

Properties of Thermally Aged Natural Esters Used as Insulating Liquid

Abdul Rajab¹, Motoo Tsuchie², Masahiro Kozako², Masayuki Hikita², and Takashi Suzuki³

¹Andalas University, Limau Manis, Padang, Indonesia.

²Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu 804-8550, Japan.

³Lion Specialty Chemicals Co., Ltd., 2-1 Hirai 7-Chome, Edogawa-ku, Tokyo 132-0035, Japan
a.rajab@eng.unand.ac.id

Abstract: An accelerated aging test is an important test to assess a long time performance of an insulation system. This paper deals with the investigation results on thermally aged natural esters insulating liquid used for transformer. Two kinds of monoesters, palm fatty acid ester (PFAE) and stearic/oleic/linoleic acids methyl esters (M182), and one tri-ester, Envirotemp (FR3), were aged at the temperature of 120 °C for 60 days. An as-received oil was used as a sample for aging test, so that the presence of a limited amount of air, and thus oxygen, in oil sample could not be avoided. The important properties like appearance, moisture content, acid value, volume resistivity, and breakdown voltage are evaluated at each 15 days interval. Experiment on mineral oil under the same condition was also conducted for comparison. It was observed that the color of the FR3 was changed from light-green to dark-green. PFAE, M182 and mineral oils which were initially transparent became yellow-green, light yellow and brown, respectively. A sludge formation was observed in the mineral oil, whereas the increase in acidity was found in the PFAE and M182 oils. The moisture content of aged PFAE and M182 oils decreased whereas that of aged FR3 and mineral oils increased. The volume resistivity of all tested oils decreased with aging time, whereas their breakdown voltage showed a different behaviours. The breakdown voltage of M182 and mineral oils increased and decreased, respectively, whereas that of PFAE and FR3 relatively unchanged.

1. Introduction

Investigation on the use of natural esters in triglyceride (tri-ester) form to be used as insulation in transformer have been tried around the same time with mineral oil [1]. At that time, they were not desirable due to the disadvantages owned by the oils. The oils, in general, are more vulnerable to oxidation, and have high viscosity and pour point. In addition, the plentiful availability of mineral oil at that time was another factor affecting the choice of mineral oils rather than natural esters of triglyceride type [2]. However, since the environmental consideration becomes an important aspect in selecting oil insulation during last decades, and the fact that the conventional insulation oils such as mineral and synthetic oils are not environmentally friendly due to their low rate of biodegradation, research and the development of vegetable (natural ester) oil for oil filled transformer application were renewed. The weaknesses of the oils were overcome by optimal selection of fatty acids composing the three branches of triglyceride structures, and proper choices of additives added into the oils [3]. The oils had been successfully implemented in small distribution transformer since the late 1990s [4] [5] and their implementation in power transformer is now rapidly growing [6].

In order to obtain the less viscous natural ester-based insulating oil, monoesters synthesized from vegetable oils were introduced. In Japan, the Lion Corporation developed a monoester type insulating oil called palm fatty acid ester (PFAE) [7]. The viscosity of PFAE is much less than tri-ester makes the cooling efficiency of the PFAE-immersed transformer better than that of tri-ester oil [8]. Its viscosity is even lower than that of the conventional transformer mineral oil [9, 10]. Nevertheless, the flash point of the PFAE is lower than that of the triglyceride type insulating oil. This makes the monoester more susceptible to the fire compared to the tri-ester. However, the flash point of PFAE is still better than that of mineral oil [11].

3. Thermal Aging

It should be noticed that the current application of monoester type insulating oil (PFAE) is at the medium voltage distribution transformer. It is a common field practice in Japan that moisture content of an oil is not strictly controlled before being used in the distribution transformer. Therefore, to simulate the initial condition of oil in distribution transformer, all oil samples were used without any pretreatment in this investigation. The presence of oxygen, the air in general, in sample oil cannot be avoided. It is well known that the presence of oxygen allows the occurrence of oxidation in the tested oils, as will be mathematically demonstrated in the next section.

Sample oil of about 4 kg was prepared for each oil type in tightly sealed oil tank and aged in an oven at the temperature of 120 °C for 60 days. The photograph of oil tank used in the thermal aging is shown in Figure 2. Properties of oil such as appearance, moisture content, acid value, volume resistivity and breakdown voltage were evaluated at each 15 days interval. At each step of aging, a sample of about 1 kg for each oil type was taken out from the oil tank for properties measurement.



Figure 2. The oil tank used for the thermal aging test.

4. Appearance

The color of all tested oils change with aging time, as shown in Table 2. PFAE, M182 and mineral oils which were initially transparent became yellow-green, light yellow and brown, respectively, at the end of aging, whereas FR3 was changed from light-green to dark-green. The most severe change in color was experienced by mineral oil, indicating the occurrence of oxidation in the oil.

The oxidation of both mineral and natural ester oils could result in color change, although the occurrence of oxidation cannot be judged by the color change alone [14]. However, a sludge was formed in mineral oil at the end of aging (Figure 3), which is absence in other tested (esters) oils, provides additional evidence of the occurrence of oxidation in the oil. This sludge is non-soluble substance resulted from a combination of the intermediate product of free radicals during the oxidation process. Other oxidation products of mineral oil are ketone, alcohol, aldehyde, organic acid and ester.

Oxidation of hydrocarbon, in general, is expressed by equations (1) – (11) [15]. The reaction starts by removing hydrogen radical H^* from hydrocarbon RH , based on equation (1).



If oxygen (O_2) is available, R^* will react with oxygen forming peroxide radical ROO^* , based on equation (2). It should be remembered that all oil sample were used in the experiment without pretreatment. Therefore, the existence of oxygen in oil cannot be avoided.



The peroxide radical ROO^* will react with hydrogen radical H^* forming hydroperoxide $ROOH$ (equation (3)). This reaction could lead to the formation of water, based on equations (4) - (6).

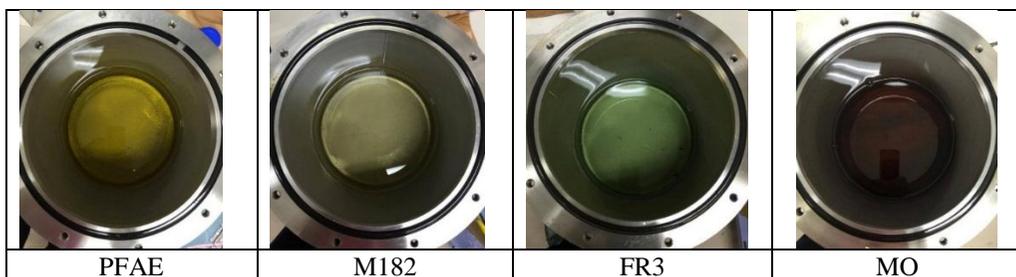


Figure 3. The appearance of oils in oil tank after aging test.
The sludge was observed in mineral oil (MO)

Table 2. The change in oils color at each 15 days duration of the aging.

Days	PFAE	M182	FR3	MO
0				
15				
30				
45				
60				

Two peroxide radicals ROO^* could react each other (equation (7)), and this reaction could lead to the formation of acid, based on equations (8) - (11).



Based on equations (6) and (11) the occurrence of oxidation can also be verified by the increase in both moisture content and acidity of oil. The formation of sludge provides an additional evidence of the occurrence of oxidation in the mineral oil.

5. Moisture Content

The moisture content of the oil sample was measured using a moisture meter (CA-06, Mitsubishi Corp., Japan), as shown in Figure 4. The results are depicted in Figure 5. An absolute moisture content might help in indicating the degradation of the aged oils, but relative moisture is more helpful in explaining the dielectric properties of the oils like volume resistivity and breakdown voltage.



Figure 4. Moisture content measurement device.

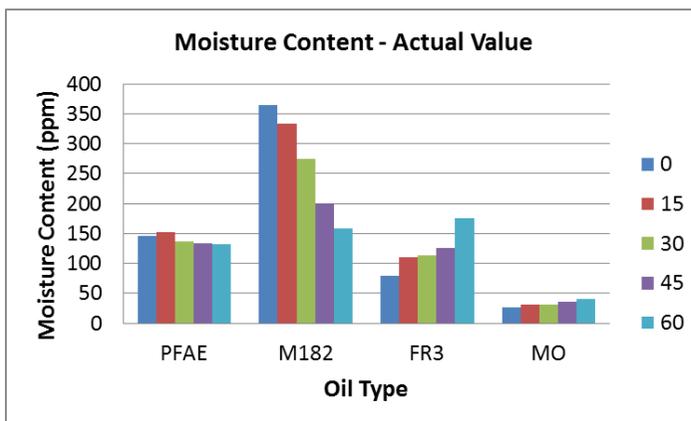
It can be seen from Figure 5 that moisture content of all tested oils changes with the aging time. The moisture content of mineral oil and FR3 increased during the aging period. The increase in moisture content of mineral oil supports the claim that the mineral oil was oxidized during the aging. Water is also known as one of the results of oxidized oil [14] [16]. Therefore, the FR3 is also suspected to be oxidized.

Differing from previously mentioned oils, the relative moisture content of M182 and PFAE reduce significantly and slightly (Figure 5). The reduction in moisture content of natural esters can be attributed to the hydrolysis reaction which consumes water, based on equation (12). It can also be perceived from Equation (12) that the increase in acidity can also be used to indicate the occurrence of hydrolysis in aged natural ester oils.

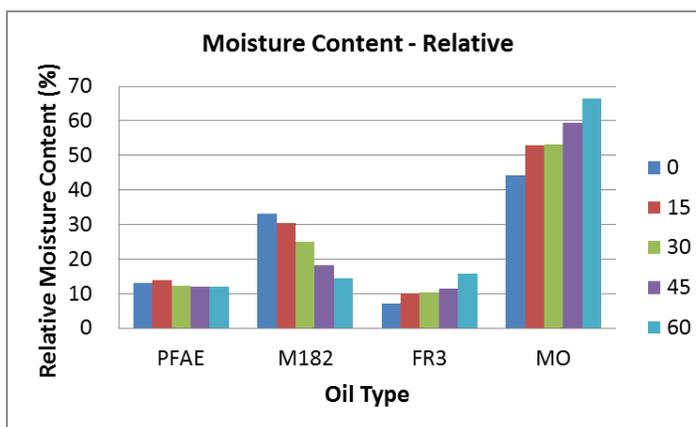


In term of absolute moisture content, mineral oil was experiencing the smallest change during the aging period (Figure 5a), but in term of relative moisture content, such change is larger than that of FR3 and M182 and comparable with that of M182, but with opposite directions (Figure 5b). This is because mineral oil can only hold a very small amount of water compared to natural esters at the same temperature. The saturation limit of mineral oil at room temperature is about 60 [17], whereas that of natural esters is about 1100 ppm (the saturation limit of FR3 is taken from [18], whereas those of monoesters are approximated from [19]). Relative moisture content (M_{rel}) of an oil is the ratio between absolute moisture content (M_{abs}) and moisture saturation limit of the oil (M_{SL}), based on equation (13) [14].

$$M_{\text{rel}} = M_{\text{abs}}/M_{\text{SL}} \quad (13)$$



(a). Absolut moisture content



(b) Relative moisture content

Figure 5. The moisture content of the oils as the function of aging duration.

It is interesting that even though all natural esters were treated under the same condition, the way they degrade under thermal aging is different. PFAE and M182 were hydrolyzed, while FR3 was oxidized. These tendencies could be attributed to the initial moisture content of tested oils and the existence of C-C double bond in hydrocarbon chain of oil molecules which is known to be prone to oxidation. The M182 was severely hydrolyzed due to its very high initial moisture content, 364 ppm or about 33 % relative moisture content. The PFAE was slightly hydrolyzed because of its initial moisture content was not too high, 145 ppm or about 13 %. The very low initial moisture content of FR3 (79 ppm or about 7 % relative moisture content) and the existence of C-C double bond in its hydrocarbon chain are suspected to be the factors responsible for the oxidation of the oil.

6. Acid Value

The acidity of tested oils is indicated by their acid values. In this investigation, the acid value was measured using Potentiometric titration (COM-1700A, HIRANUMA SANYO Co.), in accordance with JIS C2101. Acid value measurement was conducted only for PFAE and M182, and the results are depicted in Figure 6. It is clear from the Figure that acid value of both oils increases with aging duration. The increase in the acid value of M182 is larger than that of PFAE,

indicating the more severe hydrolysis occurred in M182 than that of PFAE. This evidence confirms the occurrence of hydrolysis in both oils.

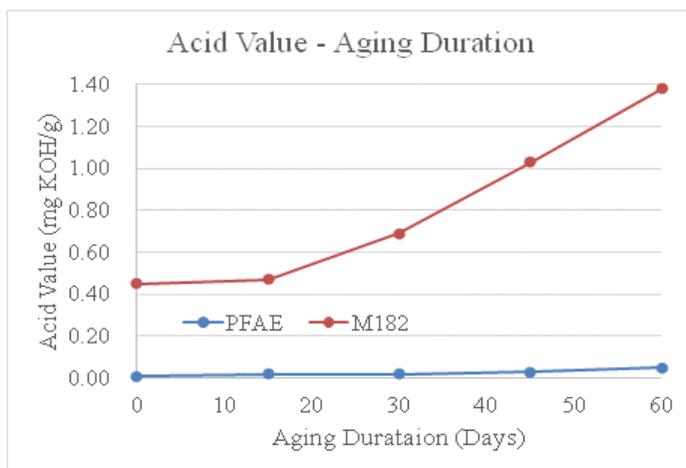


Figure 6. The acid value of PFAE and M182 as the function of aging duration.

7. Volume Resistivity

The volume resistivity (ρ) measurement was performed in accordance with JIS C 2101. The schematic test circuit and the test cell used for the measurement are depicted in Figure 7 [20]. A DC power supply with output voltage set to 10 Volt was applied to the oil-contained cell at room temperature for about 5 minutes. The current was measured using the electrometer (ADVANTEST, R8240) having a minimum detection level of 10 pA. A null (0) minute value extrapolated from the measured current was used to calculate the volume resistivity of tested sample, as expressed by equations (14) and (15).

$$R_x = V / I_0 \tag{14}$$

$$\rho = K R_x \tag{15}$$

where R_x is resistance in Ω , V is applied DC voltage in volt, I_0 is current at 0 minute in ampere, ρ is volume resistivity in $\Omega \cdot \text{cm}$ and K is a constant of an electrode in cm. In our experiment, a coaxial cylinder electrode system (OBE-2, Soken Electric CO., LTD., Japan) with $K=1000$ was used. The reported volume resistivity is the average of two measurement results.

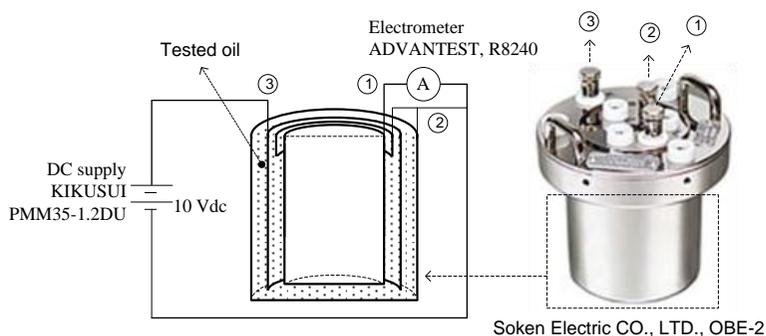


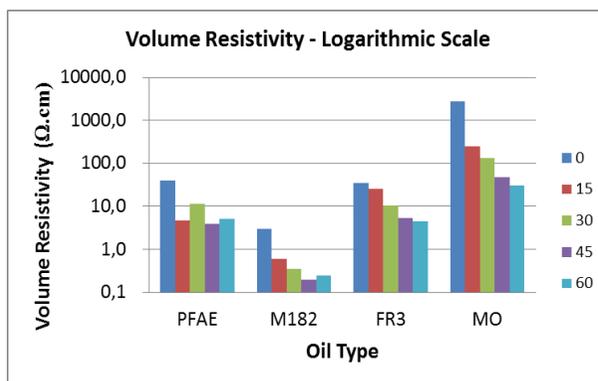
Figure 7. Test circuit of volume resistivity measurement

The volume resistivity of all tested oils is shown in Figure 8. It can be seen from the Figure that volume resistivity of all oils decreased with aging duration. M182 and mineral oil exhibited the remarkable decrease in volume resistivity during the first 15 days of aging, and the rates of their volume resistivity remain lower than that of PFAE and FR3 at the end of aging period

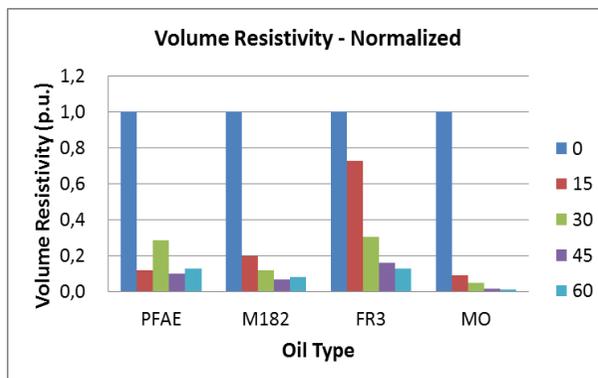
(Figure 8b). These changes, again, reflect the more severe degradation being experienced by both oils compared to PFAE and FR3 oils. M182 was hydrolyzed resulting in the production of acids and the reduction of moisture content (see equation (12)).

The combination of higher concentrations of acids and moisture is suspected to be the factors responsible for the significant reduction in volume resistivity of the M182 oil [21]. Although the moisture content of M182 reduced significantly, it remained the highest among other oils until 45 aging days and became comparable to FR3 at 60 days (Figure 5a). This is because the initial moisture content of M182 is very high, 364 ppm or about 33.1 %. The similar factors (acid and moisture) seem to contribute to the noticeable decrease in volume resistivity of mineral oil, but with a different mechanism. Mineral oil was oxidized, resulting in the productions of acids (Equation (11)) and moisture (Equation (6)) [14] [16]. Both hydrolytic and oxidative degradations produce acids, hence, it is indicative that the effect of acid is more dominant in decreasing the volume resistivity of oils than that of moisture content.

The similar explanation applies to the relatively smaller change in the volume resistivity of PFAE and FR3. PFAE and FR3 are suspected to be slightly hydrolyzed and oxidized, respectively. The very low volume resistivity of PFAE at 15 days of aging is thought to be a bias and caused by other unrecognized factors.



(a) Logarithmic scale



(b) Normalized scale

Figure 8. The volume Resistivity of the oils as the function of aging duration.

8. Breakdown Voltage

Breakdown voltage (BDV) measurement was conducted in accordance with JIS C2101:2010, using the oil insulation tester (3811 IP-SSD, Musashi Corp. Japan), as shown in Figure 9. It utilizes a test cell containing electrode pairs of sphere-sphere configuration. The diameter and

the gap distance of sphere electrodes are 25 mm and 1 mm, respectively. The tester was set to the automatic operation mode with the rate of voltage rise of 3 kV/s.

Application of voltage was started at least 5 and 15 minutes after pouring the mineral and FR3 samples, respectively, into the test chamber. Standing times for PFAE and M182 follow that of mineral oil since the viscosity of both oils is lower than that of mineral oil. The measurements were conducted six times for each sample with a time delay between two consecutive measurements at least 2 minutes for mineral oil, PFAE, and M182 samples, and 6 minutes for FR3 sample. The delay time after the measurement is intended to allow a breakdown of products to disperse and gas to expel before the subsequent measurement was conducted so that the later measurement was not influenced by the previous one. The reported breakdown voltage is the average of twelve measurement results.

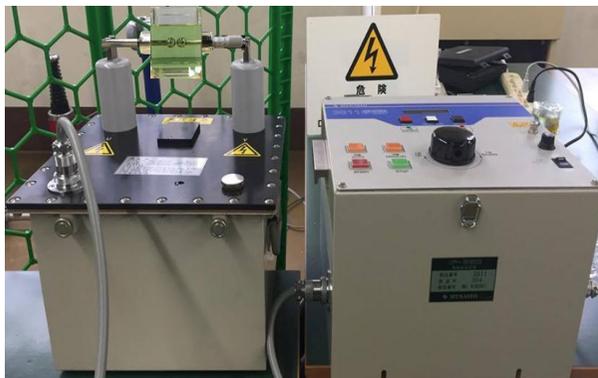


Figure 9. Breakdown voltage measurement device.

The breakdown voltage of all tested oils is depicted in Figure 10. It is clear from the Figure that the breakdown voltage of M182 and mineral oil significantly increased and decreased, respectively, during the aging period. These are the expected results since the relative moisture content of M182 decreased from 33.1% to 14.5 % as a consequence of hydrolysis, and that of mineral oil increased from 44.2 % and 66.6 % as a consequence of oxidation. It is well recognized that clean oils can hold water in dissolved form up to 30 % relative moisture content without significantly affecting the breakdown voltage of oils, irrespective of the oil types [18].

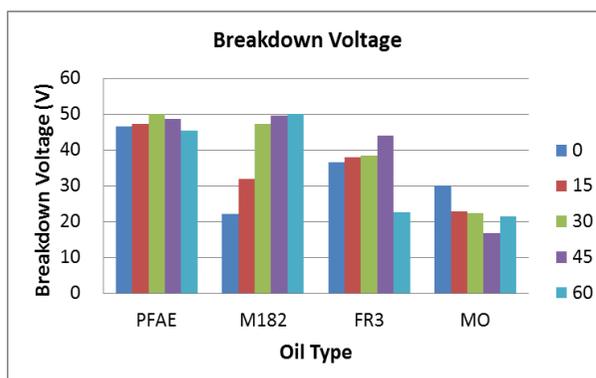


Figure 10. The breakdown voltage of the oils as the function of aging duration.

An increase in acidity is also known to decrease the breakdown voltage of oils [17]. However, it is interesting that even though both M182 and mineral oils produce acids from the hydrolysis and oxidation, respectively, the effects on the breakdown voltage of, respectively, M182 and

mineral oil are different. Acids do not affect the breakdown voltage of M182 oil but possibly contribute in decreasing the breakdown voltage of the mineral oil.

It can also be seen from Figure 10 that the breakdown voltages of PFAE and FR3 relatively unchanged during the aging period. These results confirm a negligible effect of acids, produced from a slightly hydrolyzed PFAE and a slightly oxidized FR3, on the breakdown voltage of both oils. The presence of acids of low molecular weight (LMA) or of high molecular weight (HMA) with acidity up to 4 or 9 mg KOH/g, respectively, does not cause a significant decrease in the breakdown voltage of the natural ester oil [22]. The significant decrease in the breakdown voltage of FR3 at 60 days of aging is thought to be a bias and caused by other unrecognized factors.

9. Conclusions

Properties such appearance, moisture content, acid value, volume resistivity and breakdown voltage of thermally aged natural esters of monoester and tri-ester types, as well as mineral oil, have been investigated. Some conclusions can be drawn as follows:

1. PFAE and M182 oils are, respectively, slightly and severely hydrolyzed, which are indicated by the slight and remarkable decreases, respectively, in moisture content, and by the slight and remarkable increase, respectively, in acid value of both oils.
2. FR3 and mineral oils are, respectively, slightly and severely oxidized, which is indicated by the increase in moisture content of both oils. The drastic change in color and formation of sludge indicate the severity of oxidation in mineral oil.
3. The volume resistivity of all aged oils decreased, which could be mainly due to the increase in the acid value of all oils.
4. The breakdown voltage of PFAE and FR3 relatively unchanged during the period of aging, whereas that of M182 and mineral oils significantly increased and decreased, respectively. These indicate that the change in breakdown voltage is mainly due to the change in relative moisture content of oil.

10. Acknowledgement

Publication of this article is supported by Engineering Faculty of Andalas University grant under contract No. 003/UN.16.09.D/PL/2018.

11. References

- [1]. McShane, C. P. "Vegetable Oil Based Dielectric Coolant". *IEEE Industry Application Magazine*, Vol. 8, No. 3, pp. 34-41, 2002.
- [2]. T. V. Oommen, C. C. Claiborne and J. T. Mullen, "Biodegradable Electrical Insulation Fluids", *Electrical Insulating Conference*, Chicago, 1997.
- [3]. P. Boss and T. V. Oommen, "New Insulating Fluids for Transformers based on Biodegradable High Oleic Vegetable Oil and Ester Fluid", *IET Conference*, 1999.
- [4]. C. P. McShane, G. A. Gauger and G. Luksich, "Fire Resistant Natural Ester Dielectric Fluid and Novel Insulation System for Its Use", *IEEE/PES Transmission and Distribution Conference*, 1999.
- [5]. CIGRE W. G. A2.35, Experience in Service with New Insulating Liquid, *CIGRE*, 2010.
- [6]. Daniel Martin, et al., "Further Studies of a Vegetable-Oil-Filled Power Transformer", *IEEE Electrical Insulation Magazine*, Vol. 27, No. 5, pp. 6-13, 2011,
- [7]. Y. Ohki, "Development of High-Performance Environmentally Friendly Palm Fatty Acid Ester Insulating Oil for Transformers", *IEEE Electrical Insulation Magazine*, Vol. 27, No. 3, pp. 55-57.
- [8]. J. Tokunaga, et al., "Comparative Studies on the Aging of Thermally Upgraded Paper Insulation in Palm Fatty Acid Ester, Mineral Oil, and Natural Ester", *IEEE Transaction on Dielectrics and Electrical Insulation*, Vol. 23, No. 1, pp. 258-265, 2016.
- [9]. T. Kanoh, et al., "Analyses of Electro-Chemical Characteristics of Palm Fatty Acid Esters as Insulating Oil" *International Conference on Dielectric Liquid*, 2008.

- [10]. T. Suzuki, et al., "Comparative Study of the Insulation Paper Aging in Palm Fatty Acid Ester (PF AE) and Mineral Oil", *International Conference on Dielectric Liquid*, Bled, Slovenia, 2014.
- [11]. A. Rajab, et al., "Low Thermal Fault Gases of Various Natural Monoesters and Comparison with Mineral Oil", *IEEE Transaction on Dielectrics and Electrical Insulation*, Vol. 23, No. 6, pp. 3421-3428, 2016
- [12]. C. P. McShane, et al., "Aging of paper insulation retrofilled with natural ester dielectric fluid", 2003 *IEEE/DEIS Conference on Electrical Insulation and Dielectric Phenomena*, Albuquerque, NM. 2003.
- [13]. A. Rajab, et al., "Aging Properties of Natural Esters and Comparison with Mineral Oil", *International Conference on Dielectric Liquid*, Manchester, 2017.
- [14]. S. Singha, et al., "Comparative Aging Characteristics between a High Oleic Natural Ester Dielectric Liquid and Mineral Oil", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 21, No. 1, pp. 149-158, 2014.
- [15]. CIGRE WG. D1.30, Oxidation Stability of Insulating Fluids. *CIGRE*, 2013.
- [16]. Perrier, M. L. Coulibaly and M. Marugan, "Efficiency of ageing markers for different transformer insulation systems", *IEEE International Conference on Dielectric*, Montpellier, 2016.
- [17]. R. Liao, et al., "A Comparative Study of Physicochemical, Dielectric and Thermal Properties of Pressboard Insulation Impregnated with Natural Ester and Mineral Oil", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 18, No. 5, pp. 1626-1637, 2011.
- [18]. CIGRE W.G. A2.35, Experiences in Service with New Insulating Liquids, *CIGRE*, 2010.
- [19]. Y. Kasahara, et. al., "Consideration on the Relationship Between Dielectric Breakdown Voltage and Water Content in Fatty Acid Esters", *Journal of the American Oil Chemists' Society*, Vol. 89, No. 7, pp. 1223-1229, 2012,
- [20]. H. Maryon, A. Rajab and U. Khayam, et. al., "Study on Streaming Electrification Properties of Palm Fatty Acid Ester (PFAE) Oil due to Aging" *IEEE International Conference on Dielectrics*, Montpellier, 2016.
- [21]. K. Bandara, et al., "Understanding the Ageing Aspects of Natural Ester Based Insulation liquid in Power Transformer", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 23, No. 1, pp. 246-257, 2016
- [22]. N. Aziz, "Ageing Assessment of Insulation Paper with Consideration of in-service Ageing and Natural Ester Application", *PhD thesis*, University of Manchester, 2012.



Abdul Rajab received Bachelor degree from Hasanuddin University, Makassar, Indonesia in 1996, Master degree from the Bandung Institute of Technology, Bandung, Indonesia in 2001, and Doctoral degree from Kyushu Institute of Technology, Japan in 2017. He is a lecturer at Electrical Engineering Department, Andalas University, Indonesia. His research field interest is an application of environmentally friendly insulating liquids in high voltage electrical apparatus, as well as, condition monitoring and diagnosis of electrical high voltage apparatus.



Motoo Tsuchie was born on 12 July 1949. He received the B.S., M.S., and Dr. degrees in chemical engineering from Kobe University, Japan in 1973, 1975, and 1993, respectively. He had worked for Mitsubishi Electric Corporation from 1975 to 2007. He joined Kyushu Institute of Technology in 2008. He has been engaged in research on transformer materials and diagnose of the transformer. He is a member of IEEJ and the Japan Petroleum Institute (JPI).



Masahiro Kozako (M'09) is an Associate Professor at Department of Electrical and Electronic Engineering, Kyushu Institute of Technology. He was born on 13 August 1974 in Tokyo. He received the B. Eng., M. Eng., and Dr. Eng. degrees in electrical engineering from Kyushu Institute of Technology in 1997, 1999, and 2002, respectively. He worked at Waseda University for 3 years as an Assistant Professor and a Lecturer, and at Kagoshima National College of Technology for 3 years as an Assistant Professor. He was a Visiting Researcher at the LAPLACE in Université Paul Sabatier, France, from 2011 for 1 year. His research interests concern the development of new insulating polymer nano-composite materials and the development of the diagnostic technique for electric power apparatus. He is a member of IEEJ, JIEP, CIGRE and IEEE.



Masayuki Hikita (M'97-SM'98) was born in 1953. He received the B.S., M.S., and Dr. degrees in electrical engineering from Nagoya University, Japan in 1977, 1979, and 1982, respectively. He was an assistant professor, a lecturer, and associate professor at Nagoya University in 1982, 1989, and 1992, respectively. He was a visiting Scientist at the High Voltage Laboratory at MIT, USA, from 1985 to 1987. Since 1996, he has been a professor of the Department of Electrical and Electronic Engineering, Kyushu Institute of Technology. His research interests are the development of a diagnostic technique for electric power apparatus and insulation technology development of power electronics device and apparatus such as inverter and semiconductor power module. He is a member of Japan Society of Applied Physics and IEEJ.



Takashi Suzuki was born on 11 April 1981. He received the M. Eng. in applied chemistry from Chuo University in 2006 and joined LION Corporation in 2006. He has been engaged in research on the dielectric liquid for electro-technical applications. He is a member of IEEJ.