Dielectric properties of mixtures between mineral oil and natural ester from palm oil

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Abstract: - This paper reports experimental results on dielectric properties of mixture between conventional mineral oil and a natural ester made from palm oil. The experiment was done in attempt to find new type of liquid insulating material which excellent in dielectric properties and friendly to environment. The sample used are mixtures between mineral transformer oil (Shell Diala B) and methyl ester from palm oil. The content of ester in the mixture ranged from 0 to 100 %. The breakdown voltage, losses factor and dielectric constant as function of ester content and temperature were investigated. The values of acidity, viscosity and gassing tendencies are also presented. The experimental results showed that increasing the ester content in the mixtures enhanced the breakdown voltage and slightly increased the losses factor. A higher increase of dielectric losses factor was observed at higher temperature. The dielectric constant of the mixture was stable in the range of temperature from room temperature up to 100^{o}C. Acidity as well as viscosity increased with the ester content. The viscosity decreased with temperature. Dissolved gas analysis indicated that the total combustible in the mixture are considerably lower than that threshold value for normal condition according to IEEE C57.104. Comparing the experimental results and values of several properties in standard such as ASTM D 3487, ASTM D 1289 and IEEE C57.104, the composition of 50 % ester content is a good mixture to be used as biodegradable insulating liquid.

Key-Words: - mineral oil, methyl ester, temperature, ester content, dielectric properties, dissolved gas analysis

1 Introduction

Since long time ago, petroleum-based mineral oils have been used for liquid insulation in high voltage equipments. At present time the oils are still widely used as insulation for transmission and distribution power transformers, capacitors and other high voltage equipments. Petroleum-based insulating oils, in general have excellent dielectric properties such as high electric field strength, low dielectric losses and good long term performance. However, due to environmental consideration, recently many researches have been carried out in attempt to search the alternative of liquid insulating materials which are friendly to the environment. There are some reasons why it is important to search the environmental-friendly insulating oils. Firstly, conventional transformer oils are usually non biodegradable. It can contaminate soil and water when serious spill take place[1]. This may disturb the plantation and other lives. Secondly, the mineral oils were extracted from petroleum, which is going run out in the future since petroleum is non-renewable [2].

An alternative for biodegradable high voltage insulating material is natural ester made from palm oil[3,4]. Indonesia is the 2nd largest producer of palm oil in the world. It was reported that natural ester has superior characteristic of breakdown strength and water solubility but inferior in losses factor and viscosity[5,6]. The typical of biodegradability of dielectric liquids are 97% for natural ester, 30 % for mineral oil and 20 % for high temperature mineral oil. Mineral oil has good thermal properties to evacuate heat from transformer but inferior in ageing and biodegradability. In composite state with paper, natural ester also indicates much better compatibility than mineral oils. It was reported that paper Kraft paper aged in natural ester takes 5-8 times longer to reach the same end of life point as paper aged in mineral oil[7]. Natural ester also behaves equal or better than mineral oil[8]. Mixture between different liquids may improve the dielectric as well as thermal properties of the insulating liquids[9].

This paper reports the experimental results on the properties of mixture between mineral oil and natural ester from palm oil.

2 Experiment

2.1 Sample

Sample used in this experiment was mixture of conventional mineral oil and methyl ester. Mineral oil used in this experiment is Shell Diala B which has density of 0.873 g/cm3. The oil is a highly refined base oil which is non biodegradable. Ester used in this experiment is methyl ester made from palm oil using methanol according to [10] :

Triglyceride + Methanol → Methyl Ester + Glycerol

Triglyceride in palm oil generally consists of palmytic acid (C16:0), oleic acid (C18:1) and a small amount of mysitic, stearic and linoleic acids.

Table 1
Samples used in the experiment

No	Sample name	Ester content (v/v)
1	0% Ester	0%
2	25% Ester	25%
3	50% Ester	50%
4	75% Ester	75%
5	100% Ester	100%

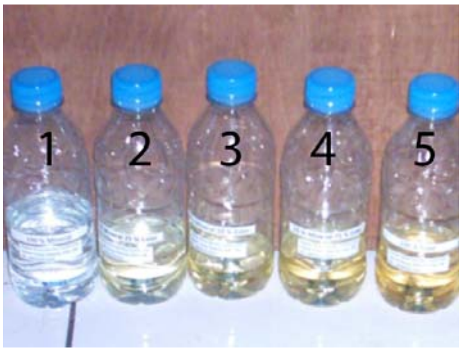

Fig. 1 Mixtures between methyl ester and mineral oil samples

The content of ester in the mixture Samples used in the experiment are mixture between mineral oil (Shell Diala B) and natural methyl ester obtained from palm oil. The concentration of ester in the mixture ranges from 0 to 100 % as shown in table 1 and the appearance of the samples are shown in fig. 1.

2.2 Breakdown voltage measurement

The breakdown voltage was measured using bispherical standard cell with spacing of 2.5 mm in Liquid Dielectric Test Set LD60 from Phenix Technologies as shown in figure 2. The experimental arrangement is in accordance with IEC 156 (1990)[11] and ASTM D 877 (1980)[12]. AC voltage with frequency of 50 Hz was applied with increasing rate of 2 kV/s. The temperature of the sample oils was varied from 25^{o}C to 60^{o}C.

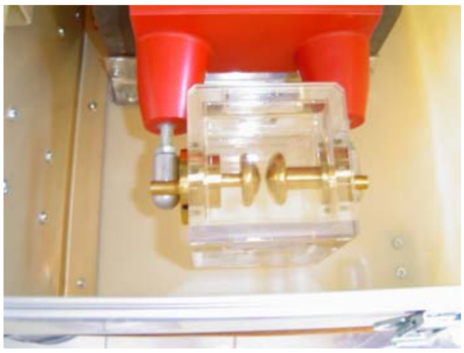

Fig. 2 Electrode for measuring the breakdown voltage of liquid insulation

2.3 Dielectric measurements

The dielectric losses factor (tan δ) and dielectric constant (ε_r) of the samples were measured according to IEC 247 (2004)[13] using a Schering bridge with a gas standard capacitor of 37.92 pF as shown in figure 3. The oil sample was put in a liquid test cell from Tettex Instruments and its capacitance (C_x) was determined under balance bridge indicated by null indicator N. This condition was obtained by controlling the variable resistance and capacitance.
Ones the capacitance C_x is obtained, then the dielectric constant can be determined by using the following formula

$$\varepsilon_r = \frac{C_x}{C_o} \qquad (1)$$

where C_o is the capacitance of test cell without liquid inside.

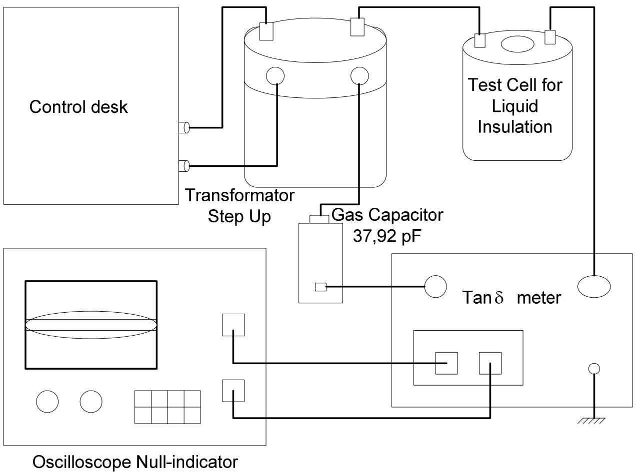

Fig. 3 Schering Bridge to measure losses dissipation factor and dielectric constant

2.4 Acidity measurement

Good liquid insulation is chemically neutral. Acid may arise in liquid insulating materials during fabrication or operation. During operating condition this acid appearance indicates degradation of insulation quality. Excessive content of acid is not tolerable. In this experiment acidity of the sample oil was determined by titration according to ASTM D 974[15]. The acidity number indicates the number of mg potasium hydroxide (KOH) to neutralize per g sample oil. The end point of titration was determined using phenolptaline indicator.

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The Dissolved Gas in the mixture was measured using a gas chromatograph HP 6890 integrated with Automated Liquid Test HP 7649 according to ASTM D 3612[16] as shown in figure 4. Oil sample of about 10 ml is put in a glass test bottle. The gas chromatograph is run for about 60 minutes for each sample. A chromatogram which indicates the species and the concentration of gas can be obtained. The data of the dissolved gasses were analyzed using total combustible gas (TCG) method[17].

Fig. 4 Gas Chromatograph HP 6890

3. Experimental Results

3.1 Breakdown voltage

Fig. 5 shows the dependence of breakdown voltage on the methyl ester content at several temperature. The figure indicates that breakdown voltage of mixture between mineral oil and natural methyl ester from palm oil increased with the content of methyl ester. This also shows that the breakdown voltage of pure natural methyl ester (i.e. 100 percent ester) is significantly larger than pure mineral oil (i.e. 0 percent ester). Therefore, in term of breakdown voltage the increase of methyl ester content improved the quality of the mixture. From the figure it is also clearly seen that breakdown voltage increase with temperature.

Oxidation of mineral oils release contaminants in the form of sludge and this reduces the breakdown of the oils.. This phenomenon is not observed in ester [18]. This because the aromatic content of conventional mineral oil reduced the solubility of mineral oil.

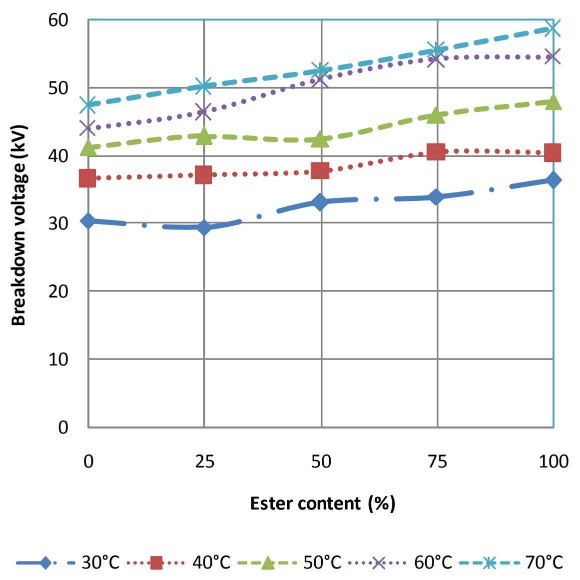

Fig. 5 dependence of breakdown voltage on ester content

Breakdown voltage is also dependent on the relative water content w_{tr}. Increasing the relative water content reduces the value of the breakdown voltage. Natural ester has much higher saturation water content than mineral oil. Therefore, ester is able to dissolve much more water compared to mineral oil in order to get same relative water content. Normally, natural ester has low relative water content. This is a reason why the breakdown voltage of natural ester is higher than mineral oil. [19].

The relative water content (w_{tr}) is determined by

$$wt_r = \frac{wt_{abs}}{wt_L} x100\% \qquad (3)$$

where wt_L is saturation water content and wt_{abs} is the absolute water content

The saturation limit of the insulating liquid depend on the insulating liquid type, its chemical composition and molar weight[20].

Figure 5 also indicates that for a given temperature, the breakdown voltage of the mixture between methyl ester and mineral oils V_{BD} (E_w) is linearly dependent on the ester content E_w. This can be expresses as

$$V_{BD}(E_w) = V_{BD0} + 0.085\, E_w \qquad (4)$$

where V_{BD0} is the breakdown voltage for 100% methyl ester fluid and E_w is the percentage of methyl ester content.

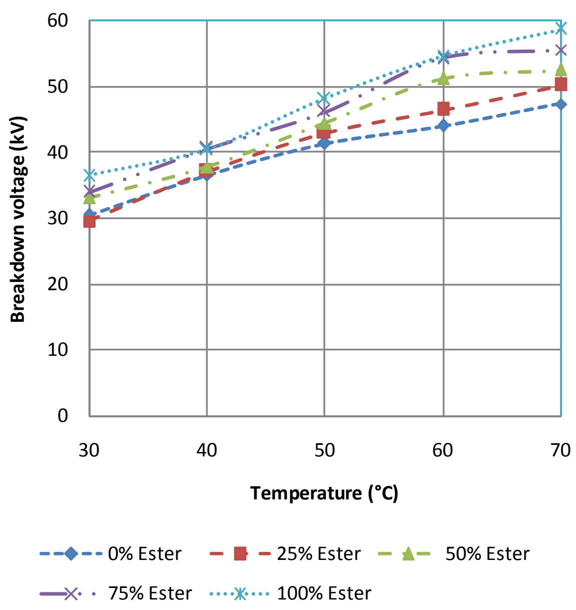

Fig. 6 dependence on breakdown voltage on temperature

Figure 6 shows the dependence of breakdown voltage on temperature. It is clearly seen that the breakdown voltage increased significantly with temperature in the temperature range from 30 ^oC – 70^oC. This is due to the increase of water solubility of the liquid.

The temperature dependence of maximum water solubility of insulating liquids is described by the following equation

$$w_L = w_o \exp\left(\frac{-H}{T}\right) \qquad (5)$$

where W_o (ppm) and H(K) are material parameters which have to be determined experimentally. Typical values of W_o and H for mineral oil are $19.2x10^6$ and 3805 and for ester fluid are 2.61 x 10^5 and 1340 for mineral oil respectively[21]. The dependence of the water saturation limit as function of absolute temperature in semi log graph is illustrated in fig. 7.

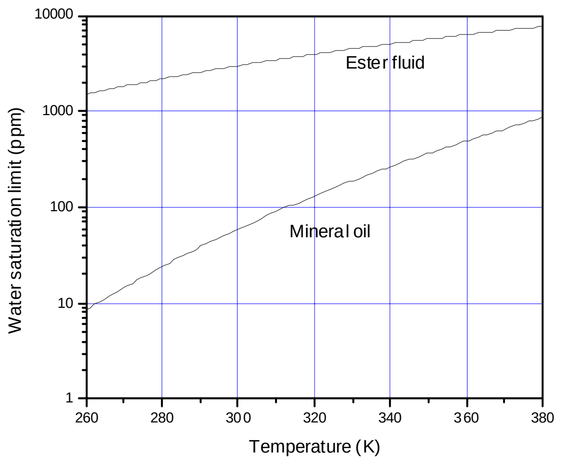

Fig 7. Water saturation limit of mineral oil and ester fluid as function of absolute temperature

Increase of temperature resulting in smaller absolute water content but increase the water solubility of the liquid. Therefore, the increase of temperature significantly reduced the relative water content in the oil. The reduction on the relative water content resulting in a higher breakdown voltage. Similar trend was also reported for the so-called Proeco TR20-ester which was designed for various kind of transformers[8] and Midel 7131for distribution transformers[22].

In ester-contained liquid, the increase of temperature also promoted the formation of peroxide which has a high affinity to hydrogen gas and reduced the formation of bubbles in the oil. The breakdown of insulating liquid is often initiated by bubbles. Therefore, increasing temperature up to about 100°C increased the breakdown voltage.

3.2 Dielectric losses factor (tan δ) and dielectric constant (ε_r)

Figure 8 shows the dependence of dielectric losses factor (tan δ) on the ester content at temperature of 25°C and 100°C. The figure indicates that at 25°C losses factor slightly increases with the ester content. At 100°C the losses factor increases significantly with the ester content. Losses factor is influenced by the degree of polarization of the oil. Chemical structure indicated that mineral oil has a symmetrical structure while methyl ester contains unbalance structure. This unbalance structure of the methyl ester enhance its losses factor. The losses factor of pure methyl ester from palm oil is much higher than mineral oil. The resistance of dipoles during polarization process increased the losses in ester sample oil. The other reason is that methyl ester contains higher absolute water. The existence of water in the methyl ester enhances the losses factor.

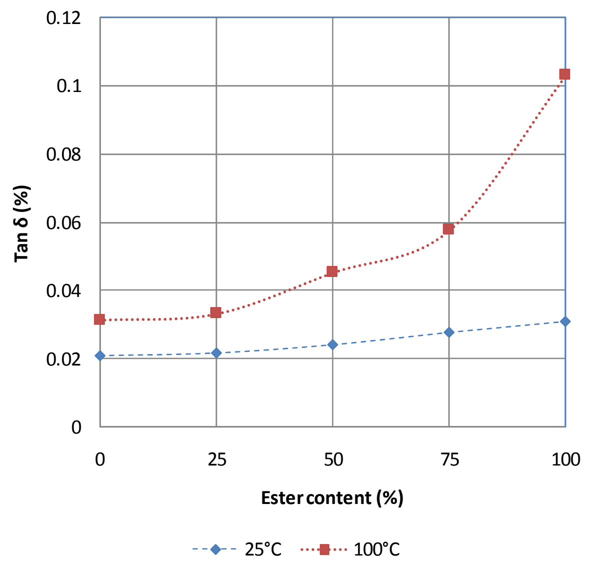

Fig. 8 Dependence of dielectric losses factor (tan δ) on ester content

The movement of dipoles during polarization resulting in displacement current. This contributes to the total current and enhances the conductivity. The absolute water content in ester also much higher than mineral oil. The losses factor correlates with absolute water content. Therefore, the losses factor of methyl ester is significantly higher than mineral oil.

The increase of losses factor was more sound at higher temperature. This is because of the decrease of sample viscosity which tend to make the charge motion more easy. The conductivity in accordance with the following equation

$$\sigma(T) = A e^{-E/kT} \qquad (6)$$

here k is Boltzmann constant, A is constant and E is activation energy which is dependent on the material. The increase of conductivity resulting in a higher losses factor (tan δ).

At high temperature oxidation may take place. This oxidation of ester may release water which contributes to the conductivity and dielectric losses factor. Under high temperature macromolecules are cleaved, releasing free charge carriers and thereby increasing the dielectric losses factor.

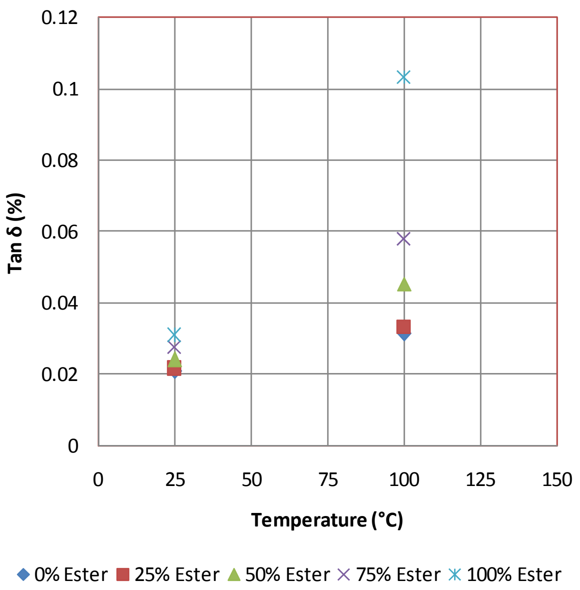

Fig. 8 dependence of dielectric losses factor (tan δ) on temperature

3.3 Dielectric constant

Figure shows the dependence of dielectric constant on ester content at different temperature. The figure indicates that dielectric constant slightly increase with the ester content. Natural ester contains higher absolute water inside compared to those of mineral oil. However, its water solubility is much higher than mineral oil. Dielectric constant is greatly affected by the absolute water absorption in the liquid. Therefore, it increases with the methyl ester content.

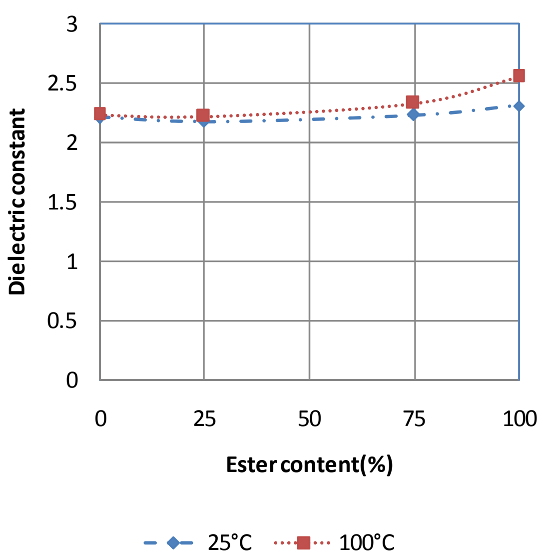

Fig. 9 dielectric constant as function of ester content

3.4 Density

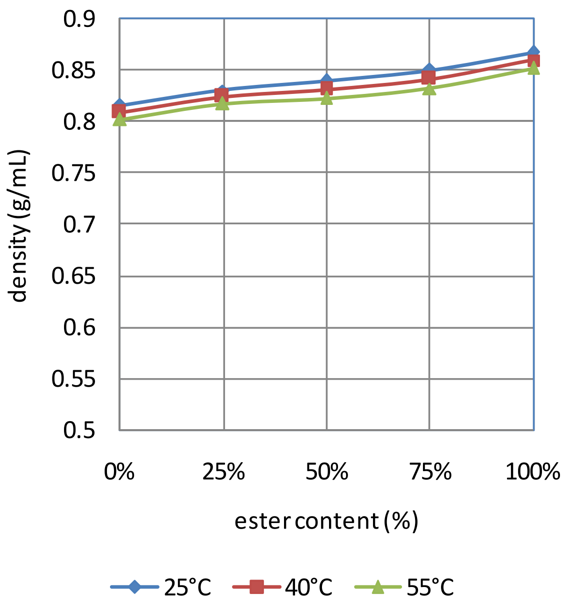

Fig 10 dependence of oil mixture density on ester content

Figure shows the dependencies of sample oil density on the ester content at different temperature. It can be seen clearly that the density of the oil mixture increased slightly with ester content. Ester has a higher density than mineral oil. Therefore, adding ester in mineral oil increased the total density.

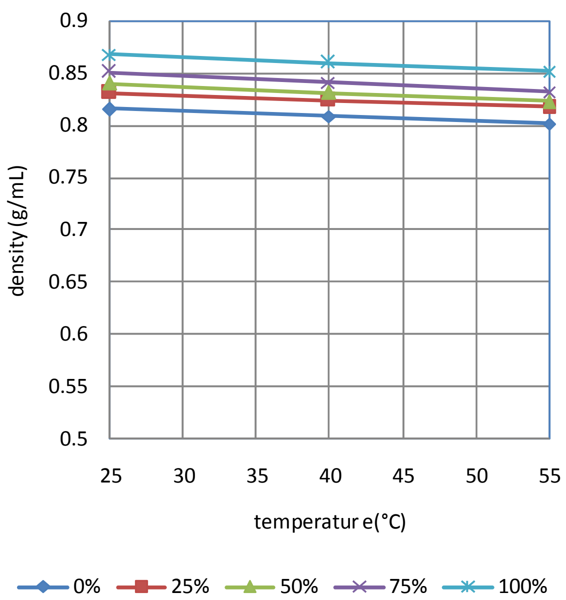

Fig. 11 dependence of oil mixture density on temperature

The figure also indicates that increase of temperature slightly reduces the density of the oil mixtures. This is because a small volume expansion as the temperature increase. The volume expansion reduce the density since the mass of the material is constant. This can be expressed as

$$\rho = \frac{m}{V}$$

V is volume, m is mass and ρ is density.

3.5 Acidity

Acidity of insulating oil is represented by the number of KOH to neutralize the acid content in the oil. Figure 14 shows the dependence of acidity on the ester content of the mixture between mineral oil and methyl ester from palm oil. The figure indicates that acidity increases with the ester content.

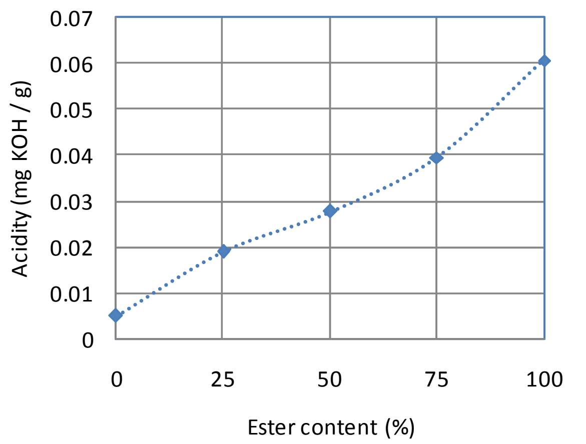

Fig. 14 acidity as function of ester content

The increase of acidity of the mixture with ester content is due to high acidity of ester. At normal condition the acidity of 100 % ester is higher than mineral oil. Higher content of natural ester in the mixture contributes a higher acid in the mixture. The acid in ester may arise as a result of oxidation which releases acid and water according to:

$$\text{R-H (ester)} + O_2 \rightarrow \text{Acid} + H_2O$$

Hydrolysis reaction of natural ester in the mixture releases fatty acid and glycerol which in turn also contributes to the increase of acidity of the mixture.

3.6 Dissolved gas analysis

Table 2 shows the gasses dissolved in the ester and mineral oil mixture. The table indicates that the concentration of the dissolved gas increases with the ester content

Table 2
Dissolved Gas Concentration in Mixtures between Methyl Ester and Mineral Oil

Ester Con-tent (%)	Gas concentration (ppm)					
	N_2	CO_2	Combustible Gas			TCG
			CO	H_2	CH_4	
0	534636	1286,05	0	0	0	0
25	515738	1537,47	40,21	67,21	0	107,4
50	514554	2100,84	87,16	146,0	0	233,1
75	516903	2193,55	148,6	218,6	0	367,2
100	426675	2468,07	471,2	457,0	6,0	934,3

Interpretation of dissolved gases using TCG method

Several gases may dissolved in liquid. In a high voltage equipment, among the dissolved gasses ,the combustible gasses are the most dangerous since these gasses may cause the burning and or explosion of the transformer. The combustible gasses commonly appear in transformer oil are H_2 (hydrogen), C_2H_6 (Ethane), C_2H_4 (ethylene) and C_2H_2 (Acetylene). The appearance of the gases relates to the degree of heating experienced by transformer oil. The analysis of dissolved gas in oil is an important tool to assess the condition of the transformers. In new liquid insulating material, the DGA is important to know the gassing tendency of the material. Total Combustible Gases (TCG) Method is a method to predict the operating condition of a transformer. This method based on IEEE C57-104-199 and ASTM D-3612 standards. According to the standard, condition 1 correlates with normal operation of transformer, the TCG should be less than 720 ppm. Condition 2 which indicates a possibility of transformer faults and necessary for investigation, the TCG is 721-1920 ppm. The TCG for condition 3 is 1921- 4630 ppm which correlates with the occurrence of high level decomposition. Detail investigation is necessary and immediate action should be done. The highest level of TCG is condition 4 with TCG of more than 4630 ppm. This indicates an excessive decomposition in the oil. Serious faults will happen if the transformer is still in operational. Immediate repair is necessary.

Table 3
TCG Method Results

Ester Content(%)	Condition
0	1
25	1
50	1
75	1
100	2

Table 3 shows the diagnostic result od the dissolved gasses using TCG method. As shown in the table the concentration of combustible gasses in the mixtures belongs to category 1 except for 100% methyl ester. This means that all mixtures except 100% methyl ester are save to be used in term of the concentration of combustible gases.

4. Comparison with standard

Table 4 shows the comparison of several dielectric properties of the mixture samples with various ester contents RBDPO with fat content varied from 3 % down to 0.5 % with the corresponding values from IEC standard. From the table it is seen that for RBDPO, the viscosity and losses factor were higher than that from standard. However, this material showed high breakdown voltage. This indicates the prospect of RBDPO to be further processed to get better dielectric properties and meet all requirements to be used as insulating materials

Table 4
Comparison between properties of several insulating liquids with standards

Dielectric fluid	Silicone oil	Mineral Oil	Synthetic Ester	0%	25%	50%	75%	100%	ASTM D3487	ASTM D6871
Breakdown Voltage (kV)	40	36.6	43	36.6	37.1	37.8	40.5	40.4	>30	>30
Tan δ (%) 25°C	0.01	0.01	0.01	0.016	0.02	0.02	0.02	0.03	≤0.05	≤0.2
Dielectric constant	2.7	2.2	3.2	2.2	2.2	2.2	2.2	2.3	-	-
Density (mg/ml)	0.96	0.87	0.97	0.81	0.83	0.83	0.85	0.86	≤0,91 (ASTM D 1298)	
Acidity (mgKOH/g)	0.002	0.01	0.03	0.005	0.019	0.028	0.04	0.06	≤0.03	≤0.06

5. Conclusion

From the experimental results some conclusions can be drawn as follows. The properties of mixture between mineral oil and natural ester from palm oil in general strongly affected by the ester content. Increasing the ester content significantly enhance the dielectric breakdown. The increase of the ester content also resulting in a higher the losses factor especially at temperature of 100°C. Viscosity and density of the mixture slightly increased with the ester content but significantly decreased with temperature. The acidity of the oil mixtures almost linearly increased with the ester content. 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.

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