RESEARCH ARTICLE

Understanding the Ageing Performance of Alternative Dielectric Fluids

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ABSTRACT Mineral oil has traditionally been used as a cooling fluid in power transformers, but its low biodegradability and low fire point have motivated the search of alternatives. In this work, six different dielectric fluids have been studied, including four vegetable liquids, from sunflower, rapeseed, soybean, and palm, one synthetic ester and a mineral oil used for comparison. These oils were subjected to an accelerated thermal ageing in glass vessels at 150°C for four weeks (672 hours) in presence of Kraft insulating paper. Different oils parameters were measured during the ageing, i.e. breakdown voltage, dielectric dissipation factor, permittivity, DC resistivity, density, kinematic viscosity, flash and fire points, interfacial tension, acidity, and dissolved gases; additionally, the degree of polymerisation (DP) of the paper was measured. Results showed that the changes of the natural esters properties, except for the palm oil, were similar along the ageing time. Palm oil results were similar to those of the mineral oil, whereas synthetic ester showed a behaviour similar to natural esters. The kraft paper degradation was higher in the mineral oil, followed by the synthetic ester and the palm oil. No significant differences were found in the ageing with the natural esters.

INDEX TERMS Insulating paper, natural esters, thermal ageing, transformers.

I. INTRODUCTION

Transformers play the major role in power grids, and their importance is expected to increase based on the foreseen evolution of electricity demand and the decarbonization policies [1], [2], [3]. Despite their high efficiency, these machines have significant losses causing the heating of their coils [4]. Their solid electrical insulation system degrades with time under high temperatures, its mechanical and dielectric performance gets worsened, leading to the occurrence of faults and, as it cannot be replaced, it determines the lifespan of the transformer [5], [6]. This harmful evolution on solid dielectric

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integrity is mitigated with their immersion in cooling fluids to dissipate the heat.

There are different kind of fluids used in transformers, such as mineral oils, silicone oils, high-molecular-weight hydrocarbons, and synthetic and natural esters [7]. The mineral oil type is traditionally the most used fluid as it is suitable for application in power transformers. The main drawbacks of mineral oils are their low biodegradability [8] and low fire points. By contrast, esters have high fire points, and they are fully biodegradable. Although discarded in the first instance for use in transformers due to their high viscosity, which reduces their cooling capacity [9], their high dielectric loss factor and their low oxidation stability [10], more recently, the concern for the environment and safety have pushed the esters as alternatives to mineral oils, even in transformers

which are currently in operation [11]. Therefore, these oils have received the attention of researchers, to improve the knowledge on their application and trying to solve their main drawbacks.

Numerical simulations carried out have shown that the temperatures reached in a transformer using esters could be similar, or even lower, to those reached with mineral oils in adapted winding designs [12], [13], [14] Some manufacturers apply special treatments to improve the viscosity or the oxidation stability of these alternative liquids [15]. The effect of the fluid used on the degradation of the solid insulation, measured by the control of the chemical [16], mechanical [17] or light techniques [18] after a thermal [19] or electrical [20] ageing process, have also been afforded. Researchers have demonstrated that the degradation suffered by the cellulosic materials is lower when the cooling fluid is a natural ester, derived from sunflower, rapeseed, soy or palm, instead of a mineral oil at similar conditions [16], [17], [19], [21], [22], [23]. The levels of degradation depended on the specific oil and the conditions of the study, not all the natural esters protected the insulation from degradation in the same degree [19], [24], and other natural esters of different origin (corn, peanut, coconut or mustard) showed worst performance [25], [26], [27], [28] The results with synthetic esters reflects slightly lower degradation than with the mineral oils [19], [29].

This has been explained based on a reduction of the hydrolysis of the cellulose. Hydrolysis is the most important degradation mechanism, and it mainly depends on the moisture content of the cellulose, but also on the temperature and the acidity type of the oil [30]. In mineral oil, for regular kraft paper, the life expectancy is reduced by half for every doubling of moisture content [31]. The moisture reduction in cellulose and the esterification with the fatty acids of esters may protect the cellulosic materials [21].

Other general trends, shared with the mineral oils as a cooling fluid, have been noticed. The initial level of moisture content in the oil, whatever its kind, conditions the degradation. The higher the moisture content of a sample of an ester, the larger the degradation or the increase of acidity under thermal stress [16], [21], [32]. When comparing the production of water or acid during the ageing, its magnitude is always higher with the esters than with the mineral oils, excepting in the case of the palm ester [16], [23], [33], [34].

Despite these discoveries on the general trends of alternative esters, the dispersion in the design of the studies has hindered finding which are, among them, the best options to replace the mineral oils. In the first place, in most of the available works, the performance of only one or two alternative fluids is studied (90%). It is difficult to find studies in which three (5%), four (4%) or more (1%) alternative fluids are analysed together. Additionally, the conditions of the ageing usually vary. Only respecting the researches here cited, there are examples of thermal ageing carried out at 80 [29], 100 [29], 110 [16], 120 [16], [21], [24], [29], [32], [35], 130 [16], [19], 140 [32], [35], 150 [17], [22], [25], [33], 151 [23], 160

[23], [32], [33], 165 [22], 168,5 [23], 170 [33], [36], 180 [22], 200, 400 and 800 °C [37]. This dispersion is worsened if the moisture initial content is considered. These used steel and iron vessels or glass vials and flasks to seal the samples of oil, frequently with copper and dielectric papers inside, but also alone, under vacuum, air or N_2 atmospheres. The quantity of each element usually varies. It is also frequent that some of this data is missed in the explanations given by the researchers [19], [25], [29], [32], [33], [35]. Finally, changes in the properties analysed between the different studies have been noticed.

Despite the ageing of the alternative fluids is well known, most of the works are comparing one or two fluids, with discrepancies in the samples' preparations, ageing processes, and testing methods. Thus, it is not possible to compare the results obtained in different works, which is also noticed in the bibliographic reviews on this topic [8], [34]. It is difficult to draw conclusions about the performance of each ester in comparison to the other ones in order to determine which one is more suitable to be used in a certain application. Moreover, if the knowledge of this fluids is enhanced, this would lead to the development of more precise specific standards.

In view of the need to analyse the oils in the same conditions, this work studies the ageing of six different dielectric liquids, between the most promising, and a commercial kraft paper. The intention is to follow the evolution of the most relevant parameters of oils (BDV, tan δ, permittivity, resistivity, density, viscosity, flash and fire points, interfacial tension, acidity, and dissolved gases) and paper (degree of polymerization, DP) during the ageing to understand their degradation. Results are compared to the corresponding standard for maintenance of transformers, in order to compare the degradation of all the fluids in terms of life expectancy.

II. MATERIALS AND METHODS
In this section, the materials studied in this work are defined. Also, the applied methods, including the samples preparation and thermal ageing are presented.

TABLE 1. Properties of kraft paper.

Property	Kraft
Density [g/cm^3]	1
Tensile strength (machine direction) [MPa]	91
Elongation (machine direction) [%]	2,8
Moisture content [%]	< 8
Electric strength in air [kV/mm]	7
Electric strength in oil [kV/mm]	55

A. MATERIALS
A commercial kraft paper of 200 μm thickness was used as solid insulation. The properties of this cellulosic material are shown in Table 1.

Six different dielectric oils were studied, including an uninhibited mineral oil, three natural esters derived from different vegetables (sunflower, rapeseed, and soybean), one

TABLE 2. Properties of dielectric fluids.

Property	Mineral	Sunflower	Rapeseed	Soybean	Palm	Synthetic
Density 20ºC [g/cm^3]	0.839	0.91	0.92	0.92	0.86	0.97
Kinematic viscosity 40ºC [mm^2/s]	9.98	39.2	37	32-34	5.062	29
Flash point [ºC]	176	330	> 315	320-330	188	260
Fire point [ºC]	-	362	> 350	350-360	206	316
Pour point [ºC]	- 48	- 25	- 31	-18 to -21	-37.5	- 56
Acidity [mg KOH/g]	< 0.01	0.05	≤ 0.04	0.01-0.05	< 0.01	< 0.03
Water content [ppm]	15	150	50	4-50	52	50
Dissipation factor 90°C	0.00198	0.03	< 0.03	0.01-0.03	0.0029	< 0.008
Dielectric Breakdown [kV] (IEC 60156)	46	65	> 75	≥ 55	85	> 75
Biodegradability [%]	-	85	98	>99	77	89

modified natural ester from palm, and a synthetic ester. Their main properties, provided by their manufacturers, are listed in Table 2. There are big differences between the mineral oil and the esters in some relevant parameters, as the viscosity, which affects the cooling capacity, or the flash and fire points, which determines the fire risk.

B. SAMPLES PREPARATION

The fluids and paper were dried as in the real process of the manufacturing of a transformer, in which the cellulose moisture content is reduced below 0.5% [38]. Drying of the oils was carried out in a vacuum oven at 60°C for 24 hours. Cycles of 4 hours of vacuum (10 mbar) and 1 hour in a nitrogen atmosphere (600 mbar) were applied to facilitate heat transfer. The paper was dried inside the 125 ml glass vials used lately for the ageing. This process was carried out in an air circulating oven at 105°C for 3 hours, reducing its moisture content to 0.43%. Moisture contents of the oils after the drying, measured through Karl Fischer volumetric titration following the IEC 60814 standard [39], are listed in Table 3. All values are within the limits set by IEEE [40].

Then, the vials were filled with 100 ml of oil and copper plates were also introduced in them. A 6 g paper / 100 g oil / 8 g copper ratio was applied in all the vials, following the procedure established by the IEEE Standard C57.100 [41]. Finally, the vials were sealed with a PTFE/butyl septum and an aluminum cap in an air atmosphere. Before applying the ageing temperature, it was ensured that the paper was completely impregnated by the oil. For it, the vials were placed in a temperature-controlled oven at 60°C for 2 hours.

C. ACCELERATED THERMAL AGEING

After that, five vials were taken for the initial point analysis. The other vials, 18 vials for each oil, were placed in the ageing oven, in which the temperature was raised up to 150°C and 4 weeks ageing process began.

To evaluate the evolution of the ageing of the dielectric materials, samples of the oils and papers were extracted and analysed in 7 different ageing states, which were 0, 16, 40, 70, 168, 384 and 672 hours. Two vials of each oil were extracted at 16, 40, 168 and 384 hours, whereas 5 vials were extracted at 70 and 672 hours, in order to carry out more measurements at these ageing states.

D. CHARACTERISATION OF THE MATERIALS

The properties on which the performance of both the oils and paper depend were measured at different ageing states to quantify their degradation. Tests were carried out following the standards when available.

TABLE 3. Moisture of samples after the drying process.

Fluid	Min.	Sun.	Rap.	Soy.	Palm	Synt.
Moisture [ppm]	11.1	53.3	54.2	50.2	56.9	107.2

Some critical dielectric properties of the oils were determined. AC BDV was measured with a BAUR DTA 100C dielectric oil analyser. This equipment allows to carry out the measurements with a 1 kV accuracy, following the IEC 60156 standard [42]. Test cell, filled with 400 ml of oil at 20°C, has semi spherical electrodes separated by 2.5 mm. According to the methodology set by the standard, voltage was increased at a rate of 2 kV/s from 0 kV to the voltage at which the arc between electrodes is established. Each sample was subjected to six consecutive breakdowns delayed between them 2 minutes in which the oil was homogenized by magnetic stirring. Breakdown voltage was calculated as the mean value of the six measurements. BDV is usually analysed together with moisture content, measured through Karl Fischer titration according to the IEC 60814 standard [39].

A BAUR DTL C was used to measure the dielectric dissipation factor (tan δ), relative permittivity (ε) and resistivity. All the parameters were determined in the same test, which was carried out according to the IEC 60247 [43]. The accuracy of the test equipment is 1×10^{-6} for the tan δ, 1×10^{-2} for the ε and 1×10^{-2} GΩ·m for the resistivity. Following this methodology, 45 ml of oil were heated up to 90°C and tan δ and ε were measured applying an AC sinusoidal voltage at rated frequency, whereas resistivity was determined under DC power.

Considering that oils are used in transformers not only for electrical insulation, but also as cooling fluids, some parameters that affect their cooling capacity were measured. The density and, especially, the viscosity are of vital importance on the design of the cooling system. They were measured

with a Stabinger Viscometer SVM 3000 at 15 and 40°C, respectively.

Moreover, flash and fire points of the oils were measured following the ASTM D92 standard [44], which corresponds to the open cup method. An OilLab 670 equipment was used, testing the flash and fire points every 2°C.

The interfacial tension was measured with a force tensiometer K11, following the ring method at room temperature, with an accuracy of 0.01 mN/m.

One of the main indicators of the oil degradation is its acidity. Acidity was measured through potentiometric titration according to the IEC 62021-1 [45] for the mineral oil and IEC 62021-3 [46] for the esters. These tests were carried out in automatic titrator, where the sample of oil reacts with ethanolic KOH until the pH is 11.5. The acidity is represented by the amount of KOH consumed respecting the sample size, which was 10 g for mineral oil and 5 g for esters.

Dissolved gases (DGA) were also analysed. Samples for gas analysis were previously prepared in 20 ml vials, sealed with argon to avoid sample contamination and gas leak. Then, they were placed in a headspace sample Agilent 7697A and measured in a gas chromatograph Agilent 7890B. The gases studied include the most important for transformer analysis: O_2, N_2, CO, CO_2, C_2H_6, H_2, CH_4 and C_2H_4 [8]. After that, the results have been processed through manual integration.

Dissolved gases have been analysed following three different criteria, including IEEE 60599 standard [47] and the Rogers and Doernenburg methods [48]. These methods can be used for detecting some faults occurred in the transformer. They are based on five gas ratios:

- R1 = CH_4/H_2
- R2 = C_2H_2/C_2H_4
- R3 = C_2H_2/CH_4
- R4 = C_2H_6/C_2H_2
- R5 = C_2H_4/C_2H_6

The IEC 60599 standard has been usually used as reference. According to this standard, it is necessary to analyse the concentrations of the gases, to ensure that they are not higher than the usual values, collected in [49]. Also, the typical rates of gas increase have to be calculated. If any of the dissolved gases shows abnormal values, the ratios R1, R2 and R5 have to be analysed, following the indications of table 1 of [47].

Respect to the Rogers method, it only considers the ratios R1, R2 and R3. The interpretation of this method has to be done following the flow chart of figure 5 of [48].

The Doernenburg method analyses both the gases concentration and the ratios R1, R2, R3 and R4. If the concentration one of the gases (H_2, CH_4 C_2H_2 or C_2H_4) is higher than twice the limit set in table 4 of [48] and at least the concentration of one of the other two gases (C_2H_6 or CO) is higher than the limit set in that table, the ratios can be analysed. The concentration of at least one of the gases considered in each ratio must be greater than the limit to determine the fault accurately. The ratios' limits for each type of fault are collected in table 5 of [48].

Additionally, the gases have been analysed through the Duval triangle method, applying the triangle for each kind of fluid when available [50].

Finally, DP of paper was determined following the ASTM D4243 standard [51]. The paper was crumbled and solved in 22.5 g of deionized water and 24.75 g of cupriethylene-diamine hydroxide solution. The solution was subjected to stirring for 16 hours with glass spheres filling the air gap of the vial. Then, its viscosity was measured.

III. RESULTS AND DISCUSSION
Results of the properties measured are shown and discussed in this section.

A. MOISTURE CONTENT
The evolution of the moisture content at three different ageing states is shown in Fig. 1. Here, the moisture content of the mineral oil remained almost constant during the ageing, being always the lowest. In the case of the esters, a different behaviour was found. The unmodified natural esters, that includes sunflower, rapeseed, and soybean, showed an increase in their moisture content at the beginning of the ageing, followed by a reduction. This behaviour has been found in other studies [16], [52]. Respecting the modified natural ester (palm oil) and the synthetic ester, their moisture content increased during all the ageing.

This evolution can be explained based on the available knowledge. During the ageing, both the fluids and the paper generate water [53], more slowly as the degradation progresses [22], [24], that is distributed between the fluid and the paper [54]. Thus, it would be expected to find increases of moisture content, as it is the case of the esters. The mineral oils are much less hydrophilic than the cellulosic and the esters (Table 3), explaining the stable level of water in this case as it tends to migrate to the paper.

The unmodified natural esters can react with the water through hydrolysis, generating high molecular weight acids [16], contrary to the other studied esters which are more stable [33], [55]. As the degradation produces less water its consumption by hydrolysis could lead to a final reduction in moisture content, as it was here noticed.

B. AC BREAKDOWN VOLTAGE
BDV results of all the tested oils at three ageing states are collected in Fig. 1. If considering the new samples, all the alternative fluids had higher BDV than the mineral oil. At the end of the ageing, BDV was reduced in all the fluids, due to degradation. This reduction was higher in the esters than in the traditional oil. This could be caused by the combination of the higher moisture content of the esters which eases the arc formation in the fluid, and their hydrolysis processes, creating free acids. It is noteworthy that modified palm ester maintained a higher BDV than the other fluids throughout ageing, as it was shown in [33].
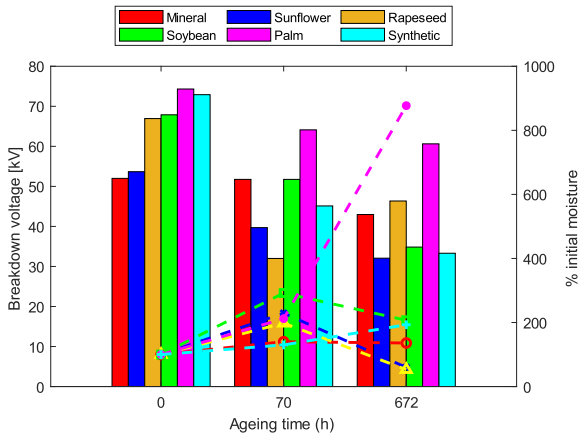
FIGURE 1. Evolution of BDV and moisture content of the dielectric fluids.

C. DIELECTRIC DISSIPATION FACTOR AND RELATIVE PERMITTIVITY

These parameters depend on the changes on the polarity and conductivity of the insulating fluid.

Tan δ of all the fluids increased with the degradation, as can be seen in Fig. 2. As expected, the mineral oil had the lowest tan δ, as in other previous works [19], [21], since natural esters always have a higher polarity due to their chemical structure and their polar affinity [33]. Also, differences between esters are due to this cause, because their different plant origin. The increase of tan δ with the ageing is commonly caused by the presence of more water or dissolved polar pollutants, as this is the case, but also due to the oxidation. Some reports agreed that even a low oxidation can strongly increase the dissipation factor of oils [56] and that the presence of long-chain fatty acids also increases this factor [57]. Moreover, the polar affinity of these fluids could result in the translocation of the polar degradation products, such as water and acids from the cellulose to the fluid, which does not occur in the mineral oil, which leads to a lower tan δ of the mineral oil during all the ageing [33].
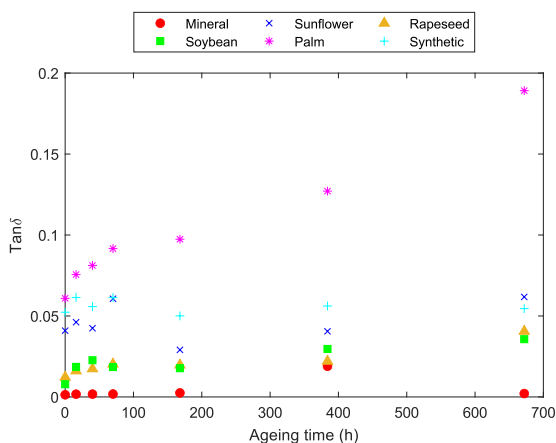
Relative permittivity of all the oils (Table 4) was practically constant, with a slight increase with the ageing. It was similar in the natural and synthetic esters, and always higher than in mineral oil. Similar results were obtained in previous works [8], [32].

TABLE 4. Permittivity of the dielectric fluids during the ageing.

State	Min.	Sunf.	Rap.	Soy.	Palm	Synt.
New	2.11	2.83	2.85	2.89	2.91	2.98
Aged 672h	2.12	2.84	2.85	2.9	2.91	3

D. DC RESISTIVITY

For new liquids the resistivity of mineral oil was approximately ten times than soybean ester and twenty times than other fluids, as it was found in other studies [23], [58]. Also, during the ageing, contrary to the tan δ, the polarity of esters results in a lower resistivity than that of the mineral oil. Esters with higher tan δ had a lower resistivity.

For mineral oil and soybean ester, the resistivity decreased rapidly with ageing, at 16 hours the values decreased 25% and 50%, respectively; these values still decreasing with time but with a slower rate. For the other fluids resistivity decreased slowly with the liquid ageing, as seen in Fig. 3.

The resistivity decrease is due to the increase of polar compounds during the ageing, caused by the rupture of bounds in the insulating system. In the case of the mineral oil, the decrease of the resistivity was mainly caused by the acids generated during the degradation. In the natural esters, resistivity decreased due to the high oxidation and the water absorption. In the synthetic ester, which is stable against oxidation according to the manufacturers, resistivity decreased less than in the natural esters and it was mainly affected by the high moisture content.
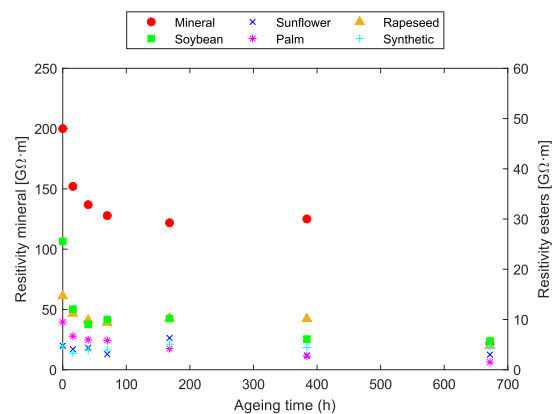

FIGURE 3. DC resistivity of the dielectric fluids.

E. DENSITY AND KINEMATIC VISCOSITY

The density of the fluids remained constant during the ageing. Moreover, the kinematic viscosity scarcely increased with

FIGURE 2. Dissipation factor of the dielectric fluids.

the degradation, as can be seen in Table 5. Since the ageing was carried out in sealed vials, samples were exposed to a few oxygen during the experiment, so the viscosity was not significantly increased [19].

This means that the differences and similitudes between the oils from Table 2 remained. The values obtained were similar to those here summarised, and reflect the suitability of mineral oil and, especially, palm oil as cooling fluids, as the remaining esters have around three times higher viscosities.

TABLE 5. Density and viscosity of the fluids during the ageing.

Property	Min.	Sunf.	Rap.	Soy.	Palm	Synt.
Density 15ºC [g/cm^3]	0.861	0.917	0.922	0.924	0.863	0.971
Visc. New 40ºC [mm^2/s]	9.9	39.43	37.41	33.21	5.03	28.78
Visc. 672 h 40ºC [mm^2/s]	9.94	39.66	37.48	33.43	5.05	28.66

F. FLASH AND FIRE POINTS

These two parameters were measured at three ageing states. Results are collected in Fig. 4. All the results agree with the values gave by the corresponding manufacturer, in Table 2. Both parameters remained almost constant during the ageing. Slight variations occurred in the rapeseed and soybean oils, in which flash point decreased up to 5% at the end of the ageing, whereas fire point decreased up to 2.5%, but they were within the test uncertainty and the standard values. This reduction could be due to the breaking of bonds with the ageing. This rupture makes the chains shorter than when they are new, which eases the gas generation, reducing the flash and fire points [56].
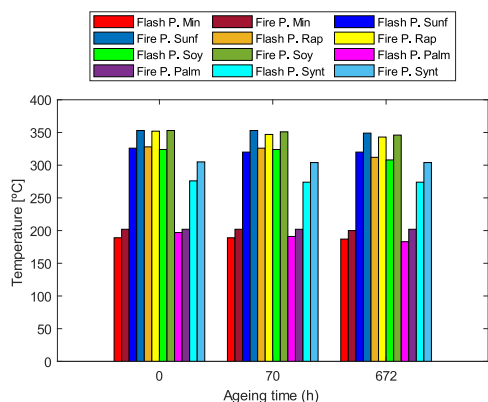

FIGURE 4. Flash and fire points of the dielectric fluids.

G. INTERFACIAL TENSION

Interfacial tension is an indirect measurement of the amount of polar compounds present in the oil, as the polar acids and other ageing subproducts [59].

Fig. 5 shows the values of the interfacial tension during ageing. The values were around 18% and 30% lower in the natural and synthetic esters, respectively, than in mineral oil; for palm oil these values were around 18% higher to mineral oil. Since the mineral oil is the only fluid that generates polar acids, interfacial tension decreased more in this oil than in the other liquids. Natural esters have lower interfacial tension because there are polar compounds in their chemical structures, and they tend to oxidize easily, so there was also a decrease of the interfacial tension, but less significant than in the mineral oil. Moreover, their interfacial tension is less sensitive to polar contaminants because of the interaction ability of the ester bonds [52]. Due to the chemical structure of the synthetic ester its interfacial tension is the lowest. Nevertheless, its high stability leads to the lowest reduction of this parameter during the ageing, in comparison with the rest of the liquids. Because of that, the interfacial tension of the synthetic ester was similar to that of the natural esters at the end of the ageing.
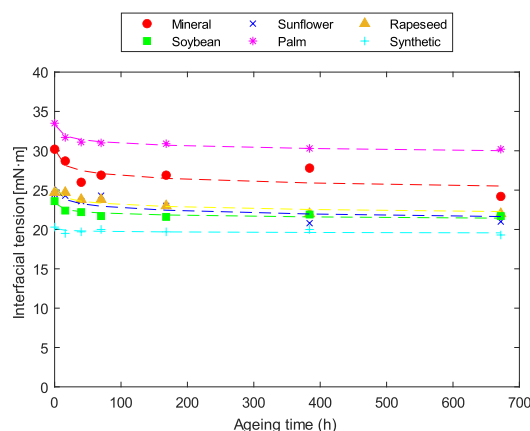

FIGURE 5. Interfacial tension of dielectric fluids during ageing.

H. ACIDITY

Fig. 6 shows the evolution of the acidity with the ageing. Unmodified esters always had higher acidity than the conventional fluid, since they have fatty acid groups in their molecular structure [21]. Acidity of new liquids was similar, and lower than 0.06 mg KOH/g in all cases, but it raised with the ageing and this increase was higher in the esters than in the mineral oil, as it was shown in other works [21], [33] for different natural esters. This increase was around 4000% in the case of all the natural esters and 2750% in the synthetic one, whereas it was 375% in the mineral oil. No relevant differences were found between esters in the increase of acidity, as in [19], excepting in the case of palm oil. This differed from that of the other natural esters and its total acid number was more similar to that of mineral oil, as it was found in [33].

This is because the acids are generated through hydrolysis and oxidation [33]. It is well known that the natural esters have a low oxidation stability [8]. Also, as already mentioned, water of the oil-paper system is consumed through hydrolysis when natural esters are used producing acids [16]. This higher increase in acidity of natural esters and their already seen reduction in moisture meet each other. It also meets with
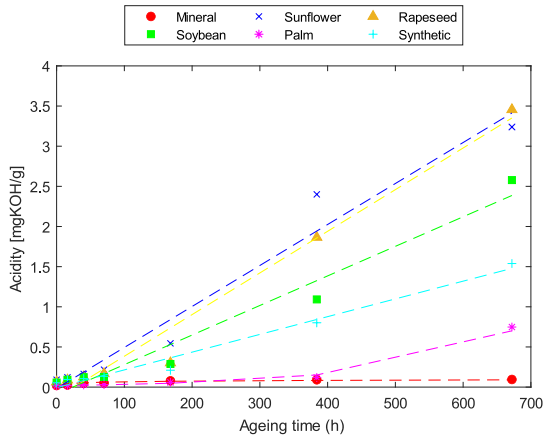
FIGURE 6. Acidity of the dielectric fluids.

the explanation regarding the loss factor, resistivity, or interfacial tension. The low acidity of the synthetic oil could be explained as it is more stable against oxidation. In the case of palm fluid, acids are only generated by the oxidation because there is no relevant hydrolysis in it [34]. Regarding the mineral oil, its acids tend to migrate from this oil to the paper and to react with it by acid hydrolysis, which also reduces the amount of free acids [30].

Acids have been usually associated with a higher degradation of oil and supposed to damage the solid insulation. Nevertheless, different kinds of acids are generated by the liquids and paper and only the low molecular weight acids play a relevant role in the degradation of cellulose [57]. Acids generated by the mineral oil are of high and low molecular weight. Due to the polarity of the last ones, they are hydrophilic and can be dissolved in the cellulose. This process, known as acid catalyst hydrolysis, accelerates the degradation of paper. By the other hand, the esters generate high molecular weight acids, and the generation of the low molecular weight ones is rarely and limited [60]. Some studies suggest that the high molecular weight acids could react with the cellulose through transesterification [21], [30], which protects it from hydrolysis, reducing its degradation [60]. Then, these higher presence of acids in the natural esters could even be, in fact, beneficial for cellulose.

I. DISSOLVED GASES

Different gasses were analysed during the ageing process. Some of them are commonly associated with the paper degradation, especially CO and CO_2, [21], whereas the others are related to the fluids. According to the IEC 60599 standard [47], the gases should be analysed considering both the concentrations and the ratios between some gases, as the CO_2/CO ratio.

O_2 decreased during the ageing due to the consumption by the oils and paper, Fig. 7. O_2 consumption of the mineral oil was the lowest, being the oxygen mainly consumed by the cellulose. The natural esters consumed most of the available

O_2 rapidly due to their tendency to oxidize [61]. This O_2 consumption led to the increase of tan δ, which agrees with those results. The synthetic ester consumed less O_2 than the natural esters due to its oxidation stability.

N_2 appeared at the beginning of the ageing and remained almost constant. The N_2 concentration was similar in all the esters (around 40000 ppm), except for the palm fluid (80000 ppm), which had the highest concentration of this gas. The mineral oil had an intermediate value of N_2 concentration (60000 ppm).
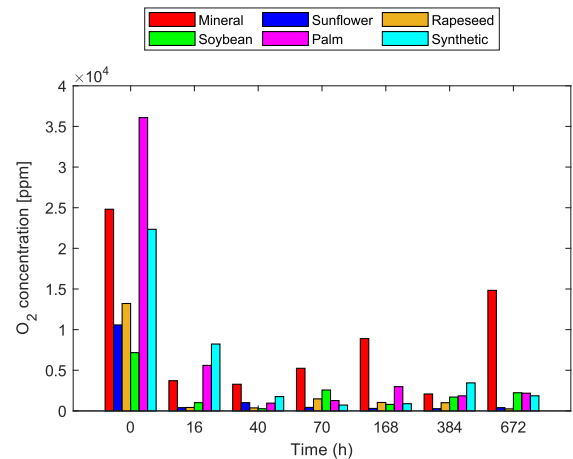

FIGURE 7. O_2 concentration of the insulating system.

C_2H_6 was generated in an appreciable concentration in all the fluids. This gas is usually related to oxidation, high temperature, light exposures, and linolenic acid content. C_2H_6 concentration was noticeably higher in the rapeseed ester than in the other fluids, approximately 2000 ppm, due to its higher linolenic acid content [50]. Soybean fluid also had a high C_2H_6 concentration, but four times lower than the rapeseed ester. The concentration of this gas in the mineral oil and the sunflower fluid was approximately 250 ppm. This gas was generated in a very low concentration in the palm and synthetic esters, which agrees with the results shown in [33].

The rest of the gases, H_2, CH_4 and C_2H_4 appeared in a low concentration during all the ageing. H_2 and CH_4 slightly increased during the ageing, and they were generated in similar concentrations in all the fluids, remaining always lower than 200 ppm. C_2H_4 also increased during the ageing but its concentration was lower than 30 ppm even at the last ageing point.

Regarding the paper degradation, the CO, CO_2, and the CO_2/CO ratio have been analysed, Fig. 8, 9 and 10.

The concentration of CO and CO_2 at the beginning of the ageing was very low due to the absence of degradation in the cellulose and it increased with the ageing. At the end of the ageing, approximately 5 times more CO_2 than CO was produced in all fluids, except in palm oil, in which the value was up to 10 times higher. Similar behaviour of the palm and soybean fluids was found in [33]. More CO was generated in the ageing with the natural esters than with

mineral oil, as it usually occurs [21]. However, it is not due to the paper degradation, but rather to the chemical structure and the acidity of the esters [50].

According to the IEC, paper degradation and/or oil oxidation is considered to exist when there is a CO_2 concentration greater than 10,000 ppm and a CO_2/CO ratio greater than 10. At the beginning of the ageing, all the oils exceeded these values.

In the case of natural esters, the CO_2 and CO_2/CO ratio increased due to oxidation and paper degradation, whereas in the mineral oil this increase was mainly caused by the paper degradation, since oxidation is not so relevant in this oil. Considering a similar increase of both factors in the mineral oil and the natural esters, a higher degradation of the cellulose in the mineral oil could be expected. Both factors are low in the synthetic ester since the O_2 consumption is low in comparison with the other esters. Also, the high ratio found in the ageing with the palm fluid could indicate a higher degradation of the cellulose in comparison with other the other esters, since oxidation was similar in all the natural esters.
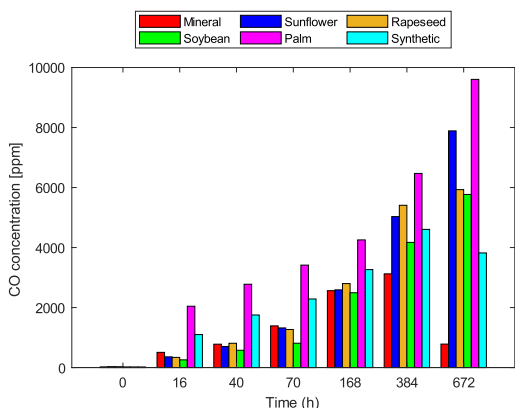

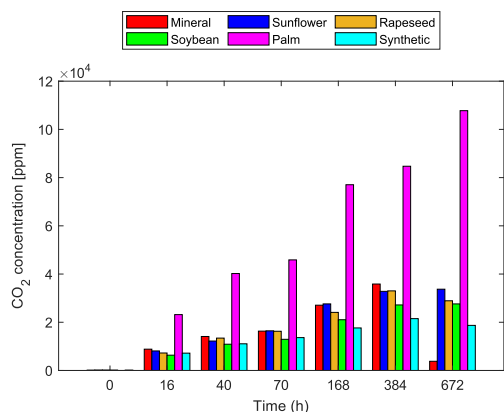**FIGURE 8.** CO concentration of the insulating system.

FIGURE 9. CO_2 concentration of the insulating system.

The dissolved gases have been also analysed according to different criteria, as the IEC 60599 [47] and the Rogers and
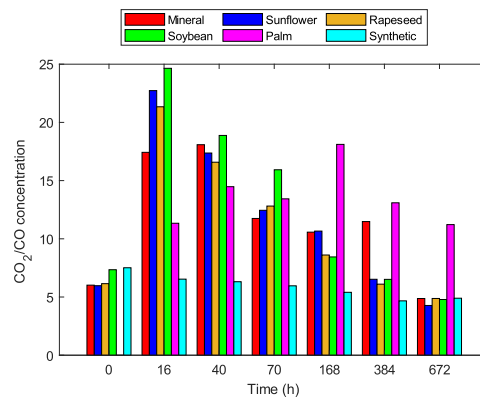

FIGURE 10. CO_2/CO of the insulating system.

Doernenburg methods [48], which are based on gas ratios. Moreover, the Duval triangle method has been applied.

The results of the IEC 60599 criteria for each fluid are collected in Tables 6-11. The values used to determine if the gas generation was abnormal in the esters are based on laboratory data, as explained in [49]. There are not typical values for the modified ester.

According to the IEC method, a thermal fault has occurred in most of the samples. In this case, it is a thermal fault T1, related to temperatures below 300°C. In the natural esters, it has been detected after 384 hours, whereas in the mineral oil this fault was detected since the beginning.

Following the Rogers method, the ratio R1 indicated the existence of a failure in all the samples. Nevertheless, it is not consistent with the ratio R5, so the fault cannot be determined in any sample.

In the case of the Doernenburg method, the typical values used as reference were those given for the mineral oil. In any case, it was not possible to analyse the gases trough this method. Acetylene (C_2H_2) was not generated in this experiment, since it is usually related to dielectric failures.

For the Duval method, each oil was analysed with the corresponding triangle. There is not a triangle designed for the palm ester. However, despite the gas concentration was different in this oil, the involved gases were generated in similar ratios to those of the mineral oil. The results of this analysis are collected in Table 12.

As can be seen, the different methods lead to different fault diagnosis, especially regarding the Rogers and Doernenburg methods, which have not been adapted for the new alternative fluids.

The IEC 60599 and the Duval triangle methods lead to similar gas interpretation for most of the fluids. Nevertheless, in the case of sunflower ester, the results are different. The typical values and the Duval triangle applied in this analysis have been obtained for a sunflower oil that differs from the one that we have studied. In this case, the Duval triangle indicates a thermal fault in all the ageing points analysed, whereas the IEC 60599 standard indicates that all the values and ratios are within the limits. In the case of palm oil, we found some

discrepancies between the methods, but it was expected since there are not typical values and a Duval triangle especially designed for this fluid. In view of this result, it would be necessary to have more data of the gases generated by each fluid, since it seems that the gases concentration and ratios differ from one fluid to another, even if they are obtained from the same plant. There is a working group that is currently preparing a reference for DGA in ester liquids.

TABLE 6. Analysis of mineral oil gases.

IEC 60599	16	40	70	168	384	672
Abnormal values	YES	YES	YES	YES	YES	YES
R1 (CH_4/H_2)	5.46	4.91	5.34	4.80	5.27	38.58
R2 (C_2H_2/C_2H_4)	0.00	0.00	0.00	0.00	0.00	0.00
R5 (C_2H_4/C_2H_6)	0.08	0.07	0.08	0.09	0.10	0.03
TYPE OF FAULT	T1	T1	T1	T1	T1	T1

TABLE 7. Analysis of sunflower ester gases.

IEC 60599	16	40	70	168	384	672
Abnormal values	YES	YES	YES	YES	YES	YES
R1 (CH_4/H_2)	0.44	0.22	0.27	0.50	1.71	2.04
R2 (C_2H_2/C_2H_4)	0.00	0.00	0.00	0.00	0.00	0.00
R5 (C_2H_4/C_2H_6)	0.07	0.10	0.14	0.13	0.19	0.22
TYPE OF FAULT	NF	NF	NF	NF	T1	T1

TABLE 8. Analysis of rapeseed ester gases.

IEC 60599	16	40	70	168	384	672
Abnormal values	YES	YES	YES	YES	YES	YES
R1 (CH_4/H_2)	1.48	1.26	1.81	1.64	1.81	3.12
R2 (C_2H_2/C_2H_4)	0.00	0.00	0.00	0.00	0.00	0.00
R5 (C_2H_4/C_2H_6)	0.01	0.01	0.01	0.01	0.02	0.02
TYPE OF FAULT	T1	T1	T1	T1	T1	T1

TABLE 9. Analysis of soybean ester gases.

IEC 60599	16	40	70	168	384	672
Abnormal values	YES	YES	YES	YES	YES	YES
R1 (CH_4/H_2)	0.66	1.11	1.33	1.44	1.65	3.69
R2 (C_2H_2/C_2H_4)	0.00	0.00	0.00	0.00	0.00	0.00
R5 (C_2H_4/C_2H_6)	0.01	0.01	0.01	0.02	0.02	0.03
TYPE OF FAULT	NF	T1	T1	T1	T1	T1

TABLE 10. Analysis of palm ester gases.

IEC 60599	16	40	70	168	384	672
Abnormal values	ND	ND	ND	ND	ND	ND
R1 (CH_4/H_2)	4.09	2.18	1.33	0.84	0.89	1.70
R2 (C_2H_2/C_2H_4)	0.00	0.00	0.00	0.00	0.00	0.00
R5 (C_2H_4/C_2H_6)	0.73	0.59	0.58	0.65	0.68	0.71
TYPE OF FAULT	T1	T1	T1	ND	ND	T1

J. POLYMERISATION DEGREE

This parameter is used as an indicator of the degradation of the solid insulation, since it measures the existing polymers

TABLE 11. Analysis of synthetic ester gases.

IEC 60599	16	40	70	168	384	672
Abnormal values	NO	YES	YES	YES	YES	YES
R1 (CH_4/H_2)	NA	2.18	1.33	0.84	0.89	1.70
R2 (C_2H_2/C_2H_4)	NA	0.00	0.00	0.00	0.00	0.00
R5 (C_2H_4/C_2H_6)	NA	0.59	0.58	0.65	0.68	0.71
TYPE OF FAULT	NF	T1	T1	NF	NF	T1

TABLE 12. Faults according to duval triangle analysis.

Fluid	16	40	70	168	384	672
Mineral	T1	T1	T1	T1	T1	T1
Sunflower	T1	T1	T1	T1	T1	T1
Rapeseed	T1	T1	T1	T1	T1	T1
Soybean	T1	T1	T1	T1	T1	T1
Plam	T1	T1	T1	T1	T1	T1
Synthetic	T1	T1	T1	T1	T1	T1

bounds in the paper. When paper is new, its DP value is around 1200 and it decreases with the ageing as the polymer degrades and they break. The relative evolution of this parameter with ageing time is represented in Fig. 11. A DP value of 200 is usually considered as the end of life for the cellulosic insulation [62], only reached in this work by the kraft paper aged in mineral oil. DP of the paper in the esters remained higher than 300 by the same ageing time (672 h). The mineral oil kraft paper took only 300 hours to reach this DP level.

As can be seen, at the beginning of the experiment the ageing rate of the paper was similar in all the oils. This rate got slowed in all the liquids as the ageing progresses, confirming that mentioned in moisture section and in references [21], [22], [24]. Nevertheless, the water consumption by the esters and the formation of high molecular weight acids slowed down the hydrolysis processes in the cellulose, reducing even more the ageing rate. On the other hand, mineral oil did not absorb water from cellulose and the low molecular weight acids generated by this oil could be dissolved in the paper. The higher moisture content in the cellulose, along with the acid hydrolysis, led to a faster degradation of the paper when aged with mineral oil in comparison with the alternative fluids. It is interesting to highlight that all the natural esters, except for palm oil, had a similar behaviour. Esters with high acid concentration protected more the cellulose, whereas palm fluid and synthetic ester, which had a low acidity, showed the worst result. Moreover, the absence of hydrolysis in these fluids could have led to higher thermal hydrolysis in the cellulose. The higher degradation of the cellulose when aged with the mineral oil and the palm fluid agrees with the analysis of the CO_2 and CO gases.

K. FLUIDS PROPERTIES AS INDICATORS OF CELLULOSE DEGRADATION

Some properties of the oils changed significantly with the degradation, and it can be related to the ageing of the
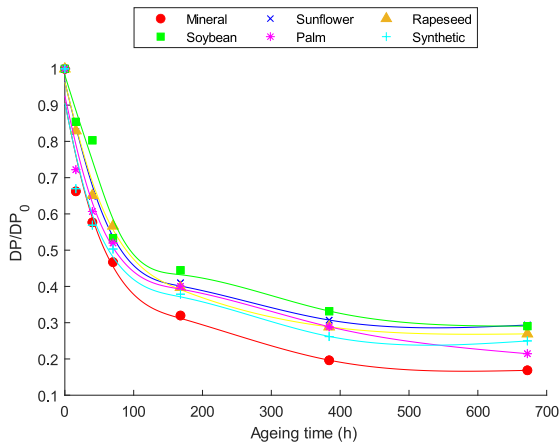
FIGURE 11. Relative DP of kraft paper with the different fluids.

cellulose. Regarding the dielectric properties, it was difficult to find a good correlation between them and the DP of the paper, as can be seen in Fig. 12. It can be caused by the large number of factors that are affecting the tan δ of the fluids. In the case of natural esters, the increase of the tan δ depended on the moisture content, acidity and oxidation, as it was also detected by [32]. On the other hand, it was found a strong linear correlation between tan δ and DP of the paper in the case of ageing with mineral oil. The Pearson correlation coefficient ($|r|$) was higher than 0.85 for this fluid.
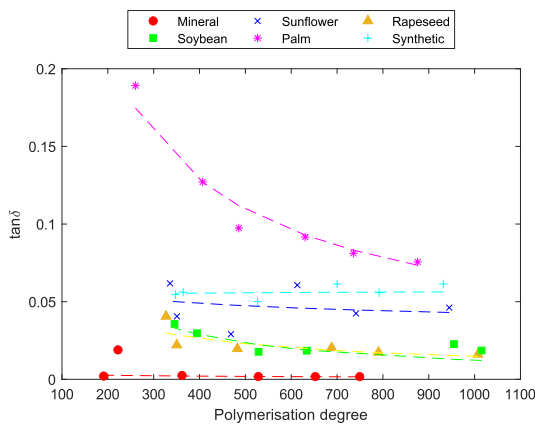

FIGURE 12. Tan δ vs DP.

With respect to the chemical properties, acidity was analysed. There is a strong potential correlation between acidity and polymerisation degree of paper when aged with the alternative fluids (higher than 0.9). This kind of correlation is given by the generation of long-chain fatty acids by these liquids. Since these acids do not damage the cellulose, a large acid content did not cause a decrease in the DP of the paper, as shown in Fig. 13. In the case of the mineral oil, we found a strong linear correlation ($|r| = 0.95$). Due to the low molecular weight acids generated by the mineral oil, a slight increase in the acid content causes a great reduction of the DP.
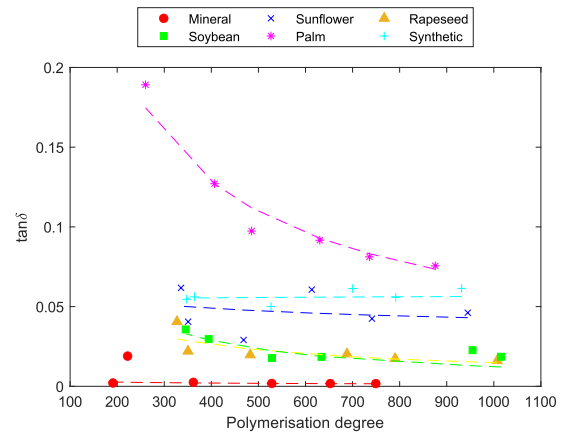

FIGURE 13. Acidity vs DP.

Regarding the physical properties, the interfacial tension has shown a strong linear correlation in all the fluids ($|r| > 0.8$), except for the synthetic ester, as can be seen in Fig. 14. Despite the interfacial tension of the natural esters did not significantly change with the ageing, the small variations can be related to the degradation of paper. Nevertheless, it is not recommended to measure the interfacial tension in the synthetic ester, according to the information given by the manufacturer, since it is not an indicator of the quality of this fluid.

Finally, considering the dissolved gases measured in the fluids, both CO_2 and CO (Fig. 15) are directly related to the degradation of paper. In this case, we found a strong correlation between both gases and DP of the paper in all the fluids ($|r| > 0.85$).
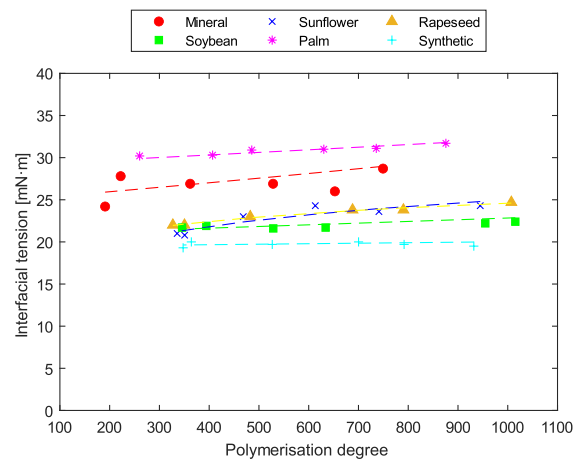

FIGURE 14. Interfacial tension vs DP.

L. ANALYSIS OF THE PERFORMANCE OF THE DIELECTRIC FLUIDS ACCORDING TO THE STANDARDS

In order to analyse the degradation of the different liquids in terms of transformer maintenance, the results obtained have been compared to the limits set by the corresponding

TABLE 13. Quality of mineral oil.

Category: O and A (>170 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	ND
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	GOOD	GOOD	GOOD	GOOD		
70	FAIR	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD	ND
168		GOOD	GOOD	GOOD	GOOD	GOOD		
384		GOOD	FAIR	GOOD	GOOD	GOOD		
672	POOR	GOOD	FAIR	GOOD	FAIR	GOOD	GOOD	ND
Category: B (72.5-170 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	ND
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	GOOD	GOOD	GOOD	GOOD		
70	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD	ND
168		GOOD	GOOD	GOOD	GOOD	GOOD		
384		GOOD	GOOD	GOOD	GOOD	GOOD		
672	FAIR	GOOD	GOOD	GOOD	FAIR	GOOD	GOOD	ND
Category: C (≤72.5 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	ND
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	GOOD	GOOD	GOOD	GOOD		
70	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD	ND
168		GOOD	GOOD	GOOD	GOOD	GOOD		
384	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD		
672		GOOD	GOOD	GOOD	FAIR	GOOD	GOOD	ND

TABLE 14. Quality of sunflower ester.

Category: O and A (>170 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	GOOD
16		GOOD	FAIR	GOOD	GOOD	GOOD		
40		GOOD	FAIR	GOOD	GOOD	GOOD		
70	POOR	GOOD	FAIR	FAIR	GOOD	GOOD	GOOD	GOOD
168		GOOD	FAIR	POOR	GOOD	GOOD		
384		GOOD	FAIR	POOR	GOOD	GOOD		
672	POOR	GOOD	FAIR	POOR	GOOD	GOOD	GOOD	GOOD
Category: B (72.5-170 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	GOOD
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	FAIR	GOOD	GOOD	GOOD		
70	FAIR	GOOD	FAIR	GOOD	GOOD	GOOD	GOOD	GOOD
168		GOOD	FAIR	FAIR	GOOD	GOOD		
384		GOOD	GOOD	POOR	GOOD	GOOD		
672	POOR	GOOD	GOOD	POOR	GOOD	GOOD	GOOD	GOOD
Category: C (≤72.5 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	GOOD
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	GOOD	GOOD	GOOD	GOOD		
70	GOOD	GOOD	FAIR	GOOD	GOOD	GOOD	GOOD	GOOD
168		GOOD	FAIR	FAIR	GOOD	GOOD		
384		GOOD	GOOD	POOR	GOOD	GOOD		
672	FAIR	GOOD	GOOD	POOR	GOOD	GOOD	GOOD	GOOD

standards. These standards are IEC 60422 [56] for the mineral oil, IEC 62975 [57] for the natural esters and IEC 61203 [63] for the synthetic esters. There is no standard for the modified ester, so the palm fatty acid ester could not be analysed.

TABLE 15. Quality of rapeseed ester.

Category: O and A (>170 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	GOOD
16		GOOD	FAIR	GOOD	GOOD	GOOD		
40		GOOD	FAIR	GOOD	GOOD	GOOD		
70	POOR	GOOD	FAIR	GOOD	GOOD	GOOD	GOOD	GOOD
168		GOOD	FAIR	GOOD	GOOD	GOOD		
384		GOOD	FAIR	POOR	GOOD	GOOD		
672	POOR	GOOD	FAIR	POOR	GOOD	GOOD	GOOD	GOOD

Category: B (72.5-170 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	GOOD
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	FAIR	GOOD	GOOD	GOOD		
70	FAIR	GOOD	FAIR	GOOD	GOOD	GOOD	GOOD	GOOD
168		GOOD	FAIR	GOOD	GOOD	GOOD		
384		GOOD	FAIR	POOR	GOOD	GOOD		
672	FAIR	GOOD	FAIR	POOR	GOOD	GOOD	GOOD	GOOD

Category: C (≤72.5 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	GOOD
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	GOOD	GOOD	GOOD	GOOD		
70	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD
168		GOOD	FAIR	GOOD	GOOD	GOOD		
384		GOOD	GOOD	POOR	GOOD	GOOD		
672	GOOD	GOOD	GOOD	POOR	GOOD	GOOD	GOOD	GOOD

TABLE 16. Quality of soybean ester.

Category: O and A (>170 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	GOOD
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	FAIR	GOOD	GOOD	GOOD		
70	FAIR	GOOD	FAIR	GOOD	GOOD	GOOD	GOOD	GOOD
168		GOOD	FAIR	GOOD	GOOD	GOOD		
384		GOOD	FAIR	POOR	GOOD	GOOD		
672	POOR	GOOD	FAIR	POOR	GOOD	GOOD	GOOD	GOOD

Category: B (72.5-170 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	GOOD
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	GOOD	GOOD	GOOD	GOOD		
70	GOOD	GOOD	FAIR	GOOD	GOOD	GOOD	GOOD	GOOD
168		GOOD	FAIR	GOOD	GOOD	GOOD		
384		GOOD	FAIR	POOR	GOOD	GOOD		
672	POOR	GOOD	FAIR	POOR	GOOD	GOOD	GOOD	GOOD

Category: C (≤72.5 kV)								
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	GOOD
16		GOOD	GOOD	GOOD	GOOD	GOOD		
40		GOOD	GOOD	GOOD	GOOD	GOOD		
70	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD	GOOD
168		GOOD	FAIR	GOOD	GOOD	GOOD		
384		GOOD	FAIR	POOR	GOOD	GOOD		
672	FAIR	GOOD	GOOD	POOR	GOOD	GOOD	GOOD	GOOD

The initial requirements have been obtained from IEC 60296 [64] for the mineral oil, IEC 62770 [65] for the natural esters and IEC 61099 [66] for the synthetic ester. Results are shown in Tables 13-17.

TABLE 17. Quality of synthetic ester.

	Category: <35 kV							
Ageing time	BDV	DDP (90ºC)	Moisture oil	Acidity	IT	Viscosity	Flash point	Fire point
0	GOOD	GOOD	GOOD	GOOD	ND	GOOD	GOOD	ND
16			GOOD	GOOD				
40			GOOD	GOOD				
70	GOOD		GOOD	GOOD				GOOD
168			GOOD	GOOD				
384			GOOD	GOOD				
672	GOOD		GOOD	GOOD				GOOD
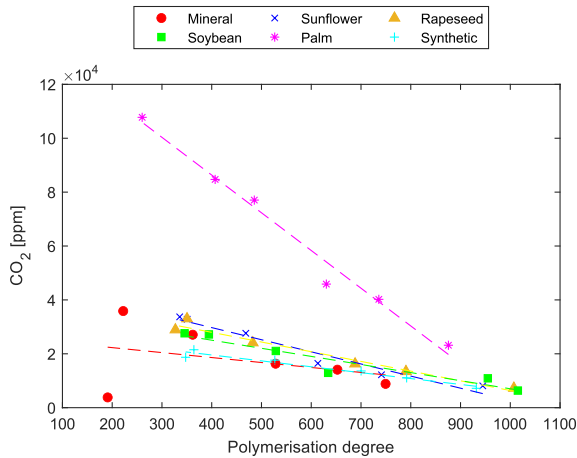
FIGURE 15. CO$_2$ vs DP.

As can be seen, despite all the esters behave similarly in terms of the evolution of their main properties, the differences found between them could lead to different requirements during the operation of a transformer. If considering the breakdown voltage, the natural esters showed a behaviour considered poor by the standard at the end of the ageing for the transformers of categories O and A. Nevertheless, in the case of transformers of category B, the rapeseed ester could be classified as ''fair'' whereas the sunflower and soybean esters state was poor, which implies the recondition or substitution of the fluid. For the transformer of category C, the rapeseed oil was the only ester which can be considered as good at the end of the ageing, whereas the others need more supervision since they are catalogued as fair.

In the case of the moisture content, we found that the esters did not reach a poor consideration in any state of ageing. Nevertheless, they require more supervision during the period of water absorption from cellulose. At the end of the ageing, moisture decreased due to the hydrolysis, so the moisture content returned to a good level for category C transformers. In the case of the larger transformers, the moisture content requirement is more restrictive, so all the esters were classified as fair. The other analysed properties, including the tan δ, interfacial tension, viscosity and flash and fire points remained at a good level during all the ageing experiment.

Regarding the acidity results, all the esters have been classified as poor at the end of the ageing in all the transformers' categories due to the high increase of acid content in the last stages. Because of the strong correlation between cellulosic

DP and oil acidity, it seems that the high acidity would not damage the paper, even if it continues to rise. Thus, despite the esters' state is classified as poor by the standard in terms of acid content it seems it would not be dangerous for the equipment, especially if we consider that most of the other properties analysed are considered good. In fact, in the case of sunflower and rapeseed esters for transformers of category C, all the properties are considered good except for the acidity.

Regarding the mineral oil degradation, we found that, except for the breakdown voltage in the case of transformers of category A and C, most of the properties remained at a good level during the ageing. The interfacial tension was reduced during the ageing as a result of the polar acids generated, reaching the fair classification at the last ageing state.

Finally, the standard of the synthetic is not as detailed. It only considers the transformers of less than 35 kV and a few parameters as the acidity, BDV, moisture content and fire point. The tan δ and resistivity are only defined for tests at room temperature, so they were not analysed in Table 17. The synthetic ester showed a low degradation since all the properties remained within the limits.

Taking into account that the paper only reached the end of life when aged with mineral oil, it would be necessary to adjust the limits set by the standard for natural esters. In the case of these fluids, the degradation of the cellulose was significantly lower than in the mineral oil, but, according to the standard, they should be reconditioned or replaced, since the acid content is significantly higher than the limit. Considering that paper is the component that can be most damaged by acids and that despite the high levels found in the natural esters the DP was not considerably reduced, it seems that the limits could be higher than they are.

IV. CONCLUSION

In this work, the ageing of a kraft paper impregnated with six different fluids has been studied. The chosen liquids were a traditional mineral oil, and five alternative ester liquids from different origin; unmodified soybean, sunflower, rapeseed esters, a modified palm ester and a synthetic ester. Ageing process was carried out in glass vials at 150°C, with the presence of copper and little air.

Different properties have been characterized during the ageing evolution. The permittivity, density, viscosity and the flash and fire points were not affected by the ageing. The nat-

ural esters, except for the palm oil, had similar properties. The palm fluid had properties similar to the mineral oil.

Dissolved gas analysis reflected that the esters generated more gases than the mineral oil during the ageing. Also, that they consumed rapidly the O_2 in the vials, due to their tendency to oxidize. The CO_2/CO ratios also reflected this trend, compared to the other fluids, as well as the high degradation of the cellulose when aged with the mineral oil.

It was also found that the unmodified natural esters increased their moisture content at the beginning of the ageing, but they consumed the water later through hydrolysis, whereas the palm fluid and the synthetic ester absorbed the water without consuming it. The moisture content of the mineral oil remained constant. This was reflected in the higher acidity of the unmodified natural esters. The palm fluid, due to the absence of hydrolysis, had a low acidity, similar to that of the mineral oil. This property scarcely changed for the mineral oil.

The oxidation, acidity and moisture content behaviour were reflected in the dielectric properties, since the AC BDV, tan δ and resistivity changed more in the esters than in the mineral oil. It was found that these properties were not related to the paper degradation when aged with the esters. In this sense, the paper degraded faster when aged with mineral oil. The sunflower, rapeseed and soybean esters showed the best performance, with a decreased ageing rate of paper. The modified and synthetic esters behaved similarly and better than the mineral oil. All the alternative fluids have proven to be a suitable alternative to the conventional oil and they could be used in both new and existing machines.

Despite the similar behaviour of the natural esters, the parameters used to characterize the degradation differed from one ester to another, differences not considered in the standards for maintenance. Some discrepancies were found when analysing the dissolved gases of the esters with different methods. Moreover, considering the low degradation of the paper with these fluids, it seems that some of the standard limits were not completely accurate, as they are for the mineral oil. Also, the lack of standards for palm and synthetic esters maintenance highlights the need to generate more data on the degradation of these fluids. This paper aims to contribute to the knowledge about alternative fluids and it could be useful to partially solve the problem in standardization.

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