Aging Assessment of Synthetic Ester Impregnated Thermally Non-upgraded Kraft Paper through Chemical Markers in Oil

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ABSTRACT

The applicability of using 2-furfural (2-FAL) and methanol as aging markers for synthetic ester impregnated paper insulation was investigated through laboratory aging experiments at temperatures of 80, 100 and 120 °C. Methanol in the synthetic ester increased linearly with paper aging until degree of polymerisation (DP) reached 400. During this period concentration of methanol in oil was higher than that of 2-FAL, which proved the concept of using methanol to indicate early paper aging in the synthetic ester. However, the rate of methanol increase against the reduction of DP in the synthetic ester was about three times higher than that seen in mineral oil. This is due to a difference in the partitioning of the marker between oil and paper. Since the synthetic ester is more polar than the mineral oil, it attracted more methanol molecules from the paper, resulting in a higher concentration of methanol in oil for the same reduction of DP. In addition, a reduction in methanol was observed at the later stage of paper aging at 120 °C. This could be due to either a change in the partitioning between oil and paper, or an esterification reaction which consumes methanol in the system.

Index Terms — Power transformers, synthetic ester, oil, paper, aging, methanol, 2-furfural, degree of polymerisation, tensile strength.

1 INTRODUCTION

THE world's first synthetic ester filled 400 kV, 240 MVA power transformer is to be connected to the UK transmission network [1], a great achievement in the perspective of going 'green' with the power system. At the same time, it might be a challenge to the asset managers for managing such transformers as their behavior and condition assessment criteria could be different from mineral oil filled transformers. Synthetic esters were first introduced into the transformer industry in the late 1970s. Over the past decades, ester based transformer oils have gained increasing popularity especially in fire or environmentally critical applications such as offshore wind turbine transformers, underground transformers and traction transformers.

Synthetic esters are manufactured by reacting polyols and acids [2]. Typical alcohols used in manufacturing synthetic esters include neopentylglycol, trimethylol-propane, pentaerythritol or dipentaerythritol [3]. Viscosity and oxidation stability of synthetic esters can be optimized during the manufacturing process by controlling the percentages of mono-, bi- and tri- functional groups in the carboxylic acids.

Therefore, synthetic esters have better anti-oxidation performance over natural esters and hence are also commonly recommended for free breathing transformers.

Similar to mineral oils, esters degrade with time through oxidation. The oxidation process will either disrupt or scissor the unsaturated bonds in the ester. In addition, esters also degrade through hydrolysis. In the presence of water, the hydrolysis process converts esters into their respective alcohol and acid. This results in high acidity values in aged esters [4].

In addition to the merits of providing biodegradability and fire safety, laboratory aging experiments have shown that esters could retard paper aging compared with the use of mineral oils [5]. Several reasons were proposed to explain the phenomenon including the absorption of more moisture from cellulose insulation due to the higher water saturation in esters; reduction of moisture in the oil-cellulose insulation system through hydrolysis of esters; and esterification of the reactive hydroxyl groups in the cellulose insulation with fatty acids through transesterification process [6, 7].

With a growing number of ester filled large high voltage power transformers, concerns have been raised on assessing the aging state of these transformers [8,9]. The molecular structure of ester based liquids is apparently different from mineral oils and hence esters are likely to behave differently from the conventional mineral oils in certain aspects. In

addition, the concentration of chemical indicators such as moisture and acids in ester liquids could be different from those in mineral oils, which makes it difficult to use the same condition monitoring criteria used for mineral oil filled transformers to assess the ester filled transformers.

Due to the poor accessibility of paper samples, the aging state of the paper insulation in transformers is commonly assessed through indirect measurements such as the amount of furanic compounds or carbon oxide gasses in oil [10]. However, it was found that the esters themselves could produce a high amount of carbon oxide gases causing difficulties in adopting carbon oxide gases to predict paper aging in esters [11]. Furthermore, only a few experiments have been conducted on furanic compounds in esters [8,9,12]. 2-FAL concentrations in synthetic esters reported in some previous work were exceptionally low compared with that in mineral oils [8,9].

In addition to the conventional paper aging indicators, it was suggested to use methanol in oil to indicate paper aging in transformers [13-16]. Experiments in oil-paper insulation systems with mineral oil showed that methanol increases linearly with paper aging and its concentration is higher than 2-FAL during the early period of paper aging [13]. However, there is lack of information on such new paper aging indicators for the esters [17].

This paper investigates the suitability of 2-FAL and methanol as aging indicators for synthetic ester impregnated paper insulation. Details of the aging experiments and the measurement techniques used to measure the aging indicators are given in Section 2. The results of the aging experiments and the variation of the aging indicators against the paper aging are shown in Section 3 and Section 4. The results of the partitioning and stability experiments conducted on methanol are presented in Section 5 followed by the kinetic study on paper aging and methanol production in the synthetic ester in Section 6. Conclusions obtained through different investigations are provided in the final section.

2 EXPERIMENTAL DESCRIPTIONS

2.1 LABORATORY AGING EXPERIMENT

The aging experiments reported in this paper were conducted under sealed conditions (with an air headspace) using thermally non-upgraded Kraft paper (thickness of 0.05 mm and density of 0.75 g/cm^3), a synthetic ester MIDEL 7131 and an IEC high grade inhibited mineral oil Gemini X (for comparison purpose). Details of the aging experiments including temperature, duration and the quantity of oil and paper are given in Table 1.

Prior to the sample preparation, oil was first preprocessed by filtering through a nylon membrane of 0.2 μm to remove particles and by drying at 85 °C inside a vacuum oven below 500 Pa to remove moisture. Synthetic ester was dried for 72 hours whereas the mineral oil was dried for 48 hours. In parallel, paper samples cut into strips of 28 mm × 220 mm were dried at 105 °C inside an air circulation oven for 24 hours to remove the water. Next, samples prepared with 200 g of oil and 10 g of paper inside 250 ml glass bottles were

left inside the vacuum oven (<500 Pa) at 85 °C for another 24 hours to impregnate the paper with oil. After the impregnation, samples were sealed with thermoplastic polyester caps (withstand temperatures up to 180 °C) and PTFE sealing gaskets before placing them inside the air circulation oven for aging. During the aging period, samples were taken out regularly from the oven and left at room temperature for 72 hours before the measurements to allow the chemical indicators to partition between oil, paper and the small headspace. Aging assessment of both oil and paper was conducted through parameters including acidity, 2-FAL, methanol, tensile strength (TS), and degree of polymerization (DP). Paper samples were de-oiled with hot hexane in a Soxhlet extractor prior to the DP measurement.

Table 1. Details of the laboratory aging experiments.

Oil: paper ratio	Oil type	Tempe rature (°C)	Duration (Days)
20:1	MIDEL 7131	80	35, 70, 140, 210, 280, 357
		100	7, 14, 21, 28, 42, 56, 70, 84, 126, 196
		120	2, 5 7, 9, 12, 14, 28, 42, 56, 70, 84
	Gemini X	80	35, 84, 140, 210, 280, 357
		100	7, 14, 21, 28, 42, 56, 70, 84, 126, 196
		120	2, 5 7, 9, 12, 14, 28, 42, 56, 70, 84

2.2 MEASUREMENT OF OIL AND PAPER AGING INDICATORS

The acidity of oil was measured using Metrohm 848 Titrino Plus titrator through a method developed based on BS EN 62021-3. TS of paper was measured according to BS EN ISO 1924 standard using INSTRON-5564 equipment. Jaw gap and cross head speed were set at 180 mm and 20 mm/min, respectively. Average TS measurements of 10 paper samples was obtained for each aging sample. DP of the paper was measured according to ASTM D4243 standard.

2.2.1 2-FAL IN OIL

Currently, there are no standard techniques available for measuring 2-FAL in synthetic esters. Hence, most laboratories follow the standards for mineral oil such as BS EN 61198 and ASTM D5837 standards, which are based on using high-performance liquid chromatography (HPLC). The BS EN 61198 standard recommends an indirect injection technique during which the furanic compounds are extracted from oil prior to the injection through either liquid-liquid or solid-liquid extraction whereas, the ASTM D5837 standard recommends either the same indirect injection technique or a direct injection of oil into the system.

Therefore, 2-FAL measurements conducted in the synthetic ester through both injection techniques were compared to select a suitable method. The direct injection technique according to ASTM D5837 standard has a detection limit of 0.01 mg/kg, whereas the indirect injection technique according to BS EN 61198/ASTM D5837 standard has a detection limit of 0.05 mg/kg. Figure 1 shows the concentration of 2-FAL measured in six synthetic ester samples prepared with a known concentration of 2-FAL in oil through both injection techniques against the reference concentration values.
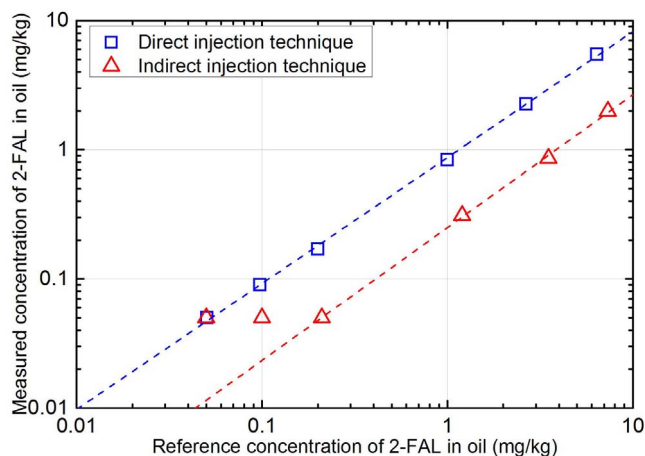
Figure 1. Concentration of 2-FAL measured in MIDEL 7131 through direct and indirect injection techniques.

Measurements conducted through the direct injection technique were similar to the reference values whereas those obtained through the indirect injection technique were about four times lower than the reference value.

The error in the indirect injection technique is due to a difference in the extraction efficiency of 2-FAL between the synthetic ester and the mineral oil. To overcome this, a calibration curve prepared from the synthetic ester is necessary for indirect injection measurements. The measurements in this work were conducted through the direct injection technique given in ASTM D5837.

2.2.2 METHANOL IN OIL

Methanol in oil was measured through an in-house method [18] developed based on [19]. The setup consists of a CTC Combi Pal autosampler unit, a Varian CP 3800 gas chromatography (GC) unit, and a Varian Saturn 2200 ion trap type mass spectrometer (MS) unit. Samples prepared with 10 g of oil in 20 ml headspace vials were heated at 90 °C to extract methanol from oil into the headspace. Next, 1 ml gas from the headspace was extracted and injected into the gas chromatography unit using a gas-tight syringe. Separation of the compounds in the injected sample was done at 40 °C through a 60 m VF-624ms column with 0.25 mm internal diameter and 1.4 μm film thickness. Extracted compounds were then scanned using the MS unit in total ion count mode with a mass to charge ratio (m/z) range of 20-100. Quantification of methanol was conducted through internal standard calibration method using ethanol-d6 as the internal standard [19]. Furthermore, calibration curves prepared with the respective oil type were used in the quantification process.

3 THERMAL AGING OF KRAFT PAPER IN THE SYNTHETIC ESTER AT VARIOUS TEMPERATURES

This section shows the results of the laboratory aging experiments including the variations of the aging indicators with aging duration.

3.1 ACIDITY OF OIL

Acids in esters are generated through both oxidation and

hydrolysis processes, whereas in the mineral oil they are generated only through oxidation. Figure 2 shows the variation of acidity of the synthetic ester and the mineral oil against the aging duration at different temperatures.
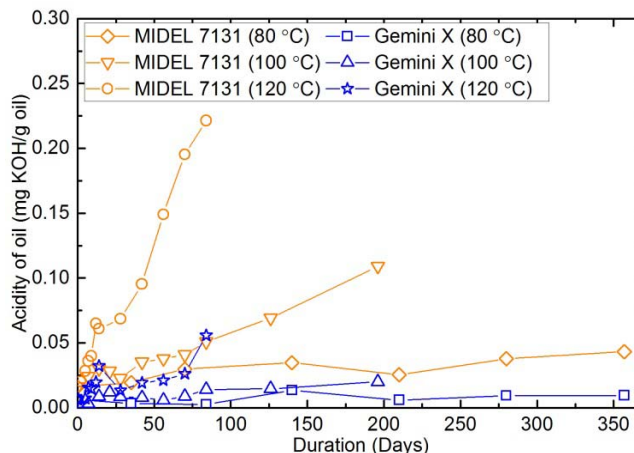

Figure 2. Variation of acidity in MIDEL 7131 and Gemini X during the aging experiments at different temperatures

Acidity of the synthetic ester showed a generally increasing trend with aging. Acidity of the synthetic ester increased from 0.02 mg KOH/g oil up to 0.04 mg KOH/g oil, 0.11 mg KOH/g oil and 0.22 mg KOH/g oil at the end of the aging experiment conducted at 80 °C, 100 °C and 120 °C, respectively. Furthermore, at all three temperatures acidity of the synthetic ester was higher than that of the mineral oil aged at the same aging duration. At the end of the aging experiments, the acidity values of the synthetic ester were about 4 to 5 times higher than the mineral oil. The hydrolysis process results in high acidity values in esters. However, it has been suggested that these acids are mainly high molecular weight acids and hence have less influence on the degradation of insulation paper [6, 20].

3.2 DEGREE OF POLYMERISATION OF PAPER

DP of paper is related to the average number of monomer units in the cellulose polymer. Typically, the larger the chain length, the stronger the paper would be. Figure 3 shows the variation of DP of paper aged in the synthetic ester and in the mineral oil against the aging duration at different temperatures.

At 80 °C, DP of paper decreased from 1126 down to 843, resulting in about 25% of DP loss over 357 days of the aging period. At 100 °C, DP of paper decreased down to 445 showing about 60% reduction in the DP of paper. At 120 °C, DP of paper reduced down to 338 resulting in about 70% loss within 84 days. DP of paper aged in the synthetic ester reduced similarly to that aged in the mineral oil during the early stage of paper aging. However, at the late stage of paper aging, mainly at 120 °C, it is noticeable that DP of the paper aged in the synthetic ester was higher than that of the paper aged in the mineral oil.

It is considered that paper aging in transformers is initiated through oxidation, and driven by hydrolysis in later stages

[21]. The synthetic ester, due to its higher water solubility, can absorb more water from paper than the mineral oil. In addition, the synthetic ester consumes water through the hydrolysis process, resulting in a reduction in the water content in the system. These reasons could have led to a lower water content in paper, and thus caused a slower hydrolysis of paper in the synthetic ester than in the mineral oil, resulting in the slower paper aging in the synthetic ester.
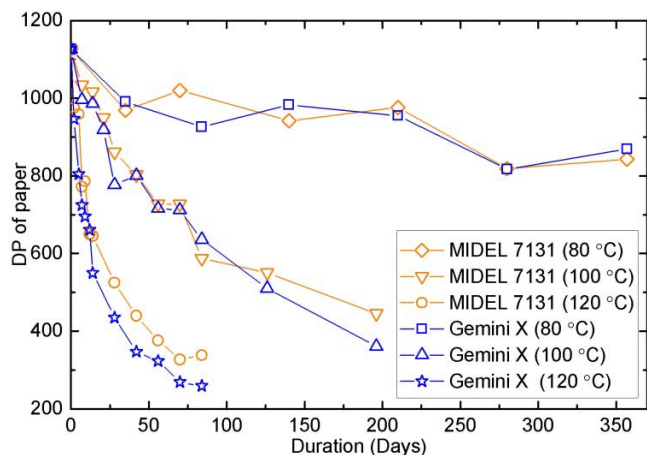

Figure 3. Variation of DP of paper aged in MIDEL 7131 and Gemini X during the aging experiments conducted at different temperatures.

3.3 TENSILE INDEX OF PAPER

Tensile index (TI) is a property calculated from the TS of paper as in (1). TI is more popular than TS as it is independent of the thickness of paper, and hence allows comparison of paper with different thickness values.

$$TI = \frac{TS}{G_m} \qquad (1)$$

where *TI* is the tensile index of paper in Nm/g, *TS* is the tensile strength of paper in N/m and G_m is the grammage of paper in g/m^2.

Figure 4 shows the variation of TI of paper aged in the synthetic ester and in the mineral oil against aging duration at different temperatures. TI of paper aged in the synthetic ester decreased with the aging duration at all the three temperatures. At 80 °C, TI of paper reduced from 90 Nm/g to nearly 80 Nm/g, losing about 11% of the TI. At 100 °C, paper aged in the synthetic ester lost about 22% of its TI, while at 120 °C, the loss was nearly 33%.

The indistinguishable variations in the TI during the early stage of the experiments conducted at both 80 °C and 100 °C could be due to the slower paper aging at these low temperatures. Similar variations have been observed by other researchers during aging experiments conducted at low temperatures [21]. Furthermore, experiments have shown that the rate of reduction in TI could be very small during the early stage of paper aging until the DP reduces to about 600 [22].

Similar to the DP, TI of paper aged in the synthetic ester at 120 °C was higher than that in the mineral oil at the later stage of the paper aging when the TI was below 70 Nm/g. This further confirms the ability of the synthetic ester to slow down the paper aging.
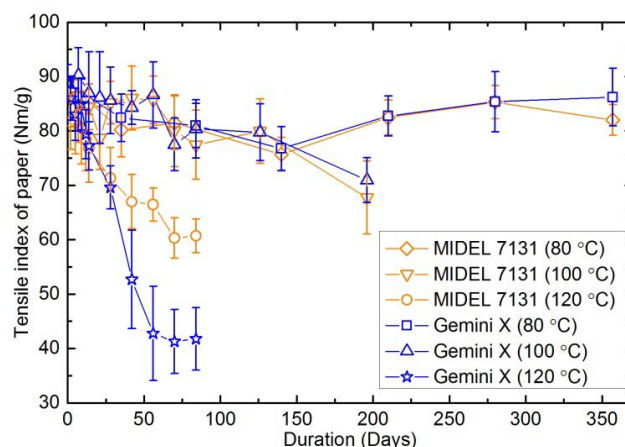

Figure 4. Variation of tensile index of paper aged in MIDEL 7131 and Gemini X during the aging experiments conducted at different temperatures.

3.4 2-FAL IN OIL

2-FAL is the most commonly used indirect paper aging indicator in the transformer industry, since its discovery during the early 1980s [23]. Figure 5 shows the variation of 2-FAL in the synthetic ester and in the mineral oil plotted in log scale against the aging duration at different temperatures. At 80 °C, 2-FAL in the synthetic ester was less than the detection limit of 0.01 mg/kg throughout the aging period. Furthermore, at 100 °C a measurable amount of 2-FAL in the ester was found only after 42 days and then it increased up to 0.13 mg/kg by the end of the aging period. At 120 °C, 2-FAL in the ester increased almost exponentially up to 3.43 mg/kg by the end of the aging period.
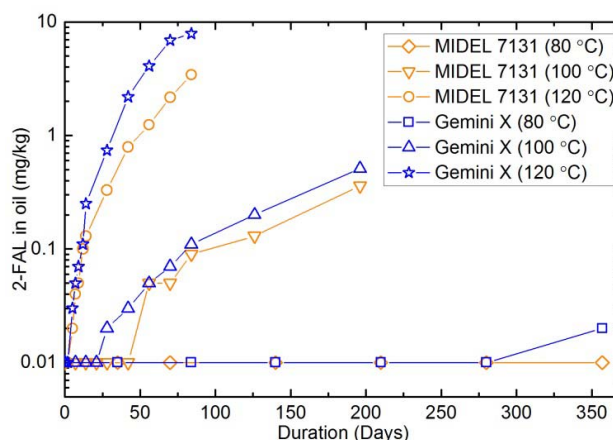

Figure 5. Variation of 2-FAL in MIDEL 7131 and Gemini X during the aging experiments conducted at different temperatures.

2-FAL in the synthetic ester varied similarly to that in the mineral oil during the early aging period. However, at the late stage of the aging, 2-FAL in the synthetic ester was continuously lower than in the mineral oil. This may have occurred either due to the lower rate of paper aging in the synthetic ester than in the mineral oil at the late stage of the aging and/or due to a difference in the partitioning of 2-FAL between oil and paper.

3.5 METHANOL IN OIL

Figure 6 shows the variation of methanol in the synthetic ester and in the mineral oil against the aging duration at

different temperatures. At 80 °C, methanol in the ester increased rapidly up to 1.72 mg/kg with a rate of about 0.005 mg/kg per day. At 100 °C, methanol increased linearly with a rate of about 0.05 mg/kg per day until 42 days of aging and later with a lower rate of increase until 4.36 mg/kg. The highest initial rate of increase in methanol was observed at 120 °C. Methanol in the synthetic ester increased linearly with a rate of 0.27 mg/kg per day within the first 14 days of aging, it then increased with a lower rate until reaching the peak value of 4.97 mg/kg at 56 days. Afterward, a reduction with the aging duration was observed resulting in a concentration of 4.19 mg/kg at the end of the aging period.

A similar reduction of methanol was observed in the mineral oil at the very late stage of paper aging i.e. the DP is less than 200 [24, 25]. Hypotheses such as a change in the partitioning of methanol between oil and paper due to a buildup of aging by-products, and reactions between methanol and carboxylic acids producing esters were proposed to explain the reduction [24, 25]. Synthetic esters are well known for their higher acidity values than the mineral oil, so the chances of methanol reacting with carboxylic acids are higher in the synthetic ester than in the mineral oil. Further experiments on the stability of methanol in the synthetic ester were conducted and the results are shown in Section 5.

On the other hand, the rate of paper aging in the synthetic ester was similar to that in the mineral oil during the early stage of paper aging and hence the generation of methanol from paper should be similar during this stage. However, the initial rate of increase of methanol in the synthetic ester was about 5 to 6 times higher than in the mineral oil. A difference in the partitioning of methanol between the ester and the paper from that of the mineral oil and the paper may have caused the difference in the rates. Partitioning experiments were conducted to verify the hypothesis and the results are given in Section 5.
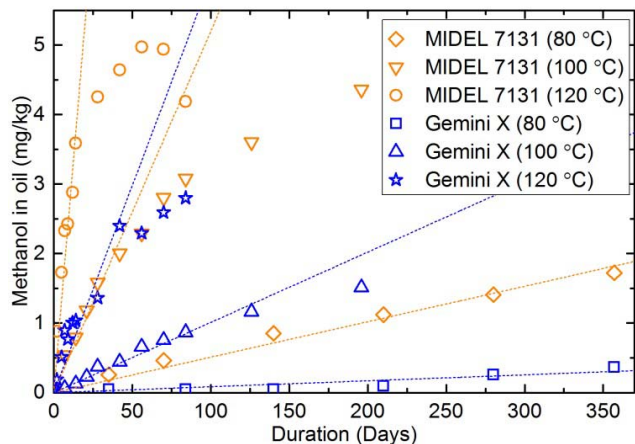

Figure 6. Variation of methanol in MIDEL 7131 and Gemini X during the aging experiments conducted at different temperatures.

4 CORRELATION BETWEEN THE PAPER-AGING INDICATORS IN OIL AND DP OF PAPER

It is well known that 2-FAL in mineral oils varies exponentially with aging and hence equations that relate the

logarithmic value of 2-FAL linearly to the DP of paper are commonly used in the industry to estimate the DP of paper through 2-FAL measurements. Figure 7 shows the variation of 2-FAL in the synthetic ester and in the mineral oil obtained during the aging experiments plotted in logarithmic scale against the DP of paper. A generally linear relationship is indeed obtained between the log-scaled 2-FAL in the synthetic ester and the DP of paper. Furthermore, the variation was similar to that obtained for the mineral oil. This suggests that the aging assessment techniques used to predict DP of paper through 2-FAL measurements in the mineral oil filled transformers would be applicable to the synthetic ester filled transformers.
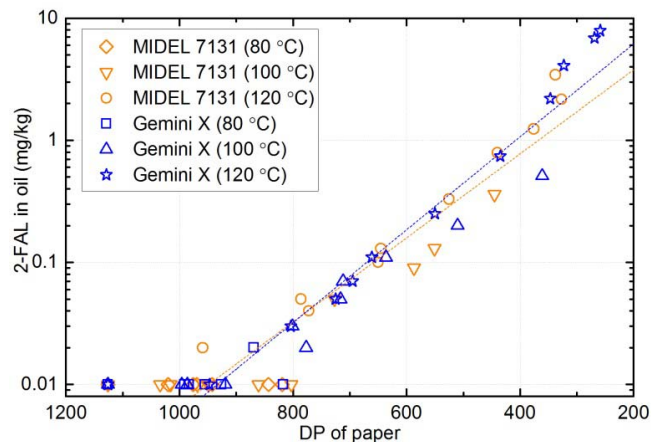

Figure 7. Relationship between 2-FAL and DP of paper aged in MIDEL 7131 and Gemini X at different temperatures.

On the other hand, methanol has been discovered recently as a paper aging indicator that has shown promising results as an early aging indicator for transformer paper insulation. Laboratory aging experiments have shown that methanol in the mineral oil varies linearly with paper aging during the early stage of paper aging until DP reaches about 400 [13, 25].

Figure 8 shows the variation of methanol in the synthetic ester and in the mineral oil against the number of ruptured bonds (NS) in paper. NS was calculated from equation (2).
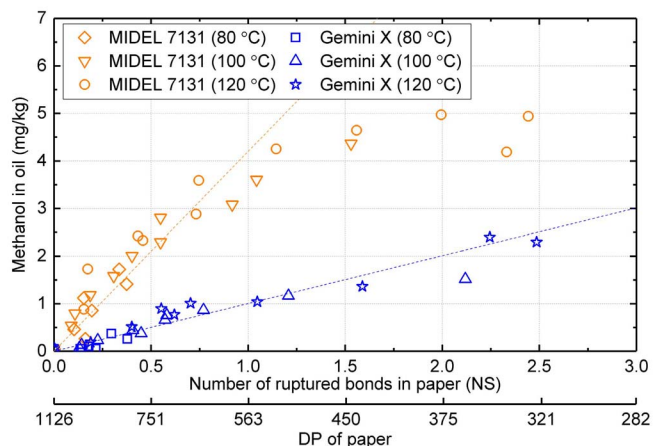

Figure 8. Relationship between methanol and number of ruptured bonds in paper aged in MIDEL 7131 and Gemini X at different temperatures.

$$NS = \left(\frac{DP_{(v0)}}{DP_{(vt)}}\right) - 1 \qquad (2)$$

where $DP_{(v0)}$ is the initial DP and $DP_{(vt)}$ is the DP value at aging time of t.

Methanol in the synthetic ester and in the mineral oil increased linearly with NS during the early stage of paper aging. In mineral oil methanol increased almost linearly until the DP reduce to about 300, while in the synthetic ester it was about 500. At the same level of paper aging, methanol in the synthetic ester was about 3 to 4 times higher than that in the mineral oil, which was found to be due to the difference in the partitioning of methanol between oil and paper (see Section 5).

5 PARTITIONING AND STABILITY OF METHANOL IN THE SYNTHETIC ESTER

Other than being generated from paper aging, the two most important characteristics of an aging indicator are its partitioning between oil and paper and its stability in oil. The aging experiments conducted in Section 3 showed that the partitioning of methanol between paper and oil for the synthetic ester could be different from that for the mineral oil. Furthermore, the aging experiments conducted at a high temperature of 120 °C showed a reduction in the concentration of methanol in oil, which raised concerns about the stability of methanol in the synthetic ester. Hence, further experiments were conducted on partitioning and stability of methanol in the synthetic ester and the results are presented in this section.

5.1 PARTITIONING OF METHANOL BETWEEN SYNTHETIC ESTER AND PAPER

Partitioning of methanol between the synthetic ester and Kraft paper at room temperature was investigated in this work. Methanol was first added to the clean synthetic ester to obtain a concentration of about 5 mg/kg. Samples for the partitioning experiment were then prepared inside 20 ml headspace vials by mixing 16 g of synthetic ester spiked with methanol and 0.8 g of ester impregnated paper. Headspace vials were then sealed tightly using crimp caps and left at room temperature of about 20 °C to allow methanol to partition between oil and paper. Samples prepared with Kraft paper and the mineral oil in a similar manner were conditioned at the same temperature for comparison. The concentration of methanol in the samples was measured regularly to observe the dynamics of the partitioning.

Figure 9 shows the variation of methanol in both the synthetic ester and the mineral oil against the conditioning period. The amount of methanol retained in oil is shown as a percentage from their initial concentrations. It is clear that methanol has a higher affinity for the synthetic ester than for the mineral oil. At the end of the conditioning period, the concentration of methanol in the synthetic ester was about 40% of its initial value whereas in the mineral oil it was less than 10%. This confirms that the difference in the methanol vs. NS relationship between the two oil types (Figure 8) is due to a difference in the partitioning of methanol in the two oil-paper systems.
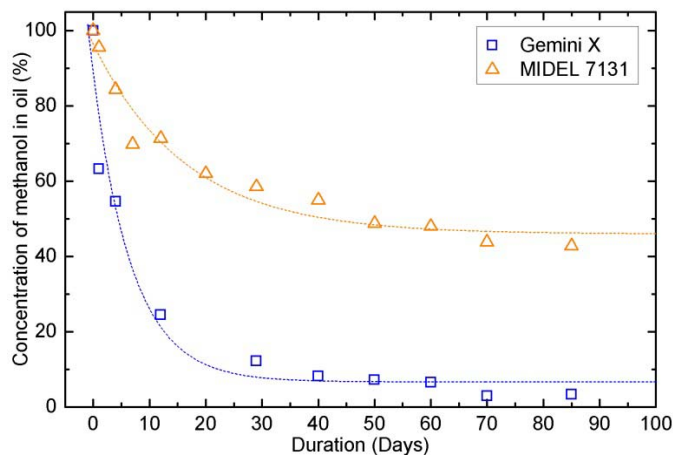

Figure 9. Variation of methanol in MIDEL 7131 and Gemini X during the partitioning experiment conducted at room temperature of about 20 °C.

5.2 STABILITY OF METHANOL IN SYNTHETIC ESTER

Stability of methanol in the synthetic ester was investigated at 130 °C. Ester samples preprocessed according to Section 2 were spiked with methanol to obtain a concentration of about 3.7 mg/kg in the ester. Samples prepared with 12 g of the ester in 20 ml glass ampoules were sealed in air and conditioned at 130 °C for up to 168 days. In parallel, ester samples prepared without spiking methanol were conditioned at the same temperature to observe the generation of methanol from the ester.

Figure 10 shows the variation of methanol in the synthetic ester conditioned at 130 °C with and without methanol being added prior to the experiment. The concentration of methanol in the synthetic ester with added methanol stayed constant only for about 7 days. Later the amount of methanol in the synthetic ester reduced with time, reaching the detection limit within 84 days of the aging period. On the other hand, the synthetic ester conditioned without methanol being added showed a slight increase in the concentration of methanol up to about 0.5 mg/kg by 50 days and then reduced to a value below the detection limit within 84 days of the aging period.
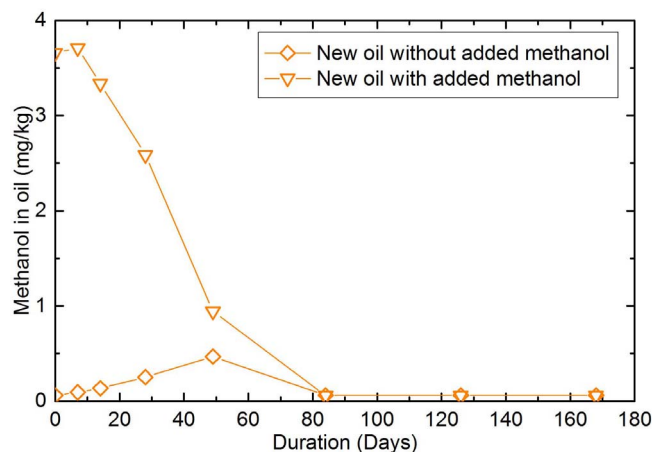

Figure 10. Variation of methanol in MIDEL 7131 during the stability experiment conducted at 130 °C

The results indicate that at high temperatures methanol in the synthetic ester could undergo further reactions that would affect its stability as an aging indicator. As expected, the esterification process during which methanol reacts with acids generating esters could have resulted in the reduction of methanol in the synthetic ester [4]. Even though it is rare that a transformer to be operated at this temperature, it is worth to investigate this issue at other lower temperatures as it could affect the reliability of methanol as an aging indicator in the synthetic ester filled power transformers. On the other hand, it pushes the application of methanol measurements in early aging stage or even during factory temperature rise tests.

6 KINETIC STUDIES RELATED WITH PAPER AGING

In transformer research, kinetic studies are mainly used to understand the degradation of cellulose and to predict the lifetime of transformers based on the condition of the cellulosic insulation [21, 24, 26-29]. Nevertheless, some of the recent studies have tried to relate the kinetics of paper aging with kinetics of methanol production in mineral oil [15].

The aim of the present study is to compare the activation energies of paper aging and methanol production in the synthetic ester and in the mineral oil calculated from the results of the aging experiments conducted in the present work. The rate of paper aging (k_1) and the rate of methanol production (k_2) during the early aging period at different temperatures were first modeled using linear functions (3) and (4) [15]. Next, the rate constant values were applied to the Arrhenius expression to obtain the activation energy values involved with paper aging and methanol production.

$$\frac{1}{DP_{v(t)}} - \frac{1}{DP_{v(0)}} = k_1 t \qquad (3)$$

where k_1 is the rate of paper aging, $DP_{v(0)}$ is the initial DP of paper, $DP_{v(t)}$ is the DP of paper at a given time, t.

$$[MeOH] = k_2 t \qquad (4)$$

where [MeOH] is the amount of methanol generated from paper and k_2 is the rate of methanol increase.

Equation (3), developed based on Ekenstams model [30] is the most commonly used equation to model the rate of paper aging. Typically, the model is used to fit DP values down to about 300 [15]. A similar approach to the literature was used to fit the data for paper aging in both the synthetic ester and the mineral oil as shown in Figure 11.

The concentration of methanol measured in oil is only a portion of the amount generated from the paper. After being generated from the paper, methanol partitions between oil, paper and the small headspace in the sample bottle. The dynamic nature of the partitioning hinders the calculation of the total amount of methanol generated from paper. Therefore, the rate of methanol increase in oil was used in the calculations as k_2 assuming it is proportional to the rate of methanol production from the paper.

Even though the paper aging showed a linear variation until the later stage of the experiments, methanol measurement in

both oil types showed clear deviation from the linear increase at an earlier stage of the experiments conducted at both 100 °C and 120 °C (Figure 6). Similar variations were observed by other researchers during the experiments conducted in the mineral oil [24]. It was suggested that a change in the partitioning of methanol due to a buildup of oxidation products could have resulted in the deviation. In addition, the instability of methanol in the synthetic esters at high temperatures as shown in Section 5 could have also contributed to the reduction. Therefore, the linear fittings in Figure 11 were only applied for the initial 42 days and 14 days for the experiments conducted at 100 °C and 120 °C, respectively.
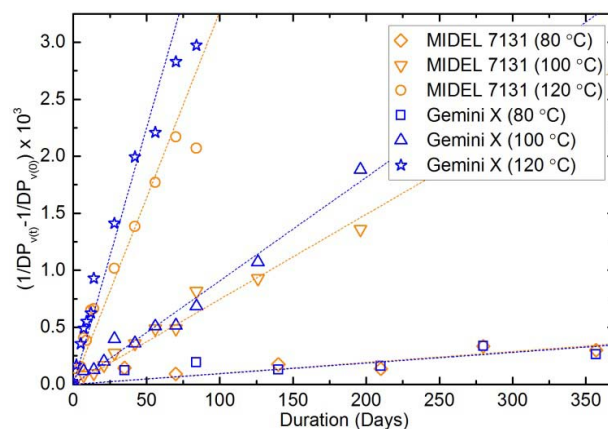

Figure 11. Linear fittings used to obtain the rate constants (k_1) for paper aging in MIDEL 7131 and Gemini X at different temperatures.

The rate constants obtained for paper aging and methanol production were then used to plot the typical Arrhenius expressions (ln K vs 1/T) as shown in Figure 12. Activation energies for both paper aging and methanol production in the synthetic ester and the mineral oil were obtained from the gradient of the plots.
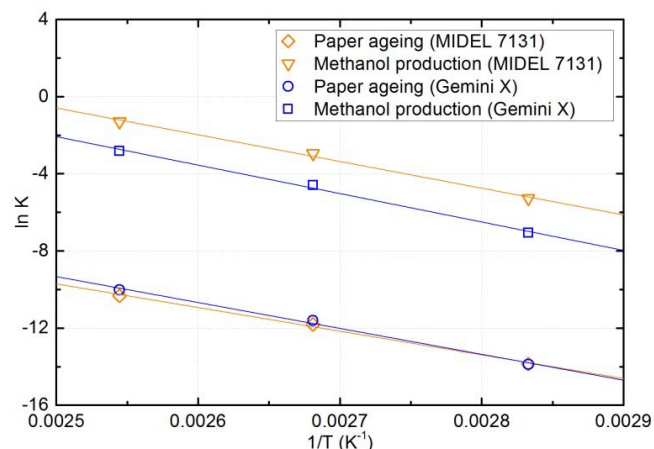

Figure 12. Arrhenius expressions obtained for the rate of paper aging and the rate of methanol production in MIDEL 7131 and Gemini X

Table 2 compares the activation energies and pre-exponential factors obtained for paper aging and methanol production in the present work and in the literature [31]. Due to the lack of data, activation energies were compared only

with those obtained during the aging experiments conducted with natural ester.

Table 2. Activation energies and pre-exponential factors for paper aging and methanol production in the oil-paper systems with synthetic ester and in the mineral oil compared to the literature [31].

	Oil Type	Temperature Range (°C)	Activation Energy (kJ mol⁻¹)	Pre-exponential factor (mg kg⁻¹ day⁻¹)
Paper Aging				
The present experiment	Synthetic ester	80 - 120	102.0	1.19E+14
	Mineral oil	80 - 120	111.9	3.58E+10
Reference [31]	Natural ester	90 - 130	99.7	
Methanol Production				
The present experiment	Synthetic ester	80 - 120	114.4	4.32E+14
	Mineral oil	80 - 120	122.3	1.17E+15

The activation energy for paper aging in the synthetic ester was 102.0 kJ mol⁻¹. The value is about 9% lower than that obtained for mineral oil in this work but similar to that obtained in the literature [31]. The main reason for the reduction in the activation energy is the slower paper aging in the synthetic ester than the mineral oil at 120 °C. The reduction in the rate of paper aging in esters is considered to be due to the inhibition of hydrolysis through different processes such as absorption of water from the paper, and esterification of the hydroxyl groups in cellulose, rather than a change in the mechanism [5].

Similar to the paper aging, the activation energy calculated for methanol production in the synthetic ester was lower (~6%) than that obtained for the mineral oil. The similar reduction in the activation energies for both paper aging and methanol production in the oil-paper system with the synthetic ester indicates that methanol production from paper may be directly related to the chain scission in paper as also suggested in [15]. However, it should be noted that the difference in the pre-exponential factors for methanol production between the mineral oil and the synthetic ester impregnated papers is due to the difference in partitioning of methanol between oil and paper.

7 CONCLUSIONS

The applicability of methanol and 2-FAL as aging markers for synthetic ester impregnated insulation paper was investigated through laboratory scale experiments. The direct injection technique given in ASTM D5837 was found to be better than the indirect injection technique to measure 2-FAL in synthetic ester because of not requiring a separate calibration curve prepared for the ester and having better detection limits than the indirect injection technique.

Methanol in the synthetic ester increased linearly with the reduction in DP and the concentration values were higher than 2-FAL during the early stage of paper aging. This confirms the prospect of using methanol as an early aging indicator for synthetic ester impregnated insulation paper. Nevertheless, the relationship between methanol and paper aging in the

synthetic ester was different from that in the mineral oil due to a difference in the partitioning between oil and paper. Therefore, different aging assessment criteria will have to be used for the transformers filled with synthetic esters compared with transformers filled with mineral oil. Similar to in mineral oil, a reduction of methanol in the synthetic ester was observed at the late stage of paper aging and the preliminary stability tests conducted at high temperature indicated a possible instability of methanol due to the esterification could have contributed to the reduction at the late stage of paper aging.

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