Analysis of the degradation of five esters and the effect of the cellulose on their properties

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***Abstract*—The need to replace mineral oils used in the cooling and insulation of transformers has led to the development of various alternatives. The most promising options include synthetic and natural esters of various origins. However, based on the available information and the studies conducted under different conditions, it is not possible to determine if the long-term behaviour and properties of all esters are the same. This work analyses the five main commercial esters (sunflower, rapeseed, soybean, palm and synthetic) and their degradation when combined with kraft and thermally upgraded papers. The insulating materials were aged along with copper at 130 ºC in sealed glass vials. The performance of the fluids was studied through the measurement of moisture content, acidity, interfacial tension, and dielectric dissipation factor. Moreover, the ageing of the cellulosic materials was monitored by the reduction of the polymerisation degree. The results showed that there are significant differences between esters of different origins. Furthermore, the properties of the esters were affected by the paper they were combined with.**

Keywords*—thermal ageing, biodegradable fluids, cellulosic materials, power transformers

I. Introduction

In recent years, there has been a growing emphasis on environmental protection and sustainable development, [1]. Various strategies are being explored to mitigate the environmental impact of the energy sector, the major contributor to CO_2 emissions, [2], including both the generation and the consumption [3]. Additionally, there is a pressing need to modernize and adapt ageing electrical systems to meet environmental standards, [4].

Transformers, crucial components of electrical substations, typically use mineral oil and cellulose-based insulation for electrical insulation and cooling, [5]. However, there is increasing interest in exploring alternatives, such as natural and synthetic esters derived from renewable resources, due to their biodegradability and high fire point, [6].

Numerous studies have investigated the long-term behaviour of the esters and the degradation of solid insulation in transformers using these alternative fluids, [7]. However, comparing results across studies is challenging due to variations in test conditions and methodologies [8]–[10] Consequently, there is a need for standardized testing protocols and comprehensive studies to determine the most suitable alternatives.

This study aims to address these gaps by examining the five main commercial esters along with two insulating papers under thermal stress conditions.

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By analysing key properties of the fluids and paper degradation, the study seeks to identify the optimal combination of materials for enhancing equipment performance and sustainability in the electrical system.

II. Experimental Procedure

A. Materials

The five most commonly used esters were selected for this study, including three natural esters (sunflower, rapeseed and soy), one modified natural ester (palm) and one synthetic ester, as well as a mineral oil for reference, whose properties are listed in Table I.

TABLE I. Properties of the Insulating Fluids

Property	Min.	Sunf	Rap.	Soy.	Palm	Synt.
Viscosity 40 ºC[mm²/s]	9.98	39.2	37	34	5.062	29
Flash point [ºC]	176	330	> 315	320	188	260
Acidity [mgKOH/g]	<0.01	0.05	≤0.04	<0.05	<0.01	<0.03
Moisture [mg/kg]	15	150	50	50	52	50
Tan δ 90 °C	0.002	0.03	<0.03	<0.03	<0.01	0.002

Moreover, two insulating papers were analysed: a regular Kraft paper and a Thermally Upgraded Kraft paper (TUK). The properties of the cellulosic materials are collected in Table II.

TABLE II. Properties of the Insulating Papers

Property	Kraft	TUK
Apparent density [g/cm³]	1	1
Tensile strength unfolded (machine direction) [MPa]	94	115
Elongation unfolded (machine direction) [%]	1.7	2
Moisture content [%]	<8	< 8
Electric strength in air unfolded [kV/mm]	10	10

B. Thermal ageing and characterisation

The insulating fluids were dried at 60 ºC for 24 hours, with a cycle of alternating 4 hours under vacuum and 1 hour in a nitrogen atmosphere at 500 mbar. The cellulosic materials were dried inside the ageing vials at 105 ºC for 3 hours. Subsequently, the vials were filled with the fluid and copper and left for impregnation at 60 ºC for 3 hours. Then, the samples underwent thermal accelerated aging at 130°C in an air circulating oven. The samples were analysed in seven degradation states by measuring their moisture content, according to IEC 60814, acidity, following the IEC 62021, interfacial tension, according to IEC 62961, dielectric dissipation factor (tan δ), according to IEC 60247, and polymerisation degree (DP), following the IEC 60450.

III. Results and Discussion

A. Moisture content

The moisture content, both in fluids and papers, varied with ageing, as can be observed in Figures Figure 1 and Figure 2. It is a key factor during the ageing of insulating since it accelerates the degradation rate [11]. Water is generated during degradation through oxidation and paper hydrolysis, while also being consumed by the latter process [12].

In the case of fluids, mineral oil maintained practically constant moisture levels during ageing, much lower than those of esters. Among the esters, moisture increased with ageing, although not uniformly across all types. Synthetic ester exhibited consistently higher moisture content than the other fluids throughout the experiment, followed by the palm fluid. In the other natural esters, moisture initially increased with the ageing, followed by a reduction due to consumption by hydrolysis, which occurred at different times depending on the paper used.

It is important to analyse the differences found in the tests conducted with Kraft and TUK papers, as moisture levels reached with the latter were consistently lower. This could be attributed to lesser water formation in the vials containing TUK paper. Since water is a byproduct of ageing, reduced degradation would result in lesser water generation.

Regarding the papers, an increase in moisture was observed, particularly in those combined with mineral oil and palm and synthetic esters. In these combinations, there was no significant reduction in moisture content in the fluids. This could explain why there was less water consumption by them and, consequently, more moisture accumulated in the paper.

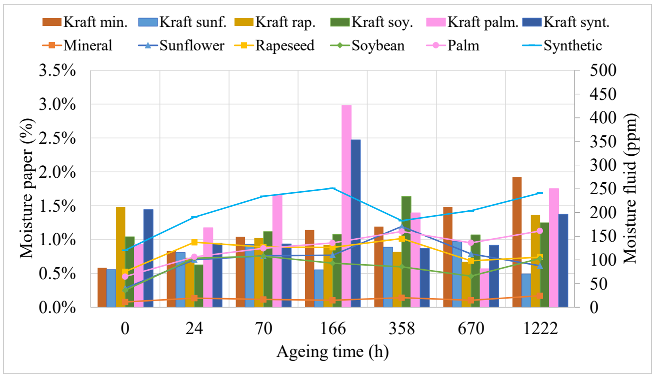

Figure 1. Moisture content of the fluids and Kraft paper.

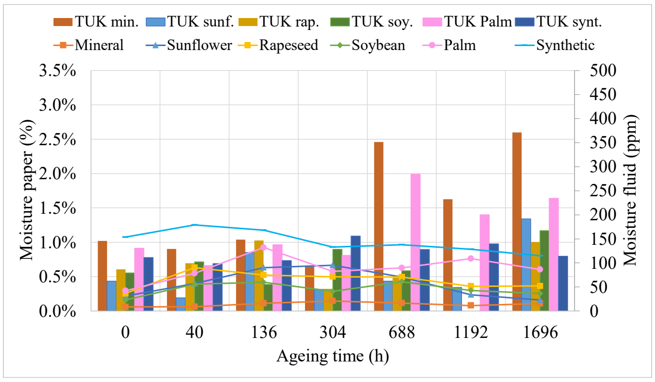

Figure 2. Moisture content of the fluids and TUK paper.

B. Acidity

The evolution of acidity is illustrated in Figures Figure 3 and Figure 4 for the samples with Kraft paper and TUK, respectively.

During the ageing, the acidity increases due to the formation of acids through hydrolysis and oxidation, both from fluids and paper.

Mineral oil exhibits lower acidity compared to esters due to its chemical structure, [13], and its increase during degradation was less pronounced. However, it is important to note that hydrolysis does not occur in this fluid, and it is also less susceptible to oxidation. Therefore, the acids primarily come from cellulose.

Differences were observed among esters concerning acid formation. Palm and synthetic esters demonstrate lower acid production, corresponding to their lower water consumption and greater resistance to oxidation compared to other esters. Notably, soybean ester exhibits minimal acid production despite having a moisture content similar to other fluids, possibly due to lesser paper degradation. Conversely, sunflower ester consistently shows higher acidity, potentially attributed to paper degradation or the chemical composition of the fluid. In these fluids, acids are generated through the hydrolysis and oxidation of both the fluid and the paper. Furthermore, only high molecular weight acids are present, [14], which are not dangerous for the cellulose, making the higher acidity less significant compared to mineral oil.

When comparing the acidity results obtained with different papers, it was observed that levels were consistently lower in samples with TUK paper. This is probably due to less available water associated with reduced paper degradation, consequently lowering acid formation.

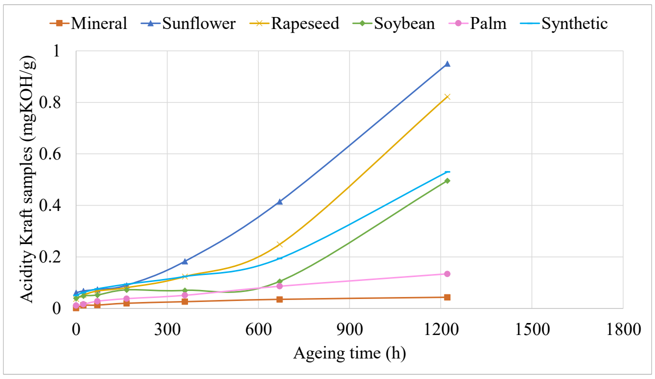

Figure 3. Acidity of the fluids aged with Kraft paper.

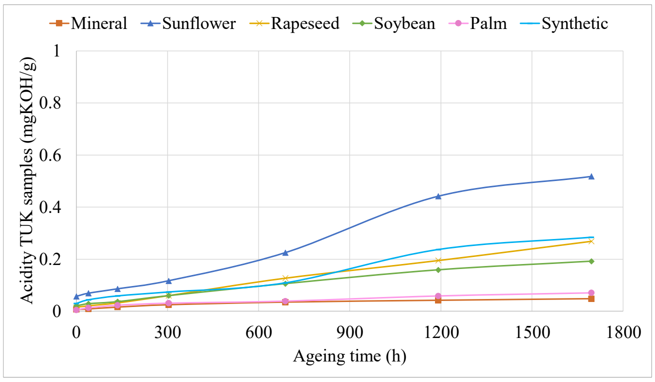

Figure 4. Acidity of the fluids aged with TUK paper.

C. *Interfacial tension*

The interfacial tension, shown in Figures Figure 5 and Figure 6, has traditionally been used as an indicator of the presence of polar substances in mineral oil. The higher the polarity, the lower the interfacial tension. Consequently, this parameter decreases with ageing due to the formation of by-products and the appearance of polar contaminants in the fluids, [15].

In the conducted tests, mineral oil and palm ester exhibited the highest interfacial tension, while the other natural esters showed lower and similar interfacial tension among them, with a noticeable reduction during ageing (approximately -15%). The synthetic ester demonstrated the lowest interfacial tension and remained relatively constant during the tests (approximately -5%). Notably, mineral oil exhibited the most significant variation in interfacial tension (-22%), likely attributable to a greater increase in polarity resulting from the generation of low molecular weight acids, which are absent in other fluids, [16].

The behaviour with both papers was similar in terms of trends and the behaviour of one fluid compared to another. However, significant differences were observed in the values of this parameter. When the fluids were combined with TUK paper, the interfacial tension was consistently lower, even in the early stages of ageing. This reduction was not observed in the mineral oil and synthetic ester, but it was particularly significant in natural esters, with a variation of up to 16% over the same ageing period. This suggests that the paper may have induced an increase in the polarity of these fluids, possibly due to some alteration in their composition or the dissolution of certain polar compounds.

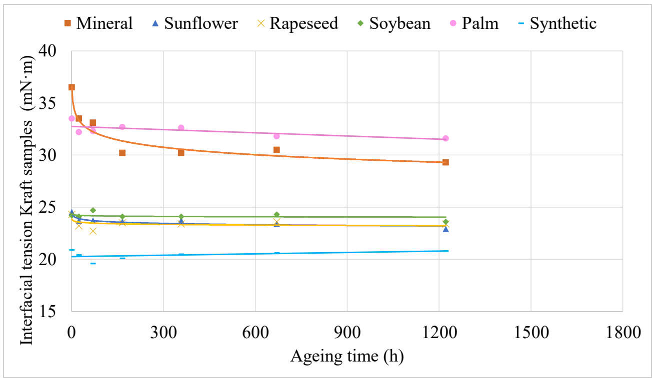

Figure 5. Interfacial tension of the fluids aged with Kraft paper.

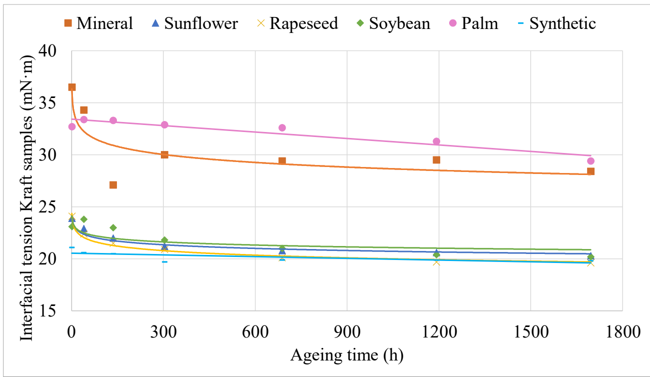

Figure 6. Interfacial tension of the fluids aged with TUK paper.

D. *Dielectric dissipation factor*

The evolution of tan δ, resulting from changes in both the polarity and conductivity of the fluids, is depicted in Figures Figure 7 and Figure 8.

Due to the polar nature of the esters, their tan δ is higher than that of mineral oil for all the ageing states, as also observed in this study, [17]. As degradation progresses, tan δ increases due to a rise in the presence of polar substances and a reduction in fluid resistivity. This increase is more pronounced in esters compared to conventional oil. Some differences were observed among the alternative fluids.

In the tests with Kraft paper, synthetic ester exhibited the highest tan δ, followed by sunflower ester, while rapeseed ester showed the lowest tan δ at all ageing points. Despite these differences, the percentage increase in tan δ was similar in all fluids.

On the other hand, in the tests with TUK paper, it was observed that the synthetic ester was the alternative fluid with the lowest tan δ, contrasting with the results obtained with Kraft paper. Furthermore, the rapeseed ester showed an unusual increase in tan δ, surpassing that of the other esters, without this occurring with the previous paper.

Moreover, when comparing the tan δ values obtained with both papers, they were higher in the tests conducted with TUK paper than with Kraft paper. This behaviour aligns with that found in interfacial tension. The fluids experiencing a significant increase in tan δ are the natural esters, which also underwent a notable change in interfacial tension. Conversely, mineral oil and synthetic ester maintained similar values in the tests with both Kraft and TUK papers, both for tan δ and interfacial tension.

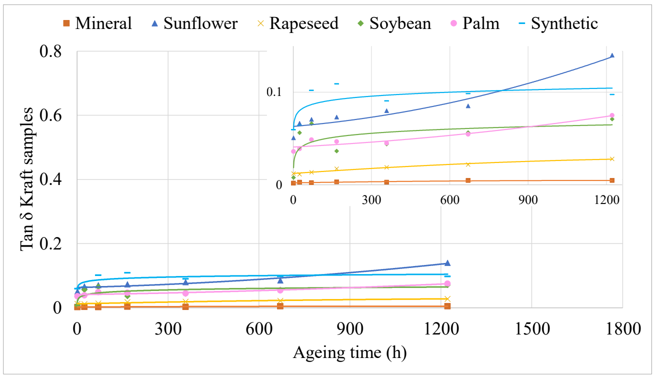

Figure 7. Tan δ of the fluids aged with Kraft paper.

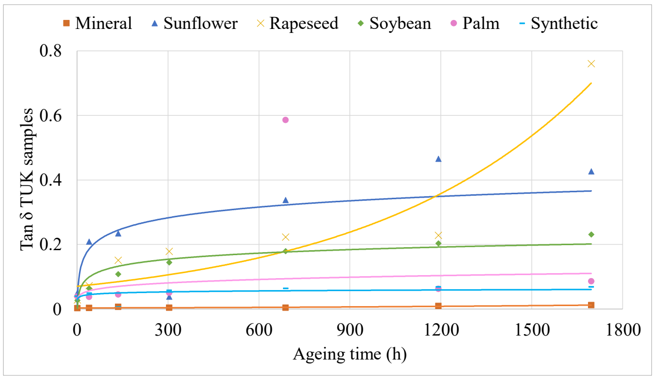

Figure 8. Tan δ of the fluids aged with TUK paper.

E. Polymerisation degree

The DP of the papers is shown in Figures Figure 9 and Figure 10. This parameter, which represents the number of glucose monomers present in cellulose, serves as an indicator of ageing. As the material degrades, the bonds break, reducing the DP, [8].

In Kraft paper, initial degradation was faster in palm and synthetic esters. However, the degradation rate began to decrease earlier than in mineral oil, resulting in a lower DP with this fluid at the end of the experiment. Natural esters showed very similar degradation among them and, in any case, provided better protection for the paper than other fluids.

On the other hand, in samples with TUK paper, degradation was minimal, and the slope is practically zero, due to the low temperature of the experiment and the absence of other types of stress, such as electrical or vibrational. With the available degradation data, clear conclusions about the performance of each fluid cannot be drawn.

When comparing both papers, a clear reduction in the ageing rate was observed with TUK paper compared to traditional one, demonstrating a significant advantage of this material.

IV. Conclusions

The ageing evolution of six fluids and two dielectric papers was studied through the analysis of five essential properties. It was observed that all alternative fluids do not behave uniformly, with notable differences between the unmodified natural esters and the palm and synthetic esters. Additionally, it was found that the paper combined with the fluids can induce changes in their polarity, which was higher with the TUK paper, particularly affecting the natural esters.

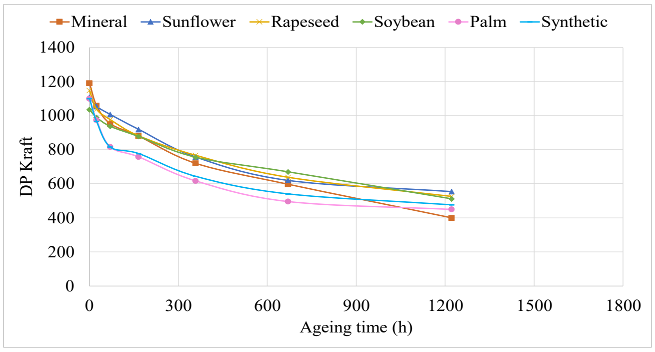

Figure 9. DP of the Kraft paper.

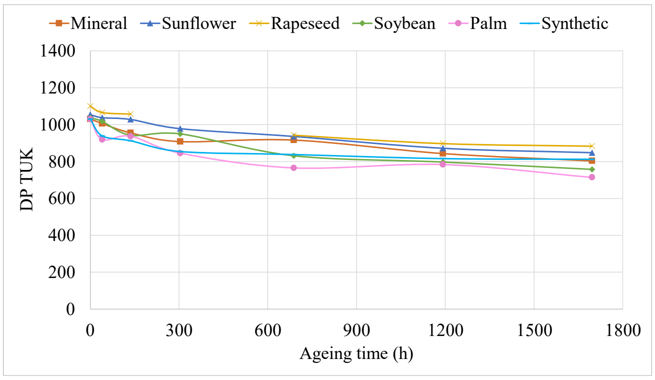

Figure 10. DP of the TUK paper.

References

[1] United Nations, "2030 Agenda for Sustainable Development." .

[2] S. Sandu et al., "Energy-Related CO 2 Emissions Growth in ASEAN Countries: Trends, Drivers and Policy Implications," Energies, pp. 1–15, 2019.

[3] G. Zsembinszki et al., "Life cycle assessment (Lca) of an innovative compact hybrid electrical-thermal storage system for residential buildings in mediterranean climate," Sustain., vol. 13, no. 9, 2021, doi: 10.3390/su13095322.

[4] T. Martin, "The role of ester fluids in Europe ' s ageing grid," Transformers Magazine, 2021.

[5] T. O. Rouse, "Mineral oil in transformers," IEEE Electr. Insul. Mag., 1998.

[6] M. Rafiq et al., "Use of vegetable oils as transformer oils-A review," Renew. Sustain. Energy Rev., vol. 52, pp. 308–324, 2015, doi: 10.1016/j.rser.2015.07.032.

[7] C. Krause, "Power transformer insulation - History, technology and design," IEEE Trans. Dielectr. Electr. Insul., vol. 19, no. 6, pp. 1941–1947, 2012, doi: 10.1109/TDEI.2012.6396951.

[8] H. P. Gasser, C. Krause, M. Lashbrook, and R. Martin, "Aging of pressboard in different insulating liquids," 2011, doi: 10.1109/ICDL.2011.6015450.

[9] T. Münster, P. Werle, K. Hämel, and J. Preusel, "Thermally Accelerated Aging of Insulation Paper for Transformers with Different Insulating Liquids," Energies, 2021.

[10] S. Y. Matharage, Q. Liu, Z. D. Wang, G. Wilson, and C. Krause, "Aging assessment of synthetic ester impregnated thermally non-upgraded kraft paper through chemical markers in oil," IEEE Trans. Dielectr. Electr. Insul., vol. 25, no. 2, pp. 507–515, 2018, doi: 10.1109/TDEI.2018.006833.

[11] T. V Oommen and T. A. Prevost, "Cellulose Insulation in Oil-Filled Power Transformers : Part II – Maintaining," IEEE Electr. Insul. Mag., vol. 22, no. 2, pp. 5–14, 2006.

[12] L. E. Lundgaard et al., "Ageing of cellulose in mineral-oil insulated transformers," CIGRE, 2007.

[13] K. Bandara, C. Ekanayake, T. K. Saha, and P. K. Annamalai, "Understanding the ageing aspects of natural ester based insulation liquid in power transformer," IEEE Trans. Dielectr. Electr. Insul., vol. 23, no. 1, pp. 246–257, 2016, doi: 10.1109/TDEI.2015.004744.

[14] G. K. Frimpong, T. V. Oommen, and R. Asano, "A Survey of Aging Characteristics of Cellulose Insulation in Natural Ester and Mineral Oil," IEEE Electr. Insul. Mag., vol. 27, no. 5, pp. 36–48, 2011.

[15] S. Forouhari and A. Abu-Siada, "Remnant Life Estimation of Power Transformer Based on IFT and Acidity Number of Transformer Oil," 2015.

[16] Cigre Working Group D1.53, "Materials and emerging test techniques - Ageing of liquid impregnated cellulose for power transformers," vol. 738, no. August, pp. 1–92, 2018.

[17] J. Tokunaga, H. Koide, K. Mogami, and T. Hikosaka, "Comparative studies on the aging of thermally upgraded paper insulation in palm fatty acid ester, mineral oil, and natural ester," IEEE Trans. Dielectr. Electr. Insul., vol. 23, no. 1, pp. 258–265, 2016, doi: 10.1109/TDEI.2015.005502.