Thermal Aging of Ester from Palm Oil and Kraft Paper Composite Insulation

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Abstract: - Since long time ago, mineral oil is being used as insulation for high voltage equipments such as transformers. Due to environment consideration and the long term availability, liquid insulation from plantation are being introduced. However, the performance of such insulation in composite with paper should be investigated in order to maintain the quality of the insulation in operating equipments under electric and thermal stresses. This paper reports the experimental results on the effects of thermal aging of natural ester from palm oil and Kraft paper composite insulation. Samples of 800 ml ester and 6 gram of kraft insulation paper were put together in heat-resistant hermetic bottles to simulate actual condition of transformator. All samples were subjected to thermal aging condition for duration of 336 hours to 672 hours at 120^{o}C and 150^{o}C in a controllable oven. Dielectric properties such as breakdown voltage, resistivity, water content were measured and dissolved gas analysis were conducted after and before aging. The morphological aging of the kraft paper was investigated using SEM (scanning electron microscopy) while chemical element change was investigated using EDS (energy dispersive spectroscopy). The experimental results indicated that thermal aging process greatly affected the breakdown voltage and resistivity. At initial stage of thermal aging application the breakdown voltage increased due to the reduction of water content. However, long term aging reduced the breakdown voltage due to the drastic increase of oxidation by product which was indicated by the darker color. Dissolved gas analysis indicated that thermal aging in ester-paper composite insulation released H_2 (Hydrogen), CH_4 (Methane), C_2H_2 (Acetylene), C_2H_4 (ethylene), C_2H_6 (ethane), and CO (Carbon Monoxide). The EDS analysis showed that during aging the C element increased while O element decreased. EDS data of krafft paper aged at 120^{o}C for a duration of 4 weeks (672 hours) taken using JEOL 6510 at accelerated voltage of 10 kV with energy range of 0-20 keV showed that the aged paper consists of 3 elements, C , O and K elements with mass percentage of 75.23 % of C at energy of 0.277 keV , O of 21.69 % observed at energy of 0.525 keV and new element of K with mass percentage of 3.08 observed at energy of 3.312 keV. It is clearly observed that C increased from 58.83 % to 75.23 %. This is due to the migration from the ester into the paper on the other hand oxygen reduced from 41.17 % to 21.69 % because the oxygen from the paper reacted with oil in an oxidation and release CO gas as confirmed by DGA (dissolved gas analysis). Similar behavior was observed for aging at 150^{o}C.

Key-Words: - Ester , Kraft paper, Dissolved Gas Analysis, dielectric properties, SEM, EDS

1 Introduction

High voltage equipments play important role in an electric power network. In the high voltage equipment, insulation is one of the most important parts to withstand a high electric field during the operation of the equipments. Liquid insulation is widely used in a power transformer. Petroleum-based mineral oils have been used as insulation for power transformer since long time ago. However, due to the environmental aspects and the availability in the future, researchers are searching new types of insulating materials, which are friendly to environment and renewable. Some of natural ester o were introduced[1-6]. Natural ester shows a high breakdown voltage and flash point. In order to obtain better performances, mixture with mineral oil was also reported. Taking into account the requirements from standard, the mixture of natural ester from palm oil and mineral oil with ester content of 50 % is considered as good enough to be used as a high voltage insulating liquid. [5].

Investigation to apply the natural ester for distribution as well as high voltage power transformers were reported [7-13].

Kraft paper insulation is composed of approximately 90% of cellulose, 6-7% hemi-cellulose and 3-4% of lignin. A dry wood Kraft paper contains 40 to 50% of cellulose, 10-30% hemi-cellulose and about 20-30% lignin [14-15]. When degradation of paper insulation occurs, hydrogen bonds are tending to breakdown causing the cellulose molecular chain to be shorter. As a result, gases are produced due to oil decompositions such as hydrogen (H_2), methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4) and ethane (C_2H_6), while carbon monoxide (CO) and carbon dioxide (CO_2) are mainly produced by paper decompositions and can be used for paper monitoring [16-18].

In this paper paper, accelerated thermal ageing test at 120 °C and 150 °C was conducted for 336 hours and 672 hours which simulated the ageing process in transformer. The effects of the thermal aging to the dielectric properties and dissolved gas in esterl were investigated. The thermal aging effects on morphological as well as chemical change of kraft paper were also investigated.

2 Experimental setup

2.1 Sample

Natural ester from palm oil and kraft paper were used in this experiment. A sample composed of 6 gram of dry paper insulation and 800 ml of ester from palm oil were inserted into heat-resistant and sealed glass bottles. Then they were placed in two iron oven and temperature of the oven was adjusted to 120°C and 150°C to simulate actual condition in transformator. 150°C temperature level selected by reference to research published in the IEEE by Mc Shane, et al [19], while the temperature of 120°C is a hot spot temperature according to the IEEE. Photograph of ester oil and paper insulation sampel are shown in figure 1 and 2.

Paper insulation and oil samples were taken out at a regular interval of 336 hours to determine the dielectric properties and dissolved gasses in oil. Here, oil samples used T0 as initial condition, while T1 and T2 are 336 and 672 hours ageing duration at temperature 120 °C and 150 °C respectively. Samples used with their aging treatments are shown in table 1.

(a) (b)

Figure.1 Ester Sample (a) Before and (b) After Thermal Aging

Figure 2. Photograph of Paper Insulation

Table.1 Sample aging treatment

Sample	Ageing
M. T0	Initial State
M. T1. 120	120^{o}C for 336 hours
M. T1. 150	150^{o}C for 336 hours
M. T2. 120	120^{o}C for 672 hours
M. T2. 150	150^{o}C for 672 hours

2.2 Dielectric Properties of ester

Dielectric properties such as breakdown voltage, resistivity and water content were measured. Breakdown voltage measurement was conducted in accordance with IEC 60156, while DC resistivity measurement was conducted using dielectric measurement system in accordance with IEC 60247 [20-21]. In this experiment the breakdown voltage was measured using bi-spherical standard cell with spacing of 2.5 mm in Liquid Dielectric Test Set LD60 from Phenix Technologies. AC voltage with frequency of 50 Hz was applied with increasing rate of 2 kV/s according to IEC 60156. Dielectric constant of the samples were measured using LCR meter and resistivity were measured using high resistance meter . Both measurements were conducted to oil sample with amount of 15 ml, and put in a liquid test cell from Tettex Instruments as shown in figure 2.

Figure 3. Liquid Test Cell and LCR Meter

2.3 Dissolved Gas Analysis

Dissolved gases in the oil samples were measured using gas chromatograph HP 6890 integrated with Automatic Liquid Sampler HP 7649. The chromatograph is shown in figure 4. The concentration of combustible gasses i.e. H_2 (hydrogen), CH_4 (methane), C_2H_6 (ethane), C_2H_4 (ethylene) and C_2H_2 (acetylene) was determined using DGA (dissolved gas analysis). The procedure to extract the gas from the oil sample refers to the standard ANSI / IEEE C57.104 (1991) and ASTM D3612[22-23].

Oil samples were placed in a vial. Vials containing about 15 ml sample then placed in the sample container. An automated sample traction device takes the vial to be analysed. Vial is shaken by an automatic shaker to extract the gas trapped in the oil. Gases accumulated in the top of the vial, then collected with a needle that also works automatically.

Figure 4. Gas Chromatograph HP 6890 integrated with Sampler HP 7649

2.4 Paper characterization

In order to understand the effects of thermal aging on the properties of kraft paper in natural ester several measurements are conducted. They are visual observation, scanning electron microscopy (SEM) and EDS measurement. Morphology of paper was observed using SEM JEOL JSM 6610 series with accelerated voltage of 0.3-30 kV as shown in figure 5 . The equipment has a built in EDS which enables to identify the chemical elements in the paper.

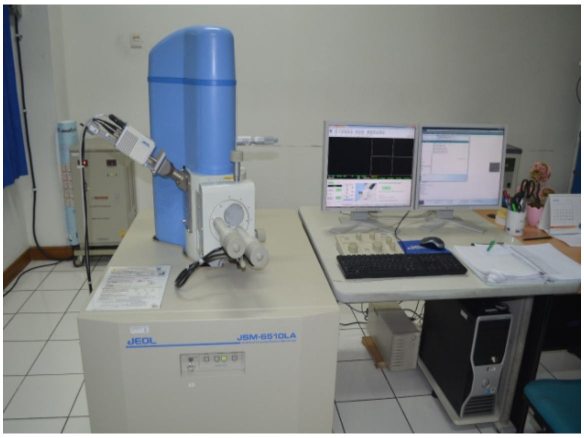


Figure 5 SEM JEOL JSM 6610

3 Experimental Results

3.1 Dielectric Properties of ester sample

Fig. 8 shows the dependence of breakdown voltage on ester oil during ageing time. The figure indicates that breakdown voltage of ester oil increased at 336 hours, then decreased after 672 hours. Under thermal ageing both of 120 ^{0}C and 150 ^{0}C, breakdown voltage in ester oil still much higher than standard IEC 60296 with limit of 30 kV. The increased of breakdown voltage at initial aging was due to the significant reduction of water content as shown in table 2. However, at longer aging the effect of water content reduction is much lower than the appearance of oxidation by product in the oil. This leads to the decrease of the breakdown voltage.

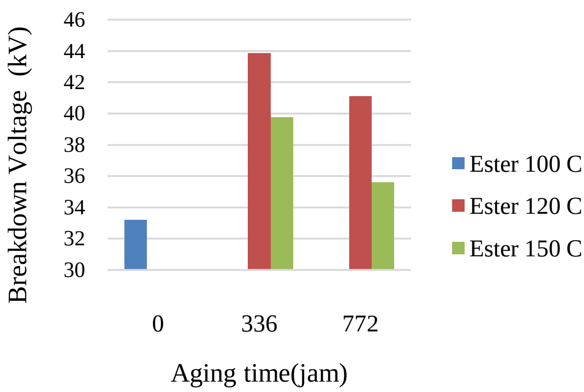


Figure 6. Breakdown Voltage Test Result in Ester Oil

Table 2 shows the visual appearance, breakdown voltage, resistivity and water content in oil before and after aging at 120^oC. The ester sample color became darker as aging became longer. The breakdown increased from 33.2 kV to 43.9 kV at 336 hours and then decrease to 41.1 kV at 672 hours. The increase of breakdown voltage was due to the great reduction of water content from 1061.9 to 478.4 mg/kg. The breakdown voltage reduction at later period was due to contaminant from oxidation by products as indicated by very dark color of the sample. Later this will be confirmed from the dissolved gas analysis (DGA).

Table 2
Dielectric properties of Ester sample before and after aging

Parameter	Sample		
	New	Aged at 120 ^oC for 336 h	Aged at 120 ^oC for 672 h
Visual appearance			
Breakdown voltage (kV)	33,2	43,9	41,1
Resistivity ($\times 10^{12}$ Ohm cm)	8.5	7	6
Water content (mg/kg)	1061,9	478,4	438,3

3.2 Dissolved Gasses Analysis

Table 2 shows the concentration of gases in the ester oil samplesThey are several gases obtained, those are H_2 (Hydrogen), CH_4 (Methane), C_2H_2 (Acetylene), C_2H_4 (ethylene), C_2H_6 (ethane), and CO (Carbon Monoxide). In this paper, we collect the concentration all of the gases and choose the most significant gases to interpret the condition of ester oil after ageing process.

From the table 3 it is clear that CO appeared in all of the samples. At high-temperature cellulose molecules are decomposed and evolve carbon oxides (CO_2 and CO). High level of dissolved carbon oxides in oil indicates the thermal degradation of cellulose insulation in the system. Hence, it is possible to assess the level of solid insulation degradation using amount of CO2 and CO concentration in oil.

Table 2. DGA test on Ester Oil

Samples	Gas Concentration (ppm)					
	H_2	CH_4	C_2H_2	C_2H_4	C_2H_6	CO
E.T0	0	0	0	0	0	0
E.T1.120	0	30,68	0	12,54	207,95	1674,58
E.T1.150	0	55,06	0	0	309,44	2264,89

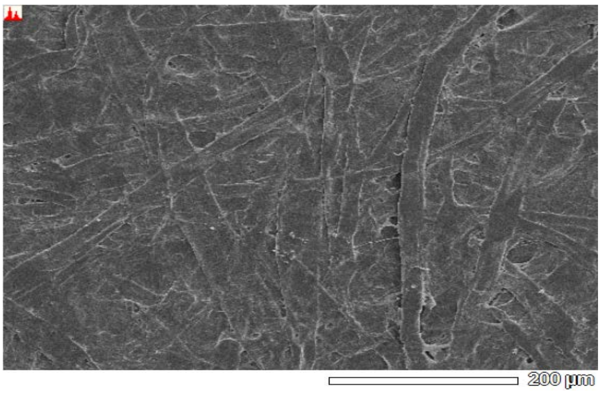
In this experiment, the amount gas concentration H_2 and C_2H_2 were little detected due to different experimental conditions. When high energy of electric defects such as partial discharge or arcs is concentrated on insulating oil, H_2 and C_2H_2 which the molecular weights are relatively small are generated in large amount because the degree of degradation of insulating oil is high.

The reason why C2H6 gas were generated in this experimental results considered to be the molecular bonding structures of natural ester fluid. Natural ester fluid is composed of unsaturated fatty acid structures which are compositely composed of double bonds and single bonds of carbon. When these structures are heated, the single bonds (C-C) that have weak binding force are degraded first to generate hydrocarbon. The hydrocarbon and water weaken the double bonds (C=C), so that the double bonds are decomposed to single bonds.

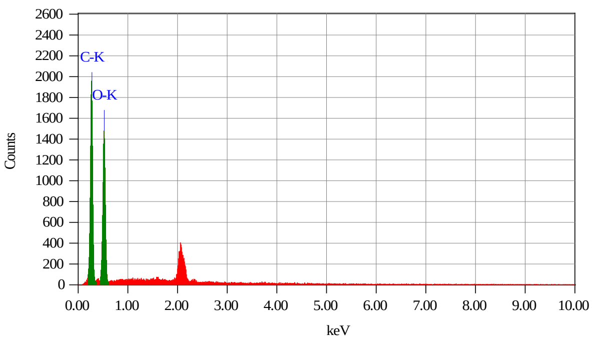
3.3 paper properties

Figure 7(a) shows the SEM picture of a new krafft paper taken using accelerated voltage of 10 kV and magnification of 200 x. It is seen that there are reasonable pore in the paper. Figure 7 (b) shows the EDS spectrum taken using JEOL 6510 at accelerated voltage of 10 kV with energy range of 0-20 keV. From the spectrum it is seen that the new paper is mainly consists of C and O elements with mass percentage of 59.83 % of C at energy of 0.277 keV and O of 41.17 % observed at energy of 0.525 keV. The results are consistent with the facts that Paper is composed of Cellulose which is an organic compound with the formula n, a polysaccharide consisting of a linear chain of several hundred to many thousands of β linked Dglucose units. The chemical formula of cellulose is ($C_6H_{10}O_5$)

Properties of new paper



(a)



Fitting Coefficient : 0.6497

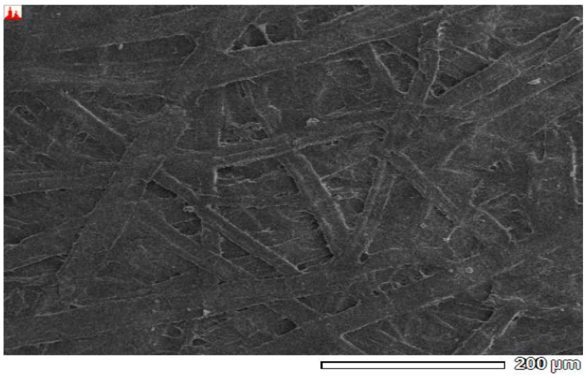
Element	(keV)	Mass%	Error%	Atom%
C K	0.277	58.83	0.23	65.55
O K	0.525	41.17	0.51	34.45
Total		100.00		100.00

(b)

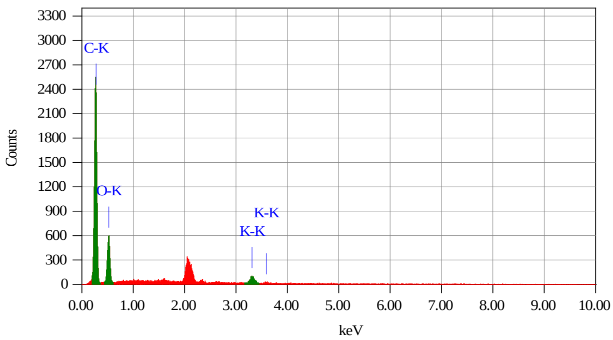
Figure 7 (a) SEM and (b) EDS spectra for new paper in ester from palm oil

Properties of paper aged at 120 deg for 336 hours in ester

Figure 8(a) shows the SEM picture of a krafft paper aged at 120°C for a duration of 4 weeks (672 hours) taken using accelerated voltage of 10 kV and magnification of 200 x. It is seen that there are reasonable pore in the paper. Figure 8 (b) shows the EDS spectrum taken using JEOL 6510 at accelerated voltage of 10 kV with energy range of 0-20 keV. From the spectrum it is seen that the aged paper consists of 3 elements, C , O and K elements with mass percentage of 75.23 % of C at energy of 0.277 keV , O of 21.69 % observed at energy of 0.525 keV and new element of K with mass percentage of 3.08 observed at energy of 3.312 keV. It is clearly observed that C increased from 58.83 % to 75.23 %. This is due to the migration from the ester into the paper on the other hand oxygen reduced from 41.17 % to 21.69 % because the oxygen from the paper reacted with oil in an oxidation and release CO gas as confirmed by DGA (dissolved gas analysis) which will be discussed later. From the EDS spectrum it is also seen that in the aged paper K element of 1.83 % mass is observed at energy of 3.312 keV. The sample used is a natural ester derived from palm oil. The main process is the transesterification reaction to get the targeted compound in the biodiesel product, the methyl ester. The Essential elements Reactants in this process are Methanol, Crude Palm Oil (CPO) and Alkali Catalyst KOH. The appearance of element K in the aged paper was due to the migration of K in the ester into the paper.



(a)

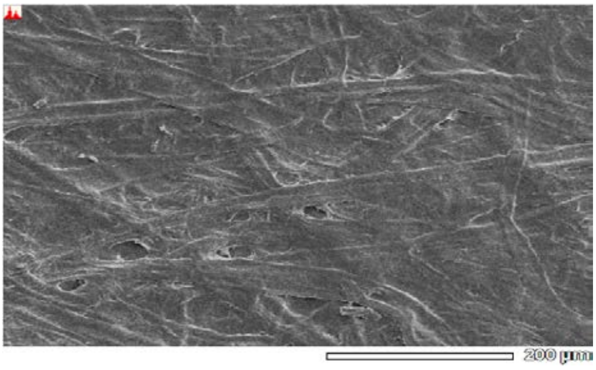


Fitting Coefficient : 0.7659

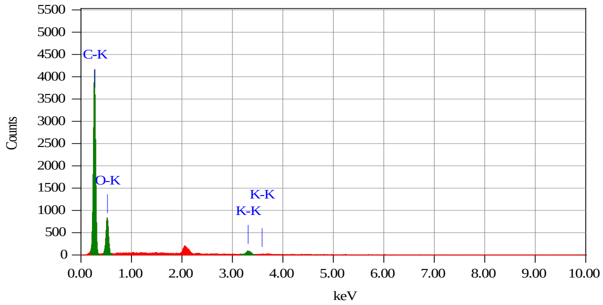
Element	(keV)	Mass%	Error%	Atom%
C K	0.277	75.23	0.29	81.37
O K	0.525	21.69	0.88	17.61
K K	3.312	3.08	1.35	1.02
Total		100.00		100.00

Figure 8 (a) SEM and (b) EDS spectra for paper in ester from palm oil aged at 120°C for 672 hours

Properties of paper aged at 150°C for 672 hours in ester



(a)



Fitting Coefficient : 0.7748

Element	(keV)	Mass%	Error%	Atom%
C K	0.277	78.19	0.30	83.40
O K	0.525	19.98	0.94	16.00
K K	3.312	1.83	1.43	0.60
Total		100.00		100.00

(b)

Figure 9 (a) SEM and (b) EDS spectra for paper in ester from palm oil aged at 150°C for 672 hours

Figure 9(a) shows the SEM picture of a krafft paper aged at 150°C for a duration of 4 weeks (672 hours) taken using accelerated voltage of 10 kV and magnification of 200 x. It is seen that pores are reasonably reduced due to oil migration into the paper pores. Figure 9 (b) shows the EDS spectrum taken using JEOL 6510 at accelerated voltage of 10 kV with energy range of 0-20 keV. From the spectrum it is seen that the aged paper consists of 3 elements, C , O and K elements with mass percentage of 78.19 % of C at energy of 0.277 keV , O of 19.98 % observed at energy of 0.525 keV and K with mass percentage of 1.83 % observed at energy of 3.312 keV. Thermal ageing of Kraft paper in ester oils yield mainly CO gas and its represent decomposition of cellulose. C_2H_6 gas generated from hydrocarbon bond that broke during ageing process, and small amount of H_2 and C_2H_2 due to different experimental ageing condition. Increasing temperature and the duration of the ageing proportional to total amount of dissolved gases. Gases that appear after ageing also affected breakdown voltage of ester oil, because gases had lower isolation capability than liquid, and hence, breakdown voltage of the ester oil decrease proportional to the ageing time.

The comparison of elements in new and aged kraft paper samples is shown in table

Element	Energy (keV)	New (%)	Aged at 120°C for 672 h (%)	Aged at 150°C for 672 h (%)
C	0.277	58.83	75.23	78.19
O	0.525	41.17	21.69	19.98
K	3.312		3.08	1.83

From the table it is seen that the thermal aging in ester-kraft paper composite insulation increased the C element due to ester permeation into the paper. However, the thermal aging reduced the O element of paper because of the usage of oxygen element to oxidize the ester to release CO or CO2 which was confirmed by DGA. The small K element appeared after aging came from the catalyst during esterification

4 Conclusion

We have investigated thye effects of thermal aging on natural ester from palm oil-kraft paper composite system. The thermal aging was conducted at 120°C and 150°C for duration of 336hours and 672 hours respectively. The experimental results indicated that thermal aging process greatly affected the breakdown voltage and resistivity. Dissolved gas analysis indicated that thermal aging in ester-paper composite insulation released H_2 (Hydrogen), CH_4 (Methane), C_2H_2 (Acetylene), C_2H_4 (ethylene), C_2H_6 (ethane), and CO (Carbon Monoxide). The EDS analysis showed that during aging the C element increased while O element degreased. EDS data of Krafft paper aged at 120°C for a duration of 4 weeks (672 hours) taken using JEOL 6510 at accelerated voltage of 10 kV with energy range of 0-20 keV showed that the aged paper consists of 3 elements, C , O and K elements with mass percentage of 75.23 % of C at energy of 0.277 keV , O of 21.69 % observed at energy of 0.525 keV and new element of K with mass percentage of 3.08 observed at energy of 3.312 keV. It is clearly observed that C increased from 58.83 % to 75.23 %. This is due to the migration from the ester into the paper on the other hand oxygen reduced from 41.17 % to 21.69 % because the oxygen from the paper reacted with oil in an oxidation and release CO gas as confirmed by DGA (dissolved gas analysis). Similar behavior was observed for aging at 150^{o}C. C element composition increased to 78.19 % of C at energy of 0.277 keV , while O element reduced to 19.98 % observed at energy of 0.525 keV and K with mass remain low at percentage of 1.83 % observed at energy of 3.312 keV. Thermal ageing of Kraft paper in ester oils yield mainly CO gas and this gas represents the decomposition of cellulose into the ester sample.

References:

[1] McShane, C.P., Vegetable-Oil-Based Dielectric Coolant, *IEEE Industry Applications Magazine*, Vol. 3, Issue 3, 2002, pp.34-41.

[2] E. Gockenbach and H. Borsi, "Performance and new application of ester liquids," *IEEE International Conference on Dielectric Liquids*, 2002, pp. 203-206.

[3] Z.H. Shah, Q. A. Tahir, "Dielectric properties of Vegetable Oils". *Journal of Scientific Research*, Vol. 3 , No. 3, 2011, pp. 481-492.

[4] H. Borsi, "Dielectric behavior of silicone and ester fluids for use in distribution transformers," *IEEE Transactions on Electrical Insulation*, vol. 26, no. 4, 1991, pp. 755-762.

[5] Suwarno, I.S Dharma, "Dielectric Properties of Mixtures between Mineral Oil and Natural Esther from Palm Oil", *WSEAS Transaction on Power System*, Vol 3, Issue 2, 20028, pp. 37-46.

[6] C. Perrier and A. Beroual, "Experimental Investigations on Mineral and Ester Oils for Power Transformers," *Conf. Rec. IEEE International Symposium on Electrical Insulation*, 20028, pp. 178-181.

[7] L. Dix; C. P. McShane; H. R. Moore; S. Moore; J. Murphy; T. Prevost; S. D. Smith,"Progress report on natural esters for distribution and power transformers" *IEEE/PES Conference and exhibition on Transmission and Distribution, Dallas, Texas, USA, 2006, pp. 15-17*.

[8] Suwarno and F. Salim, "Effects of Electric Arc on The Dielectric Properties of Liquid Dielectrics," *IEEE 8th International Conference on Properties & applications of Dielectric Materials*, bali 2006, pp. 482-485.

[9] S. Aditama, "Dielectric properties of palm oils as liquid insulating materials: effects of fat content," *Proceedings International Symposium on Electrical Insulating Materials (ISEIM)*, Vol. 1.,Kitakyushu, 2005, pp. 91-94.

[10] C. Perrier, A. Beroual, "Experimental Investigations on Mineral and Ester Oils for Power Transformers" *Conf. Rec. IEEE Int. Symp. Electr. Insul.*, 2008, pp. 178-181.

[11] Xiaohu Li, Jian Li and Caixin Sun, "Properties of Transgenic Rapeseed Oil based Dielectric Liquid," *Proceedings of the IEEE SoutheastCon*, 2006, pp. 81-84.

[12] J. Jung-Il, A. Jung-Sik, and H. Chan-Su, "Accelerated aging effects of mineral and vegetable transformer oils on medium voltage power transformers, *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 19, 2012, pp. 156-161.

[13] Christoph Krause; Uldis Kaminskis; Andreas Wild; Kevin Rapp; Alan Sbravati, Dielectric prototype test of a full-scale 420 kV power transformer HV lead exit insulated with natural ester liquid, *IEEE Electrical Insulation Conference (EIC)*, 2016, pp. 129-133

[14] A. Abu-Siada, P. Lai Sin, and S. Islam, Remnant life estimation of power transformer using oil UV-Vis spectral response, *Power Systems Conference and Exposition*,2009 , pp. I-5.

[15] M. Arshad and S. M. Islam, "Significance of cellulose power transformer condition assessment , *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 18, Issue 5,2011, pp. 1591-1598.

[16] T. K. Saha and P. Purkait, "Understanding the impacts of moisture and thermal ageing on transformer's insulation by dielectric response and molecular weight measurements, *IEEE Transactions on Dielectrics and Electrical insulation*, , vol. 15, Issue 2, 2008, pp. 568-582.

[17] Abu-Siada and S. Islam, "A new approach to identifY power transformer criticality and asset management decision based on dissolved gas-in-oil analysis, *IEEE Transactions on Dielectrics and Electrical insulation*, vol. 19, Isue 3, 2012, pp. 1007-1012.

[18] R. Tamura, H. Anetai, T. Ishii, and T. Kawamura, "Diagnostic of ageing deterioration of insulating paper," *JIEE Proc Pub A*, vol. 101, p. 30, 1981.

[19] C. P. McShane, K. J. Rapp, J. L. Corkran, G. A. Gauger and J. Luksich, Aging of Kraft paper in natural ester dielectric fluid, *IEEE 14th Int'l. Conf on Dielectr. Liquids,* Graz 2002, pp. 173-177.

[20] Insulating Liquids-Determination Of The Breakdown Voltage At Power Frequency-Test Method , *IEC Standard* , No. 60156, 1995,

[21] Insulating liquids - Measurement of relative permittivity, dielectric dissipation factor (tan d) and d.c. resistivity, *IEC Standard*, No IEC 60247:2004

[22] IEEE Guide for the Interpretation of Gases Generated in Oil-Immersed Transformers, *IEEE Standard* No. C57.104-2008, 2009

[23] Standard Test Method for Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography, *ASTM Standard*, No D3612 - 02(2009)