Quantitative Study on the Aging of Kraft Paper in Vegetable Oils

Juan Carcedo, Inmaculada Fernández, Alfredo Ortiz, Fernando Delgado, Carlos J. Renedo and Alberto Arroyo

Electrical and Energy Engineering Department
School of Industrial and Telecommunications Engineering, University of Cantabria, Avda. Los Castros, s/n. Santander, Spain

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The focus of this article is on the values of the activation energy and pre-exponential factor in the Emsley/Heywood kinetic model as applied to vegetable oil-impregnated paper as a step forward in the quantitative study of the degradation of the paper.

Introduction

Interest in using vegetable oils as dielectric coolants in power transformers dates back to the early studies on linseed- and castor-based fluids as possible replacements to mineral oil. However, interest in vegetable oils was lost due to their high viscosity and their tendency to oxidize. But, in the early 1990s and due to environmental concerns, the interest in dielectric fluids based on vegetable esters re-emerged. As a result, two vegetable ester based oils were developed; namely, BIOTEMP® developed by ABB and FR3® developed by Cooper Power Systems.

The behavior of natural esters is not yet known in detail. Because of this, the International Electrotechnical Commission (IEC) created a working group (TC10 PT-62975) that is charged with creating a document to define the limits of the parameters that determine the quality of a natural ester-based oil for power transformers. The document is entitled "Use and Maintenance Guidelines of Natural Ester Liquids in Electrical Equipment".

Over recent years, there have been many published works on the suitability of some vegetable oils as dielectrics and coolants in power transformers [1] – [9]. From the viewpoint of the lifetime of a power transformer, the assessment of the state of the dielectric system is essential. While the replacement or regeneration of oil can be done, replacing the paper is not feasible at all, so one can say that a transformer reaches the end of its life when the paper has degraded to the point of not being unable to withstand the in-service stresses [10].

Among the factors affecting the aging of paper, the nature of the impregnating oil is especially important and some studies on paper aging when impregnated in vegetable oil compared to mineral oil have been reported [11] – [15]. In particular, the degree of polymerization (DP), which is defined as the average number of repeating units (monomers) that are contained in the molecular chain of a polymer, is significant as paper degradation lowers the DP index.

To predict the behavior of the paper and therefore the life of the transformer, various kinetic models of degradation have been proposed; one of them being the Ekenstam model [16], dating from the 1930s, which established a relationship between DP and time [17].

Some years later, the working group formed by A.M. Emsley, R.J. Heywood and G.C. Stevens established a more complex kinetic model based on the Ekenstam model

but considered the variability of the aging rate [18] – [26], which better fits the experimental results that had been previously obtained with mineral oil-impregnated paper. The parameters that define this more complex model (Emsley/Heywood kinetic model [22]) have been characterized in [19] by an Arrhenius relationship through its activation energy and its corresponding pre-exponential factor.

This article focuses on the values of the activation energy and pre-exponential factor in the Emsley/Heywood kinetic model as applied to vegetable oil-impregnated paper as a step forward in the quantitative study of the degradation of the paper.

Materials and Methods

Laboratory tests consisting of thermally accelerated aging with Kraft paper impregnated in reference mineral oil (MO) and vegetable oils (VO1 and VO2) were carried out. Table 1 shows the properties of the Kraft paper used in the study as supplied by the manufacturer and Table 2 shows the measured properties of the oils prior to aging.

Table 1. Properties of the Kraft paper used in the study.

Property	Unit	Standard	Value
Thickness	mm		0.075
Weight	g/mm²		61
Density	g/cm³	IEC 554	0.8
Breakdown strength (in air)	kV/mm		7

Table 2. Properties of oils used in the study.

Property	Unit	Standard	MO	VO1	VO2
Viscosity, 40ºC	mm²/s	ISO 3104 ASTM D 445	7.6	37	39.2
Density, 20ºC	kg/dm³	ISO 12185 ISO 3675 ASTM D1298	0.877	0.92	0.9128
Breakdown voltage (2.5 mm)	kV	IEC 60156	40-60	>75	81
Acidity	mgKOH/g	IEC 62021 ASTM D 974	0.01	< 0.05	0.05
Tan delta (90ºC and 50 Hz)		IEC 60247	0.001	< 0.005	0.0134
Flash point	ºC	ISO 2719 ASTM D 92	144	327	332
Moisture content	mg/kg	IEC 60814	< 20	50	100

The sample preparation procedure used in the study was the same as described in [27]. First, strips of Kraft paper (260 × 15 mm) were placed in three steel vessels under vacuum for moisture stripping. Next, the vessels were filled with nitrogen for which hygroscopicity aids in the further removal of moisture from the paper and the vessels were heated in an oven at 100ºC for 24 hours, to attain a moisture content of

approximately 0.5%. Finally, the vessels were opened, and the three oils poured into each of the three vessels and the vacuum and nitrogen filling processes were repeated.

The prepared samples were oven aged at 110, 130 and 150 °C. This temperature range allowed us to perform an accelerated test without the risk of side effects due to pyrolysis or carbonization. The aging period varied on the aging temperature and during aging, the paper samples were removed at different intervals and tested. Because the aging rate increases with temperature, the sampling rate at 150 °C was more frequent than at 110 °C.

Moreover, as the degradation is more pronounced at the beginning of aging, the last samples were taken at longer time intervals.

Theoretical Considerations

DP represents the average number of monomers that make up the lengths of polymer chains. Thus, a polymer containing N monomers and M molecules will have Z bonds between the monomers according to the relationship

$$Z = N - M \tag{1}$$

and DP can be expressed as

$$DP = N / M . \tag{2}$$

Therefore, the number of bonds between molecules Z_t at time t is given by

$$Z_t = N - M_t = N \cdot (1 - M_t/N) = N \cdot (1 - 1/DP_t). \tag{3}$$

As the paper ages, the number of monomers does not vary over time, but the number of molecules does, as the bonds between monomers are broken. Therefore, the number of bonds at the initial time Z_0 is determined according to

$$Z_0 = N - M_0 = N \cdot (1 - M_0/N) = N \cdot (1 - 1/DP_0). \tag{4}$$

At the beginning of the aging process, several bonds between monomers are expected, that is, long polymer chains and thus, a high value DP. Assuming that the rate of chemical reaction, or the breaking of bonds between monomers, depends on the concentration of reactants, or the number of links, the number of bonds Z will decrease according to

$$- dZ / dt = k_1 \cdot Z \tag{5}$$

where k_1 is the rate of proportionality.

Integrating (5) between the initial time t_0 and t, the basis of the Ekenstam kinetic model is obtained [16]. Thus,

$$\log (1 - 1/DP_0) - \log (1 - 1/DP_t) = -k_1 \cdot t \tag{6}$$

The major limitation of the model is that it assumes that the rate of proportionality, k_1, is constant. However, as the paper ages, many of the bonds between monomers will break and since their number is limited, broken links will be less likely? From the viewpoint of chemical kinetics, this circumstance results in a progressive decrease in the rate of proportionality, which numerically means k_1 cannot be constant. Therefore, it is expected that the proportionality constant k_1 decreases with time.

Consider the value of proportionality reduces to a factor k_2, thus

$$- dk_1 / dt = k_2 \cdot k_1 \qquad\qquad (7)$$

and the instantaneous value of k_1 can be obtained from

$$k_1 = k_{10} \cdot \exp\left(- k_2 \cdot t\right) \qquad\qquad (8)$$

in which k_{10} represents the initial value of k_1.

Equation (8) is the basis of the Emsley/Heywood kinetic model [22], whose mathematical form can be obtained by substituting (8) in the differential form of (6) and integrating between the initial instant and an instant t, being necessary to consider that when the DP is high enough, the following relationship can be assumed

$$\log\left(1 - 1/DP\right) \rightarrow -1/DP \qquad\qquad (9)$$

Under such conditions, the Emsley/Heywood kinetic model is described by the following

$$\log\left(1 - 1/DP_0\right) - \log\left(1 - 1/DP_t\right) = \frac{k_{10}}{k_2} \cdot \left(1 - e^{-k_2 \cdot t}\right) \qquad (10)$$

The DP value over time has been measured through laboratory tests of the three oils at three different temperatures, according to the Standard, and a numerical analysis using MS Excel® and MATLAB® allows us to obtain the values of k_{10} and k_2 that best fit (10).

It is then assumed that of k_{10} and k_2 can be defined by an Arrhenius relationship, thus

$$k_i = A_i \cdot \exp\left(- E_{a,i} /\left(R \cdot T\right)\right) \qquad\qquad (11)$$

where
k_i	factor (k_{10} and k_2)
A_i	pre-exponential factor
$E_{a,i}$	activation energy (J/mol)
R	gas constant (8,3143 J/mol/K)
T	temperature (K)

Taking logarithms of (11) a linear function $k_i = f\,(1/T)$ whose slope is $-E_{a,i}/R$ and intercept is $\log A_i$. Thus,

$$\log\left(k_i\right) = \log A_i - E_{a,i} /\left(R \cdot T\right) \qquad\qquad (12)$$

Separate relationship for each of the tested oils is obtained from the three temperatures. The activation energy and pre-exponential factor is obtained which then defines the relationship. At any operating temperature, the values of the factors k_{10} and k_2 that define the paper degradation kinetic model for the oil is obtained.

Results and discussion

Figure 1 shows the decrease of DP with time when the Kraft paper was impregnated with the three types of oil and subjected to thermally accelerated aging at three temperatures. The results agree with that reported in previous research [28] showing a decrease of DP over time and this deterioration being more pronounced at the beginning of the process and at higher temperatures. The logarithmic difference shown in (10) was obtained and these results are shown in Figure 2.
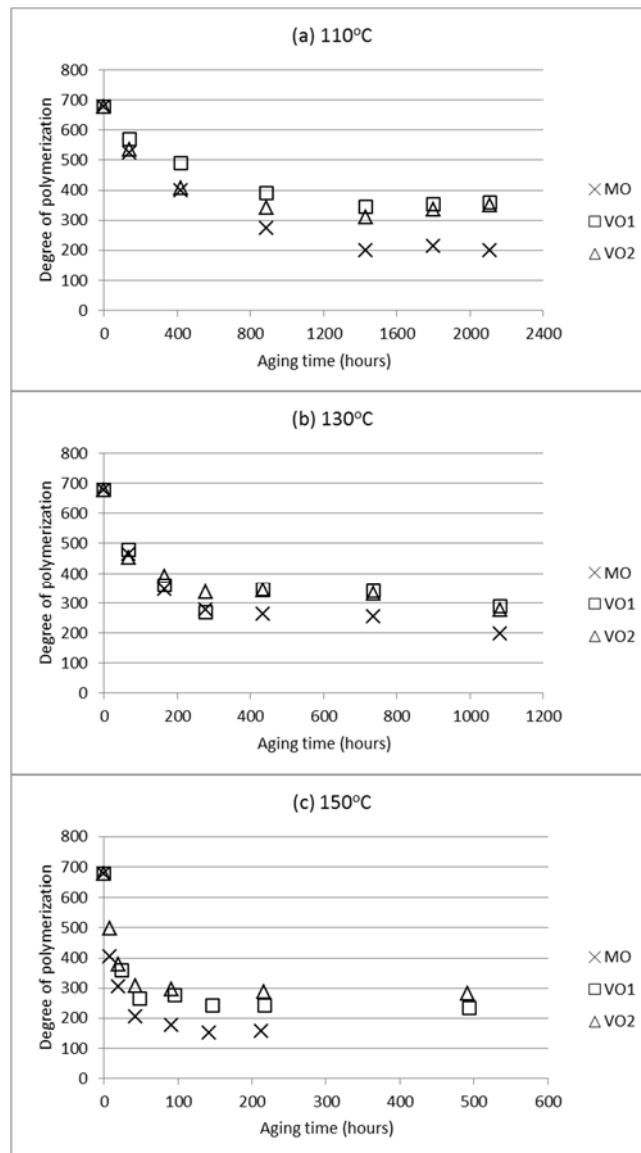

Figure 1. Decrease in the degree of polymerization of Kraft paper with aging time for MO, VO1 and VO2 oils.
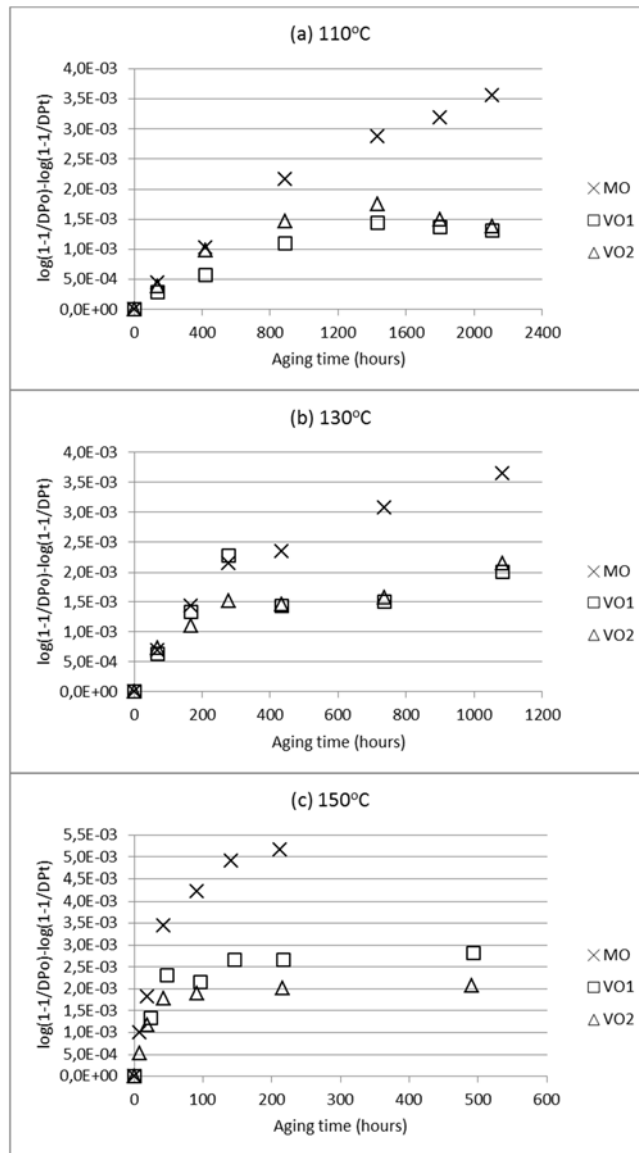
Figure 2. Decrease in the degree of polymerization in the form of equation (10) of Kraft paper with aging time for MO, VO1 and VO2 oils.

Except at the very beginning of the aging process, Figure 2 shows a significant departure of the experimentally obtained values of DP with respect to those expected from (6). However, this simplified Ekenstam kinetic model described by (6) could be useful in obtaining the factor k_{10} from the first two samples. The fit of the data to (10) was performed using MATLAB® and the results are summarized in Table 3 for each oil and at each temperature.

The numerical values of k_{10} and k_2 in Table 3 allow us to predict the aging rate of paper, in terms of DP, but only at the three temperatures tested. However, the aim is to determine the values of k_{10} and k_2 for each oil type and at any operating temperature. Assuming that factors k_{10} and k_2 can be expressed by (11), it is possible to obtain the relationship that fits (12) for each type of oil. The lines obtained are plotted in Figure 3 and from them the values of activation energy and pre-exponential factor for each type of oil have been obtained (Table 4).

Finally, in Figure 4, the DP values obtained experimentally are compared to those calculated through the Emsley/Heywood model with the numerical values of Table 4.

Table 3. Rate of proportionality constants k_{10} and k_2 in equation 10 from experimental data as in Figure 2.

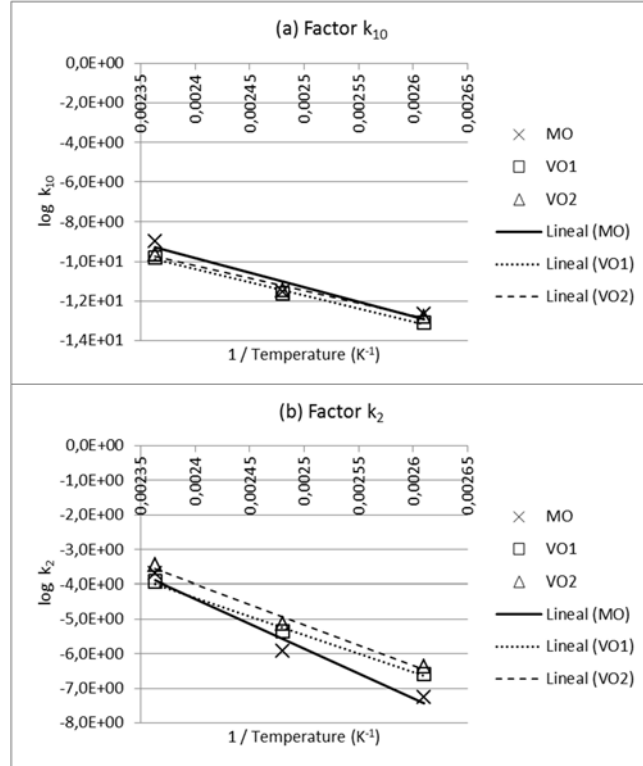| OIL		MO	VO1	VO2
110°C	k_{10}	3.084E-06	2.149E-06	3.845E-06
	k_2	6.519E-04	1.450E-03	2.791E-03
	R^2	0.9976	0.9788	0.9142
130°C	k_{10}	1.008E-05	1.418E-05	9.981E-06
	k_2	2.710E-03	7.876E-03	5.374 E-03
	R^2	0.9875	0.8064	0.9149
150°C	k_{10}	1.198E-04	7.352E-05	7.937E-05
	k_2	2.374E-02	2.742E-02	3.815E-02
	R^2	0.9942	0.9598	0.9898

Figure 3. *Rate of proportionality constants k_{10} and k_2 plotted using equation (12) for MO, VO1 and VO2 oils.*

Table 4. Activation energy E_a and pre-exponential factor A for each type of oil for rate of proportionality constants k_{10} and k_2 using equation (11).

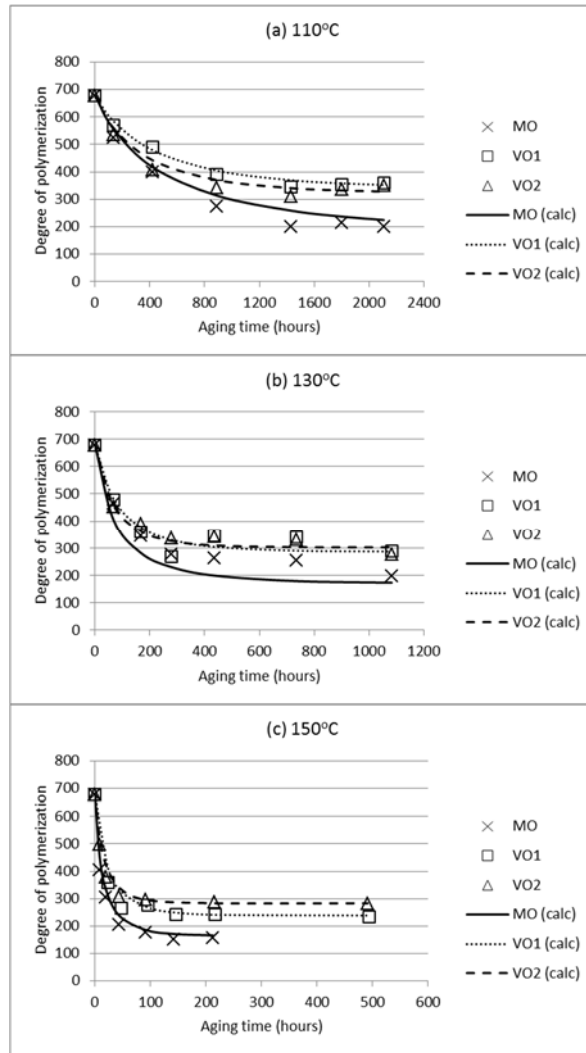|		MO	VO1	VO2
k_{10}	E_a (kJ/mol)	122.51	119.08	101.31
	A (h^{-1})	1.228E+11	3.727E+10	2.041E+08
	R^2	0.9482	0.9999	0.9440
k_2	E_a (kJ/mol)	120.64	99.23	87.33
	A (h^{-1})	1.575E+13	5.134E+10	1.790E+09
	R^2	0.9783	0.9966	0.9075

Figure 4. Experimental DP values compared to calculated values through the Emsley/Heywood model with the numerical values of Table 4.

Conclusions

The measured DP of all three oils examined in this aging study show a strong dependence on the temperature of the test. Significant deterioration of paper takes place with temperature during the initial aging period as observed by a notable decrease in DP which is followed by a relatively stable DP with further aging. These observations are consistent with other qualitative results published previously by various authors. However, the results on activation energies and pre-exponential factors defining the kinetic model make it possible to quantitatively estimate the DP in any of the three oils and at any operating temperature.

When a power transformer is operating under normal conditions, that is, at a lower temperature than that necessary to carry out accelerated aging tests, the DP value may stabilize well above 200, which is the most commonly used threshold to determine the end of life of the paper. For example, with an operating temperature of 75ºC, the paper impregnated in MO mineral oil would reach a DP value of 200 after 18 years, whereas the DP of the paper impregnated in VO1 or VO2 vegetable oils would stabilize at a value above 400. Addressing the issue from another point of view, the paper impregnated in VO1 could theoretically operate at a temperature of 175ºC with a stabilized DP value of 200, or at a temperature of 210ºC in the case of VO2. However, such high temperatures would not be feasible operating conditions, as other phenomena like carbonization of the paper would occur.

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Juan Carcedo received the MSc degree in Industrial Engineering in 2004 and worked as a freelance engineer for ten years and as a part time Lecturer at the University of Cantabria from 2009 to 2014. He received the PhD degree in 2015 and currently he is Assistant Lecturer of the Electrical and Energy Engineering Department in the School of Industrial Engineering at the University of Cantabria. His main research topic is the study of transformer ageing and insulating oils and paper.

Inmaculada Fernández received the MSc degree in Chemical Engineering in 2004 and the PhD degree in 2009 from the University of Cantabria, Spain. Currently, she is an Assistant Lecturer in the Electrical and Energy Engineering Department at the University of Cantabria. She has published two chapters in international books, over 20 works in national and international conferences, and 9 papers in journals included in the Journal of Citation Report. Her main research topic is the energy conservation.

Alfredo Ortiz graduated with a PhD in Electrical Engineer at University of Cantabria in 2005. He has published six chapters in international books, over 50 works in international conferences and 21 papers in journals included in the Journal of Citation Report. He has acted as reviewer for several international journals included in the Journal of Citation Report. He belongs to national (AEN/CTN207/SC14 and AEN/CTN207/SC10) and international committees (CENELEC/TC14/WG29, IEC60076-20 and IEC/TC10/WG33) for standardization in the field of power transformers and alternative dielectric fluids. Currently, he is the Head of Electrical and Energy Engineering Department at the University of Cantabria.

Carlos J. Renedo received the MSc degree in Industrial Engineering in 1997 and the PhD degree in 2002 from the University of Cantabria, Spain. Currently, he is an Associate Professor in the Electrical and Energy Engineering Department at the University of Cantabria. He has published over 50 works in international conferences and 24 papers in journals included in the Journal of Citation Report. His main research topic is in energy conservation.

Fernando Delgado received the MSc degree in Industrial Engineering in 1998 and the PhD degree in 2011 from the University of Cantabria, Spain. Currently, he is an Associate Professor in the Electrical and Energy Engineering Department at the University of Cantabria. He has published over 25 works in international conferences and 13 papers in journals included in the Journal of Citation Report. Currently his main research topic is the study of the alternative dielectric liquids in power transformers.

Alberto Arroyo received the PhD in electrical engineering at University of Cantabria in 2012. Currently, he is an Assistant Lecturer in the Electrical and Energy Engineering Department at the University of Cantabria. He has published 2 chapters in international books, 15 works in international conferences and 7 papers in journals included in the Journal of Citation Report. He has worked as an electrical engineer at Gamesa Electric.