermal Aging

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Abstract: Mineral oil has been widely used as liquid insulation for high voltage equipment such as a transformer. Due to environmental consideration and long-term availability, there are many efforts to find new liquid insulating materials that are environmentally friendly and renewable. Natural ester is among the candidates for those purposes. In order to be applicable, its interaction with the kraft paper as well as its degradation characteristics is essential to be studied. Accelerated thermal aging is a method that typically been used to assess the performance of oil and paper in the laboratory. In this paper, the result of the degree of polymerization (DP), tensile strength (TS), and Fourier transform infrared spectroscopy (FTIR) measurement were done to examine the degradation characteristic of kraft paper. FTIR which expected to be a new non-destructive diagnosis method of transformer insulation is used to determine the changes of the chemical bond of the kraft paper. The results show that moisture content affects the decrease of DP and TS characteristics. Hence, the FTIR measurement of kraft paper shows that the absorption intensity of C=O and C-H bond increase during the aging.
Meanwhile, the absorbance intensity of the O-H bond decreases during aging time. Through regression method, it can be shown that the correlation between DP values to the peak absorbance is influenced by oil-paper moisture equilibrium. Exponential regression method is appropriate for high moisture condition and linear regression is suitable for low moisture condition.

Keywords: Transformer, Natural Ester, Degree of Polymerization (DP), Tensile Strength (TS), and Fourier Transform Infrared Spectroscopy (FTIR)

1. Introduction

The growth of human population and industry lead electricity demand to increase from time to time steadily. The generation process of electricity is usually far from the load. Therefore, a power system must be equipped with transmission lines that carry out electricity from the power plant to the load for long distances. Converting high voltages from one level to another is necessary to minimize the power losses in the power system. In alternating current conversion, the transformer is one of high voltage equipment that is widely used to change the voltage level of alternating current. The performance of the transformer is mainly determined by its insulation. The contribution of the insulation system to the transformer failure based on the latest study is approximately about 84% [1,2]. Insulation system in power transformer is composed of paper and oil [3]. The coils for low rating transformer are made by super-enameled copper wire. Kraft paper is used to insulate between layers, between coils and between coils to ground. Besides, for high rating power transformer, the paper is wrapped around the rectangular conductors for the coil to coil or oil to ground insulation [4]. Kraft paper is composed of cellulose and has been used as solid insulation for 100 years [5]. Oil is the primary insulation for oil-filled is transformers and also used as a cooling medium [6].

Mineral oil has been used as insulation oil for the power transformer for a long time ago. It is the liquid by-product of refining crude oil and it contains thousand hydrocarbon compounds such as alkenes, cyclic alkenes, and aromatic [7]. Under transformer operation, mineral oil performs good compatibility with kraft paper. Mineral oil has excellent physical and electrical properties under thermal and electrical stress. As is well known, mineral oil is a cost-effective material [8–11]. However, it is going to run out as the raw material is taken from petroleum which is non-renewable energy resource. It is also confirmed to be non-environmentally friendly

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since it is not biodegradable and become a contaminant when spilled to water or soil [12–14]. Natural ester oil is then projected to become one of insulation liquid to replace mineral oil. It can be made from vegetable oil through trans esterification processes. Natural ester oil is a non-hazardous material which will not be a toxic product during a fire and is approved to be biodegradable oil [12,15,16]. Besides, its fire point is exceeded 300^0C and its ignition point exceeds 330^0C which is appropriate for the high voltage operation [17,18]. Natural ester from palm oil was chosen as a material to be studied because of palm oil has become the highest crop commodity especially for edible oils [19].

Inside of a transformer, oil and paper will deteriorate due to the degradation reactions such as hydrolysis, oxidation, and pyrolysis. Natural ester oil has a different chemical structure from mineral oil. Therefore, the degradation performance of cellulose immersed in the natural ester transformer may be different from conventional mineral oil. Based on previous research, the primary degradation of cellulose immersed in the mineral oil is subjected by the oxidation reaction. However, degradation in natural ester is caused by hydrolysis reaction [20,21]. Some authors also mentioned that hydrophilic structure in the natural ester tends to bind water molecule and keep the paper insulation dryer [22]. The lower moisture content of cellulose paper immersed in natural ester oil during thermal aging is claimed to be able to extend the lifetime of the transformer.

Thermal, mechanical, and electrical stresses take an essential role in determining the speed of reaction. It is an irreversible degradation and therefore in the high-level point they can be used to determine the lifetime of a transformer [12]. Degree of polymerization (DP) and tensile strength (TS) is a method widely used to determine the lifetime of the transformer based on paper degradation. However, DP and TS measurements are the kind of destructive diagnostic methods [23,24]. Not only being a destructive method but also taking a sample of paper in a transformer is also impossible to be done. Therefore, the transformer diagnostic method is generally done by analyzing the oil condition.

Several works in combining spectroscopy technique to determine the degree of polymerization and water content of the transformer paper have been reported in previous research [7,15,23,25,26]. This study discusses the experimental results of the FTIR technique to determine the degree of polymerization. The result shows that the absorption intensity in a particular peak has a good correlation with the degree of polymerization (DP). The observation was done to analyze the contribution of O-H, C-H, and C=O functional group of kraft paper to the degree of polymerization.

2. **Experimental Setup**

A. Sample Preparation

IEEE Standard C57.100-2011 recommend the way to conduct accelerated thermal aging by using copper conductor [27]. The inner part of the power transformer composed of winding made from copper, oil, and paper. Natural ester from palm oil, kraft paper, and copper shows in Figure 1 was used to conduct this experiment. The typical ratio of natural ester, kraft paper, and copper in the transformer is 20: 1: 0.875 [15,28]. In this study, each bottle of the sample contains 400 grams of natural ester oil, 20 grams of kraft paper, and 17.5 grams of copper.

The kraft paper has 0.08 cm of the thickness measured by the micrometer screw. The copper was then wrapped by cellulose paper, as shown in Figure 2(a). This study was objected to observing the chemical, electrical, and physical degradation of the sample under accelerated thermal aging in different paper moisture. Therefore, before accelerated thermal aging was performed, some of the kraft papers are dried in 100^0C for six hours. Initial moisture of kraft paper was 7.59%. After the drying process, the weight of the kraft paper was reduced by one gram from the total weight and it was assumed to be the weight of the water.

(a) (b) (c)

Figure 1. Sample composition: (a) Natural ester from palm oil; (b) Cellulose paper; (c) Copper

The natural ester oil was made from RBD palm oil through trans esterification process. This process accommodates the reaction between lipid with alcohol to form esters and a by-product, glycerol. KOH catalyst is used to accelerate the reaction between oil and methanol. Trans esterification reaction breaks triglycerides into diglycerides, diglycerides to monoglycerides, and finally monoglycerides into glycerol. It is a reversible reaction although the equilibrium condition leads to fatty acid esters and glycerol production [29–31]. The fundamental properties of the natural ester are presented in Table 1 below.

Table 1. Initial properties of natural ester

Property	Method	Result
Dielectric Strength (kV) 2.5 mm gap	IEC 60156	36.52
Dissipation Factor (25^0C) (%)	ASTM D 924	0.41
Kinematic Viscosity (cSt) 100^0C	ASTM D 445	1.97
Water content (mg/kg)	IEC 60814	283.08
Visual Examination	ASTM D 1542	Bright and Clear

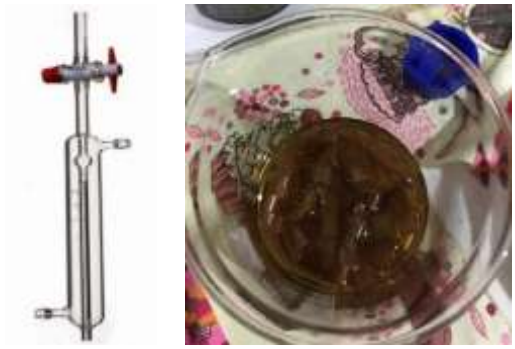
Along with the pre-treatment paper, natural ester oil is also given pre-treatment by heating in the oven at 100℃ for 24 hours [8,11,15]. After the pre-treatment process was done, the kraft paper was then immersed in the oil. Accelerated thermal aging is conducted by using a sealed system with 120^0C aging temperature for 1008 hours [32]. Sampling was taken for every 336 hours. 120^0C aging temperature was chosen since it is determined to be the hotspot temperature for transformer operation according to IEEE [33].

(a) (b)

Figure 2. (a) Copper wrapped by kraft paper; (b) Sample under accelerated thermal aging

B. Degree of Polymerization (DP) Measurement

The degree of polymerization measurement referred to ISO 5351 ES standard and was conducted by using intrinsic viscometer as shown in Figure 3(a). At the beginning of the process, kraft paper is dissolved in a particular solution that breaks the cellulose formation. The flow rate of the dissolved sample is then measured in a capillary viscometer. The test sample must be completely dissolved in the cupriethylenediamine solution. The size of the viscometer capillary is tiny. Therefore, it can inhibit the flow rate of the sample to be tested, or even it cannot be measured. Pure cellulose samples will dissolve in the cupriethylenediamine solution in a short time, but if there is an additive, it will take a long time. The paper is soaked in methylene chloride to remove the natural ester oil on it as shown in Figure 3(b).

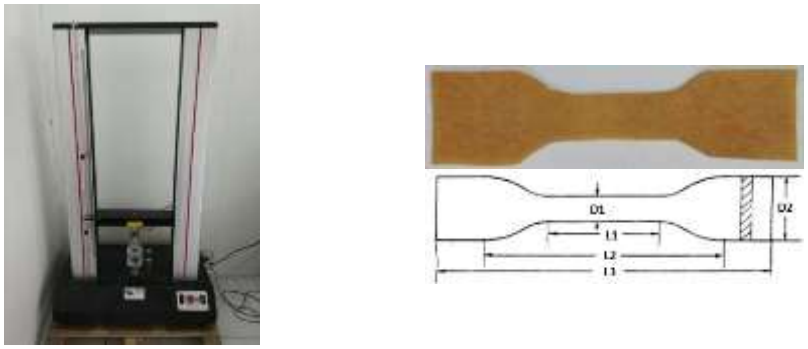


(a) (b)

Figure 3. (a) Intrinsic viscometer; (b) Oil and paper separation

C. Tensile Strength (TS) Measurement

Tensile strength measurement is carried out by using the Universal Tensile Machine is shown in Figure 4(a). The paper is cut into dumbbell shape as shown in Figure 4(b) below so it satisfies the requirements of tensile strength measurement [34]. The paper sample dimensions such as length, width, and thickness were first measured and then put in an autograph to be stretched out and measured. Paper samples are wet (oily) when the tensile test was carried out. After the paper was torn, the load size and the elongation measurement result in this tool are recorded, as well as the area of termination. The tensile speed was 5mm/min.



(a) (b)

Figure 4 (a) Universal Tensile Machine; (b) Dimension of kraft paper for TS measurement (D_1 = 1 cm, D_2 = 2 cm, L_1= 3 cm, L_2 = 4.5 cm, L_3 = 8 cm)

D. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a method that can be used to determine the specific portions of a molecule or functional groups by injecting infrared light. This experiment used Alpha FTIR Spectrometer shown in Figure 5. If a substance is radiated by infrared light,

the energy can be absorbed, transmitted, reflected, scattered, or have photoluminescence (PL). FTIR undergoes the absorption of light from an upper to a lower vibrational energy level [35]. Kraft paper and natural ester oil are placed in the path of the infrared beam and when infrared light transmitted, the radiation will penetrate the sample and goes to the detector. The detector is then measuring the intensity of the remaining radiation energy after passing through the sample. The output is a plot of absorbance level versus the wavenumber range from 4000-400 cm^{-1}. The peak observation is then done around 1700-1800 cm^{-1} to determine the existence of C=O, 3273-3325 cm^{-1} for O-H, and 2700-3000 cm^{-1} for C-H functional group.

Figure 5 Alpha FTIR Spectrometer.

3. Experimental Results

A. Degree of Polymerization (DP)

Since the nineteenth century, paper degradation has become an interesting topic to be observed [36]. Paper is mainly formed by cellulose which contains hundred to thousand links of glycosidic bonds given in Figure 6 [12]. The average number of the glycosidic bond in one chain of cellulose is then measured and called the degree of polymerization measurement. Kraft paper is composed of 90% of cellulose, 6-7% of hemicellulose and 3-4% of lignin [17,37,38]. The hydrophilic group in the kraft paper is the most dominant compound since it has a low amount of lignin, the hydrophobic group. It creates an excellent bond among hydrophilic compounds. As a result, kraft paper has a high-value degree of polymerization and mechanical strength [39]. These excellent properties make kraft paper chosen to be paper insulation for the transformer. Typical degree of polymerization of kraft paper for a new transformer is about 2000.

The solid insulation in the transformer cannot be easily replaced or repaired. Therefore, the aging of paper insulation determines the lifetime operation of the transformer. In the transformer, the paper will meet the thermal, electrical, and mechanical stress as well as react to water, acid, and other substances immersed in transformer oil. The reaction that mainly affects the degradation process is pyrolysis, hydrolysis and oxidation reaction [12]. From the previous experimental result, it has been known that the number of chain scission due to thermal activated kinetic energy can be described by equation (1) [40].

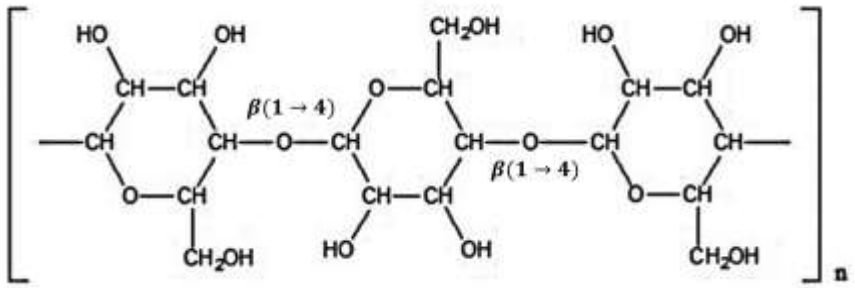


Figure 6. The molecular structure of cellulose.

$$Avg.number\ of\ chain\ scission\ = \frac{1}{DP_{new}} - \frac{1}{DP_{old}} \quad (1)$$

Pyrolysis reaction is caused by a high aging temperature, which leads to the breaking of the glycosidic bond [41]. The further product of pyrolysis is 2-furfuraldehyde [12]. In the initial process of the hydrolysis reaction, the carboxylic acids are dissociated by ion H^+ dissolved in oil. One molecule water is consumed when the acid hydrolyzes and breaks the inter-unit linkages in cellulose. The reaction then occurs in the inner part of the cellulose. The monosaccharide dissociation produces three molecules of water. The furanic compounds such as 2-furfuraldehyde, 5-hydroxymethyl 2-furfural, and 2-Furfuryl alcohol are the main products of the hydrolysis reaction. 2-furfuraldehyde is the most stable compound and will accumulate by the time of aging and dissolve in the oil. The other products are then decomposed into laevulinic and formic acid [12,40]. The accumulation of the furanic compound in the oil is claimed that is can be used to diagnose the power transformer condition. The oxidation reaction is the reaction due to the presence of oxygen. Besides reducing the value of the degree of polymerization, carboxyl groups such as aldehydes and ketones are formed [36]. The oxidation reaction depends on the oxidizing agent and the pH of the paper immersed. The product of this reaction weakens the glycosidic bond and lead the chain scission processes.

The degradation of kraft paper can be observed through the degree of polymerization and tensile strength measurement. Figure 7 shows that the high temperature of aging leads to a decrease in the degree of polymerization of kraft paper. In the initial state of aging, the rate of chain scission drops rapidly. By the time of aging, the rate of reaction decreases. The difference rate degree of polymerization is caused by the reaction, which takes part in the initial and remaining time of aging. In the initial aging time, oxygen will contribute to the oxidation reaction. As a result of this situation, the glycosidic bond is getting weakened. The high temperature of aging is then accelerating the chain scission of the cellulosic chain. It has been stated previously in equation (1) that higher temperature leads to an increase in the rate of degradation. When the oxygen levels in the air are runs out, the rate of the oxidation reaction is declining and getting slower. Moreover, weak linkage removal at the beginning of aging also leads to cause different decline rate of the degree of polymerization [42]. Based on the structural characteristic, it has been studied that cellulose insulation may contain weak links in the middle of the chain [43]. Weak links naturally exist in every 500 glucose monomer units [44]. The intensity of hydrolysis in the cellulose is dominant in the amorphous regions [44]. It is acknowledged as the site that has higher permeability so that the majority of water and acid sits in this structure [45]. On the other hand, the crystalline regions do not allow water and acid to bond with them. Breaking cellulose linkage in the amorphous regions by hydrolysis reaction also causes the rapid rate of paper degradation at the beginning of aging [40].

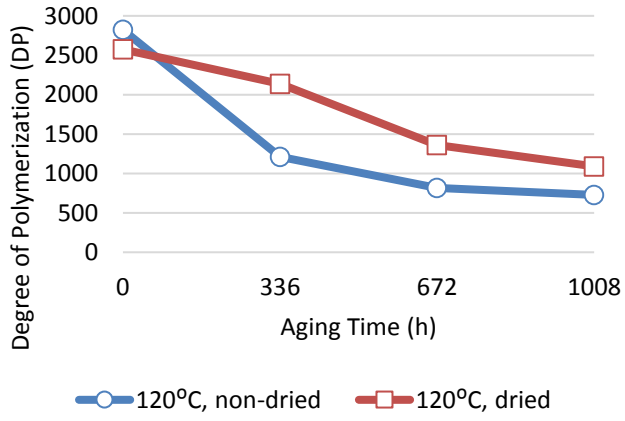


Figure 7. The decrease of the DP values over aging

It also can be seen that moisture of paper affects the decreased rate of the degree of polymerization. Samples with dried paper tend to have a lower decline rate compared to the sample with non-dried paper. The hydrolysis reaction is the main reason for this phenomenon. The amount of water as the reactant of hydrolysis reaction in the sample with given pretreatment paper is lower than the sample with non-dried paper. Thus, it proves that the initial moisture of paper affects the aging rate of kraft paper.

B. Tensile Strength

Tensile strength is one of the most essential basic mechanical and physical properties of paper. This measurement reflects the morphology, intrinsic chemistry, and structure of the cellulose fiber as well as the network structure of the kraft paper. These properties also reflect the chemical change in the paper due to chain scission. Therefore, the degree of polymerization measurement result is then compared to the tensile strength measurement. The measurement result shows that the decrease in the degree of polymerization affects the mechanical strength of kraft paper [46,47]. The degradation reaction ruins the outer part and move to the deeper part of the cellulose bond and consequently reduce the mechanical strength of kraft paper. Longer duration of aging makes the kraft paper becomes more fragile, easily torn and broken. In power transformer operation, crack in paper increase the probability of the breakdown and lead to cause failure operation of the power transformer. Figure 8 shows the tensile strength measurement result for the sample under accelerated thermal aging.

The correlation between the decrease of the degree of polymerization can be observed through the linear regression. The value of the degree of determination (R^2) can represent how close the data to the linear regression. From Figure 9 below, it can be seen that the value of R^2 in Table 2 below is 0.9972 and 0.9996 which nearly close to 1. It indicates that there is a significant correlation between chain scission in the polymeric chain to the decrease of mechanical strength of kraft paper.

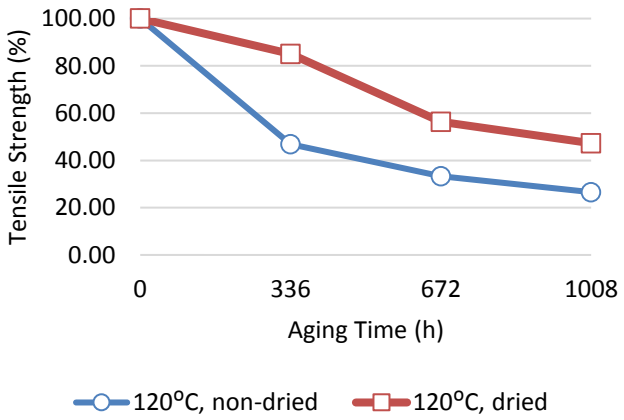


Figure 8. The decrease of TS values over aging

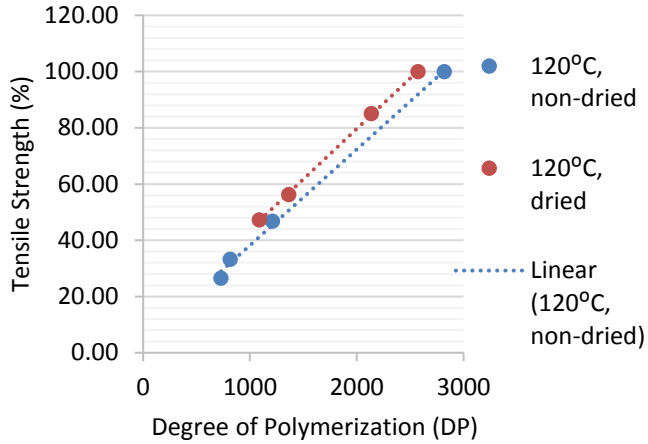


Figure 9. DP and TS correlation by using linear regression.

Table 2 Linear regression result from DP and TS

Sample	Linearity (x = DP, y = TS)	R^2
120^0C, non-dried	$y = 0.0341x + 4.084$	0.9972
120^0C, dried	$y = 0.0359x + 7.9196$	0.9996

C. Structural Changes of Cellulose

Degradation process due to thermal stress in the natural ester is mainly affected by hydrolysis reaction [20,21]. It becomes the main differences with aging characteristic in the mineral oil which is influenced by the oxidation reaction. Natural ester consists of triglyceride that has three fatty acid molecules connected at the hydroxyl groups via ester linkages [48]. Hydrolysis in natural ester consumes three water molecules to break triglyceride bond into glycerol and three fatty acids as shown in Figure 10 [20]. Moisture equilibrium between oil and paper have a high contribution to the hydrolysis reaction because water molecules act as a reactant [21,49]. A higher amount of water means higher speed of hydrolysis reaction. The speed of hydrolysis reaction refers to Arrhenius's theory of reaction kinetic energy in equation (2). From the equation below, it can also be observed that aging temperature give a contribution to the rate of the hydrolysis reaction.

$$k = Ae^{\frac{-E_a}{RT}} \quad (2)$$

Where k is the constant rate of reaction, E_a is the activation energy (kJ/mol), T is the absolute temperature in Kelvin, R is the ideal gas constant (8,314 J/mol. K), and A is a parameter depending on the chemical environment. The activation energy represents the minimum amount of energy that is required to activate the atoms or molecules which undergo a chemical reaction [40].

However, the hydrolysis reaction occurred at the same time with the oxidation reaction. The unsaturated double bond is susceptible to oxidation [48]. The more amount of unsaturated level triglyceride in the vegetable oil, make it easy to perform oxidation mechanism [50]. Oxidation is initiated from the removal of a hydrogen atom from the methylene group next to the double bond. The existence of oxygen then supports further propagation reaction. The oxidation reaction mainly produces free radical ions that respectively will accelerate the other oxidation processes. The stability level of vegetable oil can be improved by reducing the amount of unsaturated fatty acids in the oil [48,51]. Temperature operation is the main parameter that determines the rate of oxidation in the hydrocarbon [52].

The chemical structural changes of kraft paper are examined by using FTIR spectroscopy. The peak at certain wavenumbers represents the functional group of molecular bonds. In these cases, FTIR spectroscopy of the paper surface during the aging have observed. Based on the

observation, samples with dried paper have a different significant characteristic of FTIR spectroscopy compared to the non-dried paper. Besides, FTIR spectroscopy of kraft paper at particular wavenumber has a deep correlation to the aging characteristic. Table 3 and 4 show the peak absorbance of specific wavenumber. The absorbance is used to observe C-O bond, C=O bond or ester functional group, C-H bond which represent aldehyde and alkane functional group and O-H bond which include to the hydroxyl group at 1743.98 cm^{-1}, 3325.17 cm^{-1}, 2853.79 cm^{-1}, and 2921.74 cm^{-1} of peak.

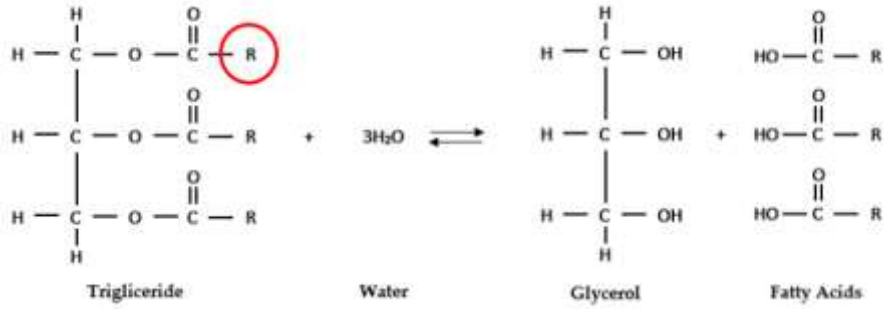


Figure 10. Hydrolysis in natural ester oil [15].

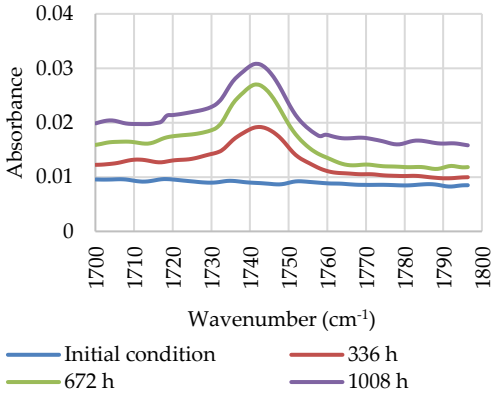
Table 3. Peak absorbance of FTIR spectroscopy of non-dried paper samples at 120^0C

Wavenumber (cm^{-1})	Functional Group	Peak Absorption			
		Initial cond.	336 hours	672 hours	1008 hours
1027.70	C-O	0.08944	0.0863	0.0656	0.0601
1104.14	C-O	0.05242	0.0515	0.0392	0.0332
1159.35	C-O	0.03494	0.0377	0.0287	0.0203
1743.98	C=O (Ester)	0.00881	0.019	0.0262	0.030
2853.79	C-H (Aldehyde)	0.01653	0.0250	0.0289	0.0382
2921.74	C-H (Alkane)	0.01567	0.0279	0.0325	0.0397
3272.80	O-H	0.02975	0.0295	0.0298	0.0278
3325.17	O-H	0.03037	0.0301	0.03	0.0282

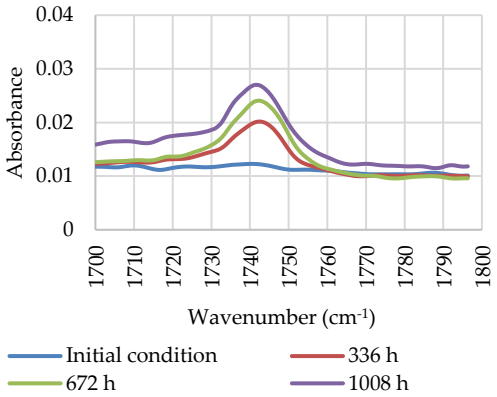
Table 4. Peak absorbance of FTIR spectroscopy of dried paper samples at 120^0C

Wavenumber (cm^{-1})	Functional Group	Peak Absorption			
		Initial cond.	336 hours	672 hours	1008 hours
1027.70	C-O	0.0904	0.0840	0.0656	0.0814
1104.14	C-O	0.0530	0.0502	0.0392	0.0491
1159.35	C-O	0.0352	0.0365	0.0287	0.0375
1743.98	C=O (Ester)	0.0120	0.0199	0.0236	0.0262
2853.79	C-H (Aldehyde)	0.0166	0.0210	0.0242	0.0266
2921.74	C-H (Alkane)	0.0162	0.0213	0.0264	0.0308
3272.80	O-H	0.0329	0.0298	0.0284	0.0276
3325.17	O-H	0.0335	0.0315	0.0290	0.0281

Figure 11 is the FTIR result of kraft paper at spectroscopy around 1700 cm^{-1} to 1800 cm^{-1}. The peak was observed at 1744 cm^{-1} that indicate the existence of the C=O bond. It can also be observed that kraft paper that has not been immersed in the oil does not have C=O bonds. FTIR spectroscopy results in this condition match with the molecular structure of cellulose showed in Figure 6. It does not contain a C=O functional group in its polymeric chain. As the duration of aging increases, kraft paper starts to gain a C=O bond. The peak absorbance of samples with non-dried paper treatment is higher than samples with dried paper treatment. It means that sample with higher moisture level tends to absorb a higher amount of fatty acid which consist of C=O bonds. This condition supports the statement before that water equilibrium between oil and paper affects the hydrolysis reaction.



(a)



(b)

Figure 11. FTIR spectroscopy at wavenumber 1700-1800 cm^{-1} of kraft paper: (a) 120^0C, non-dried; (b)120^0C, dried.

Binding processes of fatty acid (-COOR group) to the cellulose in the paper surface is caused by a transesterification reaction. Fatty acid replaces the reactive OH group in the fifth atom carbon were located in the outside of pyranose rings. Transesterification reaction in the natural ester was claimed to be a reaction that slows down the chain scission process in cellulose. Figure 12 shows how transesterification happens in the cellulose. Chain scission process in the non-esterified glucose chain happens as the -OH group in the outside of cellulose reacts with the hydrogen atom to produce a water molecule, which is called hydrolysis reaction. The oxidation reaction then transforms alcohol into a ketone. Hydrogen in the -OH group is then replaced by the carbon group and -CH_2OH formed reacts with oxygen to break the glucose chain. However,

transesterification is claimed to be a reaction that prevents chain scission processes. The presence of fatty acids will block the reactive group (-CH_2OH) [20]. In the other study, the formation of -COOR group may reduce the rate of chain scission by giving protection to the cellulose from water molecule [53]. Instead of its role as the water barrier, transesterification may strengthen the C-O and C-C bonds in the cellulose [53].

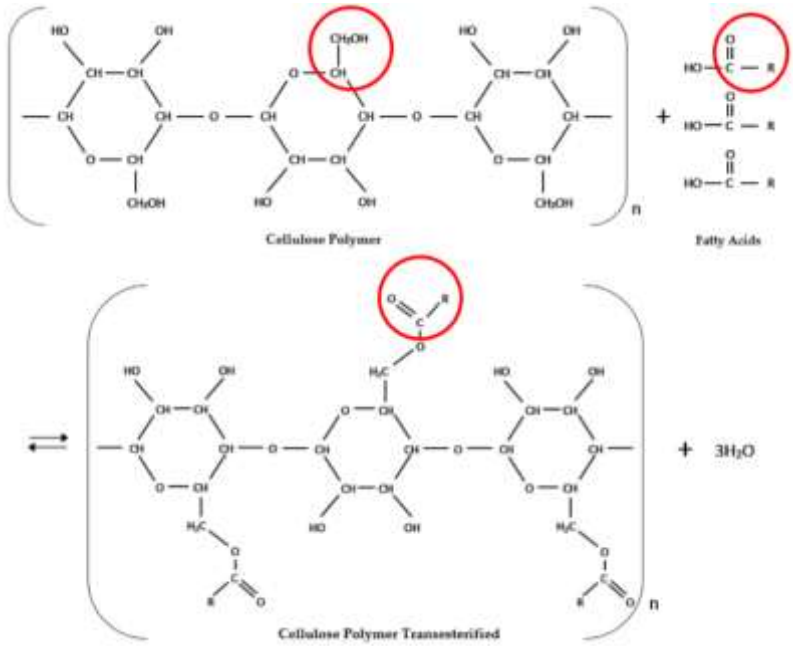
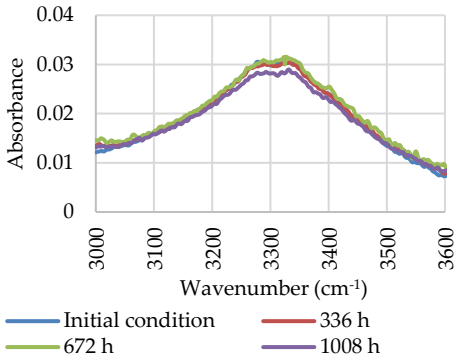


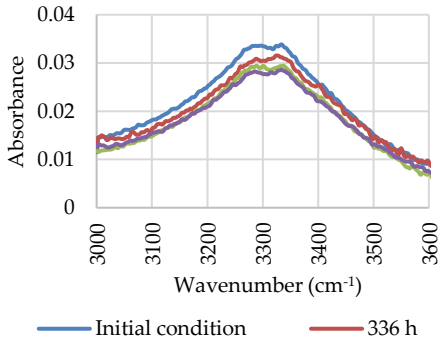
Figure 12**.** Transesterification reaction [15].

The other observations are also conducted at wavenumber range from 3000 cm^{-1} to 3600 cm^{-1}. Figure 13 below shows the comparison of the absorbance values of kraft paper during the aging. The peak is located at 3273 cm^{-1} and 3325 cm^{-1} which indicate stretching vibration of hydroxyl groups in the cellulose [12,54]. The intensity of absorbance of O-H peak is getting lower by the time of aging. The decrease in O-H peak absorption is mainly due to the reduction of inter and intermolecular hydrogen bonding [12]. Loss of hydrogen bonds that strengthen the cellulose chain will accelerate paper degradation. As the weak bond has already been removed, further degradation which is caused by hydrolysis and oxidation will break the linkage of the long glucose chain. It will give a contribution to the decrease in the molecular weight of cellulose [15]. The main products of paper degradations are CO, CO_2, H_2O, CH_4, and furans that during the aging will dissolve to the natural ester. Cleavage chain of the cellulose also contributes to the decrease of peak absorbance in this range. As the reactive hydrogen bond (-OH) in the outside of the ring reacts with hydrogen to form water molecules, the value of hydrogen absorbance will decrease over the aging. In the previous research, observation under this wavenumber shows how durable kraft paper can bind the water molecule [55].

Figure 14 illustrates the variation of FTIR spectra at 2700-3000 cm^{-1} with the peak around 2853.79 cm^{-1} and 2921.74 cm^{-1}. The peak at those wavenumbers determines the stretching vibration of C-H groups. The absorbance intensity is getting higher with the increase of the aging duration. This condition is caused by absorption of the hydrolysis and oxidation product to the paper surface. Low molecular weight particles may attach the surface of kraft paper and lead to the formation of hydrocarbon layer or lamination, which increase the stretching vibration of C-H groups. Degradation in the paper surface may also give a contribution to the C-H attachment because of the deterioration process can form a more reactive site that enhances this process.

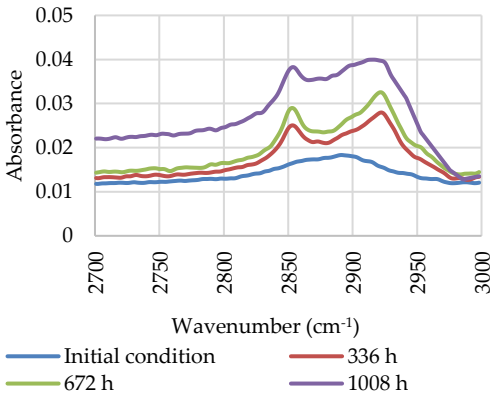


(a)

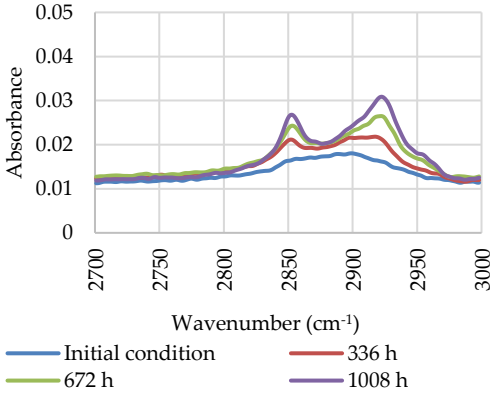


(b)

Figure 13. FTIR spectroscopy at wavenumber 3000-3600 cm^{-1} of kraft paper: (a) 120^0C, non-dried; (b)120^0C, dried.



(a)



(b)

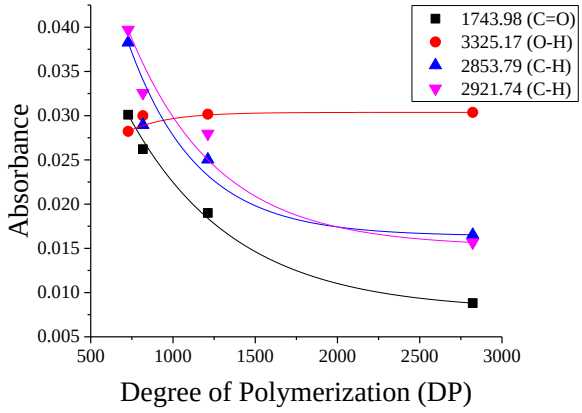
Figure 14. FTIR spectroscopy at wavenumber 2700-3000 cm^{-1} of kraft paper: (a) 120^0C, non-dried; (b)120^0C, dried.

D. Analysis of Aging Processes

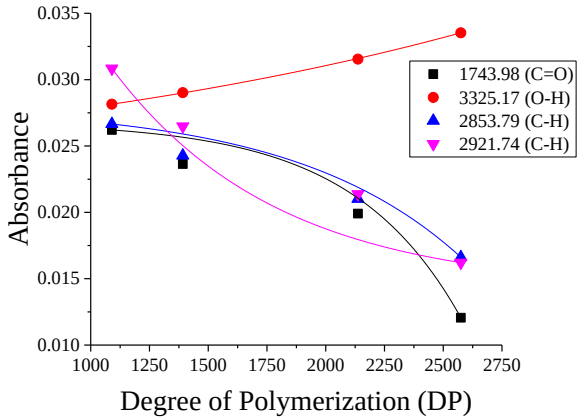
Degree of polymerization and tensile strength measurement are generally used to diagnose the lifetime of a transformer. This method is also useful in determining the irreversible degradation characteristic of kraft paper. Aging process in this study is also being observed by using FTIR spectroscopy. The results show that the value of particular peak absorbance, which represents a specific functional group, is correlated to the decrease of the degree of polymerization and tensile strength value. Exponential and linear regression is used to analyze the correlation between these two parameters.

Surprisingly, moisture content determines the suitable regression method to be chosen in this experiment. Figure 15 shows the result of exponential regression between the degree of polymerization and peak absorbance at 1743.98 cm^{-1}, 3325.17 cm^{-1}, 2853.79 cm^{-1}, and 2921.74 cm^{-1} which represent C=O, O-H and C-H functional group respectively. Besides, Figure 16 shows the linear regression result for those two parameters. The R^2 is again called the coefficient of determination which has a range of 0–1 and can be used to represent how close the data to regression method used. A value of R^2 near to 1 means that among the parameters observed has a strong relationship.

Exponential regression is found to be a better method for modeling the correlation between DP and peak absorbance for high moisture sample. However, exponential regression does not give a good result for the low moisture content of kraft paper. Linear regression is more appropriate for modeling this case. It is strengthened by the value R^2 shown in Table 5 below. In high moisture condition, the value of R^2 for exponential regression is higher than the value of R^2 for linear regression in every wavenumber. Meanwhile, the value of R^2 for low moisture content is good if they are modeled by using linear regression. This behavior can be explained as follows: the decrease of DP in the initial aging for high moisture condition is faster than the sample in low moisture condition. Hydrolysis in oil and kraft paper takes an essential part in this degradation process. The low molecular weight cellulose chains are easier to be chopped down among the high molecular weight cellulose. Therefore, the decomposition processes are rather intense during the initial aging period. The high molecular weight cellulose chains will decrease sharply during the end of the aging period, leading to a decrease in cellulose degradation rate. The existence of water molecule and aging temperature will also affect the rate of other reactions between natural ester and kraft paper during the aging. Changes in the DP value to the variations in paper moisture was also being observed in the latest experiment by using mineral oil [56]. The DP value can then be approached with the value of peak absorbance because the C=O, O-H, and C-H functional groups replace the presence of the other bonds during chain scission in the cellulose.

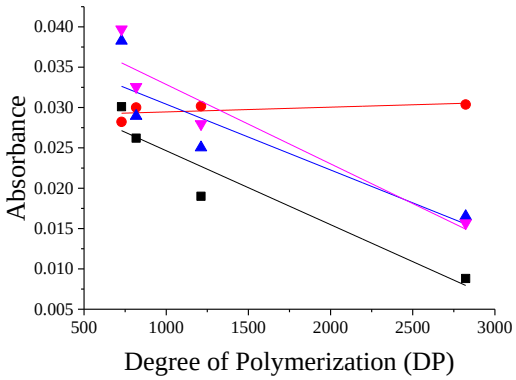


(**a**)

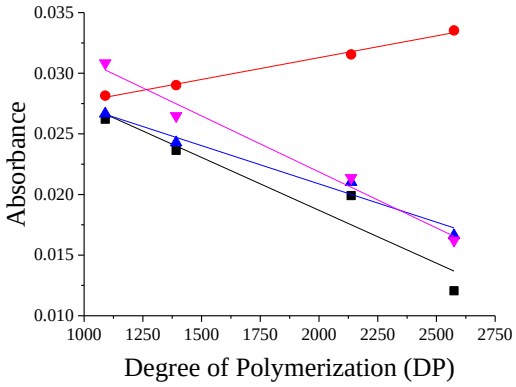


(b)

Figure 15. DP and FTIR exponential regression: (a) 120^0C, non-dried; (b) 120^0C, dried.



(a)



(b)

Figure 16. DP and FTIR linear regression: (a) 120^0C, non-dried; (b)120^0C, dried.

Table 5**.** Exponential and linear regression result from DP and peak absorbance

Sample	Wavenumber (cm^{-1})	Functional Group	R^2	
			Exponential Regression	Linear Regression
120^0C, non-dried	1743.98	C=O	0.9837	0.9115
	3325.17	O-H	0.5679	0.3374
	2853.79	C-H	0.8796	0.7757
	2921.74	C-H	0.9352	0.9012
120^0C, dried	1743.98	C=O	0.8572	0.9234
	3325.17	O-H	0.9996	0.9940
	2853.79	C-H	0.8200	0.9718
	2921.74	C-H	0.6559	0.9831

4. Conclusion

This study verifies that initial moisture of paper influences the aging performance of kraft paper and natural ester oil. During the aging, the decline rate of the degree of polymerization and tensile strength is fast in the beginning and getting slower later on. A rapid removal of weak linkage of the cellulose chain as well as inter and intermolecular hydrogen bonds due to the hydrolysis and oxidation reaction lead to generating high rate decline value in initial aging. As the weak bond removed, the remaining strong crystalline structure slows down the rate of the chain scission. It also confirms that there is a correlation between chain scission of cellulose to the decrease of mechanical strength. From the FTIR analysis at kraft paper in 1744 cm^{-1} of peak, there is an indication that C=O functional group, which is the product of hydrolysis reaction in the natural ester, bind with the paper surface. Trans esterification reaction involves the fatty acid molecule (C=O bond) to bind with the surface of the paper and creates a form of water barrier. The formation can keep paper insulation drier and it is claimed that it can extend the lifetime of the transformer. Besides, FTIR spectra at wavenumber 3000-3600 cm^{-1} indicate stretching vibration of hydroxyl group decline during the aging duration. The observation of FTIR spectra at wavenumber 3000-3600 cm^{-1} indicates stretching vibration of C-H groups increases with the aging duration. It may be caused by low molecular weight particles attach to the surface of kraft paper and lead to form a hydrocarbon layer or lamination. The result of FTIR shows that the amount of peak absorbance of C=O, O-H and C-H bond has a strong correlation with the decrease of the degree of polymerization and tensile strength value. For high moisture condition, the correlation between these two parameters can be well modeled by using exponential regression. On the other hand, linear regression fits better for modeling low moisture condition. The peak

absorbance can be used to identify the DP value because C=O, O-H and C-H functional group replaced other bonds in the cellulose when chain scission process took place.

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6. References

[1]. Genutis, D.A. Importance of Electrical Insulation Electrical Equipment Condition Assessment Using On-Line Solid Insulation Sampling

[2]. Stone, G.C.; Culbert, I.; Boulter, E.A.; Dhirani, H. Electrical Insulation for Rotating Machines: Design, Evaluation, Aging, Testing, and Repair: Second Edition; 2014; ISBN 9781118886663

[3]. Banović, M.; Sanchez, J. Basics of Power Transformers. Transformers Magazine 2014, 1, 12–15

[4]. Wadhwa, C.L. High voltage engineering; New Age Science, 2010; ISBN 1906574723

[5]. Mildemberger, L.; Andreoli, M.C.; Silva, G.C. da; Motta, H.N. da; Gulmine, J.V.; Munaro, M.; Mildemberger, L.; Andreoli, M.C.; Silva, G.C. da; Motta, H.N. da; et al. Correlation between stabilizer consumption and degree of polymerization of thermally upgraded paper aged in insulating natural ester and insulating mineral oil. Polímeros 2016, 26, 61–65

[6]. Rajab, A.; Sulaeman, A.; Sudirham, S.; Suwarno, S. A Comparison of Dielectric Properties of Palm Oil with Mineral and Synthetic Types Insulating Liquid under Temperature Variation. *ITB Journal of Engineering Science 2011*

[7]. Munajad, A.; Subroto, C.; Suwarno Fourier transform infrared (FTIR) spectroscopy analysis of transformer paper in mineral oil-paper composite insulation under accelerated thermal aging. *Energies 2018*

[8]. Rahmat, S.; Pasaribu, R.A.; Suwarno Effects of thermal aging on Dielectric Properties and DGA of oil-paper insulations. In *Proceedings of the 2016 3rd Conference on Power Engineering and Renewable Energy (ICPERE); IEEE*, 2016; pp. 231–234

[9]. Suwarno; Munajad, A.; Subroto, C. Dissolved gas analysis (DGA) and fourier transform infra red (FTIR) spectroscopy of thermal-aged natural ester-paper composite. In *Proceedings of the 2017 52nd International Universities Power Engineering Conference, UPEC 2017; 2017*

[10]. Martins, M.A.; Gomes, A. Comparative study of the thermal degradation of synthetic and natural esters and mineral oil: effect of oil type in the thermal degradation of insulating kraft paper. *IEEE Electrical Insulation Magazine* 2012, 28, 22–28

[11]. Suwarno, S.; Pasaribu, R.A. Thermal Aging of Mineral Oil -Paper Composite Insulation for High Voltage Transformer. *International Journal on Electrical Engineering and Informatics 2016*, 8, 820–835

[12]. Bandara, K.; Ekanayake, C.; Saha, T.K.; Annamalai, P.K. Understanding the ageing aspects of natural ester based insulation liquid in power transformer. *IEEE Transactions on Dielectrics and Electrical Insulation* 2016, 23, 246–257

[13]. Suwarno; Widyanugraha, T.; Hs, P.D.; Suharto Dielectric properties of silicone oil, natural ester, and mineral oil under accelerated thermal aging. *Proceedings of 2012 IEEE International Conference on Condition Monitoring and Diagnosis, CMD 2012 2012, 1139–1142*

[14]. Hamid, M.H.A.; Ishak, M.T.; Din, M.F.M.; Suhaimi, N.S.; Katim, N.I.A. Dielectric properties of natural ester oils used for transformer application under temperature variation. *In Proceedings of the PECON 2016 - 2016 IEEE 6th International Conference on Power and Energy, Conference Proceeding; 2017*

[15]. Munajad, A.; Subroto, C.; Suwarno Study on the effects of thermal aging on insulating paper for high voltage transformer composite with natural ester from palm oil using fourier

transform infrared spectroscopy (ftir) and energy dispersive x-ray spectroscopy (EDS). *Energies 2017, 10, 1857*

[16]. Suwarno, M. Ilyas, Rubadi, Effects of temperature on dielectric properties of rhicinnus oils as insulating liquid, Proceedings of 2008 International Conference on Condition Monitoring and Diagnosis, Beining, 21-24 April 2008, pp. 286-289

[17]. Pillai, R.; Havaldar, F.; Chitnis, C. Natural esters for life and capacity enhancement of distribution transformers. CIRED - Open Access Proceedings Journal 2017, 2017, 355–358

[18]. Oommen, T.V.; Claiborne, C.C.; Mullen, J.T. Biodegradable electrical insulation fluids. *In Proceedings of the Proceedings: Electrical Insulation Conference and Electrical Manufacturing and Coil Winding Conference; IEEE; pp. 465–468*

[19]. Cai, S.; Chen, C.; Guo, H.; Chen, S.; Zhou, Z.; Guo, Z. Fire resistance test of transformers filled with natural ester insulating liquid. *The Journal of Engineering 2018*

[20]. Murphy, D.J. Future prospects for oil palm in the 21st century: Biological and related challenges. *European Journal of Lipid Science and Technology 2007, 109, 296–306*

[21]. Garcia, B.; Garcia, T.; Primo, V.; Burgos, J.C.; Urquiza, D. Studying the loss of life of natural-ester-filled transformer insulation: impact of moisture on the aging rate of paper. *IEEE Electrical Insulation Magazine 2017, 33, 15–23*

[22]. Rapp, K.J.; McShane, C.P.; Luksich, J. Interaction mechanisms of natural ester dielectric fluid and kraft paper. *In Proceedings of the IEEE International Conference on Dielectric Liquids, 2005. ICDL 2005.; IEEE; pp. 387–390*

[23]. Frimpong, G.K.; Oommen, T. V.; Asano, R. A survey of aging characteristics of cellulose insulation in natural ester and mineral oil. *IEEE Electrical Insulation Magazine 2011*

[24]. Baird, P.J.; Herman, H.; Stevens, G.C. On-site analysis of transformer paper insulation using portable spectroscopy for chemometric prediction of aged condition. *IEEE Transactions on Dielectrics and Electrical Insulation 2008*

[25]. Saha, T.K. Review of modern diagnostic techniques for assessing insulation condition in aged transformers. *IEEE Transactions on Dielectrics and Electrical Insulation 2003, 10, 903–917*

[26]. Herman, H.; Shenton, M.J.; Stevens, G.C.; Heywood, R.J. A new approach to condition assessment and lifetime prediction of paper and oil used as transformer insulation. *In Proceedings of the ICSD'01. Proceedings of the 20001 IEEE 7th International Conference on Solid Dielectrics (Cat. No.01CH37117); IEEE; pp. 473–476*

[27]. Przybylek, P. A new method for indirect measurement of water content in fibrous electro-insulating materials using near-infrared spectroscopy. *IEEE Transactions on Dielectrics and Electrical Insulation 2016, 23, 1798–1804*

[28]. C57.100-2011 IEEE Standard Test Procedure for Thermal Evaluation of Insulation Systems for Liquid-Immersed Distribution and Power Transformers.; ISBN 9780738171968

[29]. Sun, P.; Sima, W.; Yang, M.; Wu, J. Influence of thermal aging on the breakdown characteristics of transformer oil impregnated paper. *IEEE Transactions on Dielectrics and Electrical Insulation 2016, 23, 3373–3381*

[30]. Anastopoulos, G.; Zannikou, Y.; Stournas, S.; Kalligeros, S. Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. Energies 2009

[31]. Zhang, Y.; Dubé, M.A.; McLean, D.D.; Kates, M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Bioresource Technology 2003

[32]. Meher, L.C.; Vidya Sagar, D.; Naik, S.N. Technical aspects of biodiesel production by transesterification - A review. Renewable and Sustainable Energy Reviews in 2006.

[33]. IEEE Power Engineering Society. Transformers Committee.; Institute of Electrical and Electronics Engineers.; *IEEE-SA Standards Board. IEEE guide for loading mineral-oil-immersed transformers; Institute of Electrical and Electronics Engineers, 1996; ISBN 9780738108834*

[34]. Acker, C.R. Loading Guide for 65 C Rise Distribution Transformers. *IEEE Transactions on Power Apparatus and Systems 1964, 83, 893–901*
[35]. Liu, K.; Yang, K.; Wang, W.; Zhou, K.; Lu, J. Tensile strength research of PC and PET under high temperature in mineral oil. *In Proceedings of the 2014 IEEE Conference on Electrical Insulation and Dielectric Phenomena, CEIDP 2014; 2014*
[36]. Cui, H.; Abu-Siada, A.; Li, S.; Islam, S. Correlation between dissolved gases and oil spectral response. *In Proceedings of the 2017 1st International Conference on Electrical Materials and Power Equipment (ICEMPE); IEEE, 2017; pp. 28–32*
[37]. Fellers, Christer. Ageing/degradation of paper : a literature survey / Christer Fellers ... [et al.]; Fellers, C., Ed.; Rapport (FoU-projektet for papperskonservering (Sweden)) ; no. 1E.; FoU-projektet for papperskonservering: Stockholm, 1989
[38]. Levchik, S.; Scheirs, J.; Camino, G.; Tumiatti, W.; Avidano, M. Depolymerization processes in the thermal degradation of cellulosic paper insulation in electrical transformers. Polymer Degradation and Stability 1998, 61, 507–511
[39]. Heywood, R.J.; Xiao, X.; Ali, M.; Emsley, A.M. Degradation of cellulosic insulation in power transformers. Part 3: Effects of oxygen and water on ageing in oil. IEE Proceedings - Science, Measurement and Technology 2000, 147, 115–119
[40]. Brantaco, A.A. Effect of progressive recycling on cellulose fiber surface properties, Georgia Institute of Technology, 2008
[41]. Lundgaard, L.E.; Hansen, W.; Linhjell, D.; Painter, T.J. Aging of Oil-Impregnated Paper in Power Transformers. *IEEE Transactions on Power Delivery 2004*
[42]. Unsworth, J.; Mitchell, F. Degradation of electrical insulating paper monitored with high performance liquid chromatography. *IEEE Transactions on Electrical Insulation 1990, 25, 737–746.*
[43]. Bandara, K.; Ekanayake, C.; Saha, T.; Ma, H. Performance of natural ester as a transformer oil in moisture-rich environments. *Energies 2016*
[44]. Hill, D.J.T.; Le, T.T.; Darveniza, M.; Saha, T. A study of the degradation of cellulosic insulation materials in a power transformer. Part III: *Degradation products of cellulose insulation paper. Polymer Degradation and Stability 1996*
[45]. Emsley, A.M.; Stevens, G.C. Kinetics and mechanisms of the low-temperature degradation of cellulose. Cellulose 1994
[46]. Dissado, L.A.; Hill, R.M. Anomalous low-frequency dispersion. Near direct current conductivity in disordered low-dimensional materials. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics 1984*
[47]. Stevens, G.C.; Emsley, A.M. Review of chemical indicators of degradation of cellulosic electrical paper insulation in oil-filled transformers. *IEE Proceedings - Science, Measurement and Technology 1994*
[48]. Tang, F.; Zhang, Y.; Yuan, B.; Li, Y.; Zhang, W.-B.; Zhang, G.-J. Ageing condition assessment of oil-paper insulation using near infrared spectroscopy detection and analytical technique. 2018
[49]. Fox, N.J.; Stachowiak, G.W. Vegetable oil-based lubricants—A review of oxidation. Tribology International 2007, 40, 1035–1046
[50]. Scheirs, J.; Camino, G.; Tumiatti, W. Overview of water evolution during the thermal degradation of cellulose. European Polymer Journal 2001, 37, 933–942
[51]. Sherwin, E.R. Oxidation and antioxidants in fat and oil processing. *Journal of the American Oil Chemists' Society 1978, 55, 809–814*
[52]. Warner, K.; Knowlton, S. Frying quality and oxidative stability of high-oleic corn oils. *Journal of the American Oil Chemists' Society 1997, 74, 1317–1322.*
[53]. Hodges, P.K.B. Hydraulic Fluids; 1996; ISBN 0419-4217
[54]. Yang, L.; Liao, R.; Caixin, S.; Zhu, M. Influence of vegetable oil on the thermal aging of transformer paper and its mechanism. *IEEE Transactions on Dielectrics and Electrical Insulation 2011*

[55]. Hinterstoisser, B.; Åkerholm, M.; Salmén, L. Effect of fiber orientation in dynamic FTIR study on native cellulose. Carbohydrate Research 2001, 334, 27–37
[56]. Olsson, A.-M.; Salmén, L. The association of water to cellulose and hemicellulose in paper examined by FTIR spectroscopy. Carbohydrate Research 2004, 339, 813–818
[57]. Wang, Y.; Xiao, K.; Chen, B.; Li, Y. Study of the impact of initial moisture content in oil impregnated insulation paper on thermal aging rate of condenser bushing. Energies 2015.

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