Vliv antioxidantů na rostlinné oleje

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Effect of Antioxidants in Natural Ester Oil

Abstract – **Main features of the insulating fluids based on natural esters are biodegradability, a good thermal and insulating features, a high fire resistance etc. Compared to the mineral oil, the fluids based on natural esters still have a problematic development of a trend of dissipation factor in the long-term period due to lower oxidative stability. This paper primarily presents a comparison of key dielectric parameters of clean natural ester insulation fluid (rapeseed oil) and several mixtures of this rapeseed oil with 1 wt% of different antioxidants. The aim of this paper is to choose the antioxidant which contributes to achieving the best dielectric parameters of oil based on various measurement. Part of the evaluation was establishing the oxidative stability.**

Keywords –antioxidants; breakdown voltage; dissipation factor; natural ester oil; oxidative stability.

I. Introduction

There has been great emphasis on the development of the biodegradable insulating fluids usable in power and distribution transformers. This type of oil can be manufactured locally, have good electrical insulation properties and also being easily biodegradable [1]. As stated above, most of its parameters are acceptable or even better compared to the common mineral oil (sulphur content, high fire resistance, low toxicity etc.) [2].

The aim of this research is to examine and improve the properties of rapeseed oil using a different kind of inhibitors. Several properties in which rapeseed oil could be improved, as breakdown voltage, dissipation factor, oxidative stability etc. were monitored and compared with other results in order to find the best possible blend of rapeseed oil and the given type of inhibitors. All the samples were then exposed to accelerating heat ageing and the changing properties development were examined as part of the test of oxidation stability.

II. Theoretical Background

There is one problem with long term usage of the natural ester oils – they tend to oxidize rapidly. The goal is to make the oil properties as steady as we can for as long as we can, but on the other hand they are naturally highly biodegradable. That is of course countering the previously stated. So the balance point must be found out via adding some ingredients.

Oxidation is a process between molecules of unsaturated fatty acids and oxygen molecules. Most affected are double C=C bonds. In this process the free radicals are created, which are highly reactive. Free radicals can damage the oil by reacting with other molecules, creating more free radicals which will further react. The oxidation is undergo slowly but is accelerated rapidly by the presence of light, heat or metal ion particles [3-4].

The protection of insulating fluids against oxidation can ensure specific additives (antioxidants) which influence the degradation of chemical structure in an oxidizing atmosphere. It is a common way to slow, prevent or even to stop the oxidation processes. These additives scavenge free radicals and neutralize. The oxidation process with reduced amount of free radicals is less dangerous for the deterioration [4].

In our experiment four antioxidants were used. One natural antioxidant - Citric Acid (CA) and three synthetic antioxidants - Propyl Gallate (PG), tert-Butylhydroquinone (BTHQ) and Butylated Hydroxyanisole (BTHX). Abbreviations in brackets are used for identification of antioxidants in the following text.

III. EXPERIMENT

The rapeseed oil was is natural ester oil which fatty acids content can be seen in Table I. This can tell a lot about properties of the oil, as is the oxidative stability – the higher content of unsaturated acids means worse oxidative stability and therefore faster deterioration of the properties of the oil itself. The higher content of saturated fatty acids means higher chemical stability but also means higher melting point. On the other hand, the unsaturated fatty acids are not only disadvantage, the higher their content is, the longer the oil stay liquid in low temperatures [3].

TABLE I. FATTY ACID CONTENT [9]

Acid	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Content (%)	4	2	62	22	10

Each oil sample was set in the oven for 24 hours at 80 °C for more water reduction. Then the oil was heated up to the melting point of the antioxidant which was then added and properly mixed so the proper bonding with oil was assured. Each sample consists of pure rapeseed oil (500 ml) and an antioxidant at 1wt% of the oil. Table II provides coverage of all samples used in this paper and will function as a guideline further.

TABLE II. SAMPLES IDENTIFICATION

Sample No.	1	2	3	4	5
Antioxidant	none	PG	BTHQ	BTHX	CA

Measured electrical parameters were dissipation factor tan δ, breakdown voltage and real part of relative permittivity ε' under high AC voltage. The dissipation factor was measured according to the IEC 60247 at a voltage of 500 V in the temperature range from 30 °C to 90 °C. The breakdown voltage U_b was done by the IEC 60156 with high voltage source (maximum 200 kV) with the frequency of 50 Hz and with a rate of 2 kV/s until breakdown. The distance between electrodes was 2.5 mm. The detailed analysis was done by BDS (Broadband Dielectric Spectroscopy) in frequency range from 0.5 Hz to 1 MHz and in temperature range from -60 °C to 90 °C. The amplitude of measuring AC voltage was set to 1 V.

Test of the oxidation stability (TOS) was done by IEC 61125 in two steps. First one is the ageing of oil samples at 150 °C for 164 hours. After the ageing is finished the dissipation factor is measured again. The IEC 61125 provides a limit value of dissipation factor that the oil must comply.

IV. Results and Conclusion

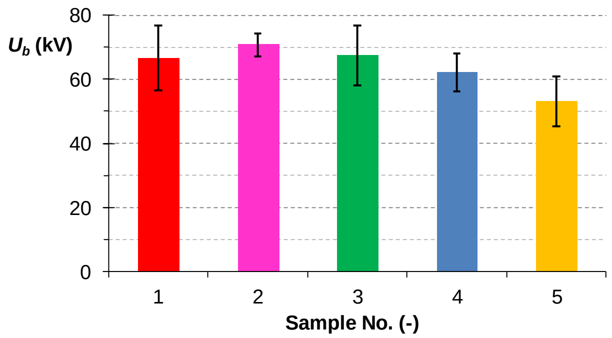

Figure I. **Results of breakdown voltage measurement of samples before TOS**

The results of Ub (Fig. 1) were not a surprise. The addition of the antioxidants had small effect on the value of breakdown voltage compared to the pure rapeseed oil (sample 1). The standard deviations of Ub are slightly smaller with antioxidants.

The main goal of these measurements was the dissipation factor (Fig.2). It is compared to the limit factor from IEC standard.

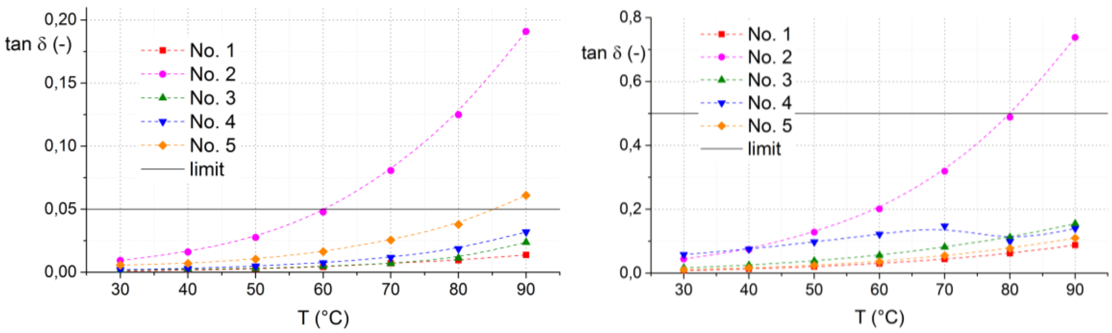

Figure II. **Temperature dependencies of dissipation factor before and after TOS**

The following Fig. 3 show the results of the dielectric analysis performed by BDS. The growth of tan δ with decreasing frequency and increasing temperature is associated with an increasing influence of conductivity.

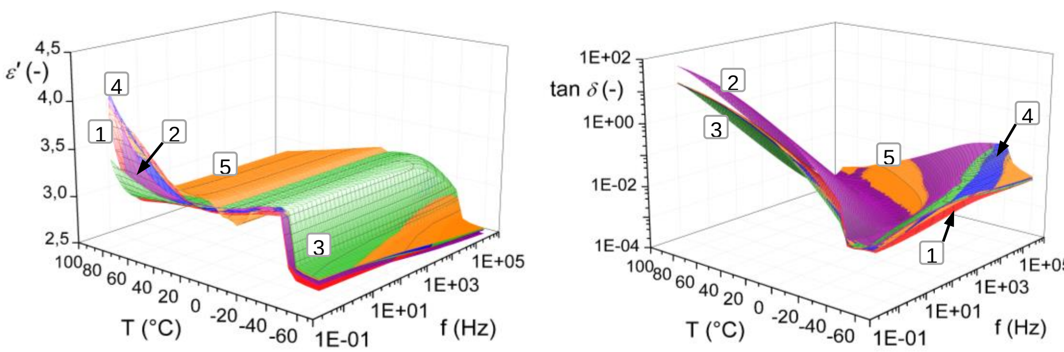

Figure III. **3D interpretation of temperature-frequency dependencies of real part of relative permittivity and dissipation factor of samples after TOS**

The results of dissipation factor clearly show that samples 2 and 5 failed the limit right at the start after preparation of the samples. We can also see that every sample with antioxidant has a higher tan δ than clear rapeseed oil. After TOS the sample 2 (oil with PG) only confirms that. It is not a good choice as an antioxidant for rapeseed oil.

For an evaluation of oxidative stability the comparison of tan δ at 90 °C was made. It is visible in Table III. We can state that lower the coefficient is, the less susceptible the oil is to oxidation. From this we can say that antioxidants in samples 2, 4 and 5 are viable for long term usage as they have significantly lower relative oxidation speed coefficients compared to the pure rapeseed oil sample.

TABLE III. VALUES OF DISSIPATION FACTOR AT 90°C AND COEFFICIENT OF RELATIVE OXIDATION SPEED

Sample No.	1	2	3	4	5
tan δ before TOS	0.0138	0.1910	0.0238	0.0320	0.0610
tan δ after TOS	0.0881	0.7380	0.1550	0.1400	0.1100
Coefficient	6.38	3.86	6.51	4.37	1.80

With all this in mind, we can recommend antioxidants in samples 4 and 5 (BTHX and CA) for further use in combination with rapeseed oil, and antioxidant in sample 2 (PG) for further research because of its improvement of pour point.

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REFERENCES

[1] J. Souček, J. Hornak, M. Svoboda, M. Gutten and T. Koltunowicz, "Comparison of the electrical properties of canola oil with commercially available mineral oil," 2015 16th International Scientific Conference on Electric Power Engineering (EPE), Kouty nad Desnou, 2015, pp. 634-637.

[2] A. Ciuriuc, P. V. Notingher, R. Setnescu, L. M. Dumitran and T. Setnescu, "Lifetime estimation of vegetable oil for transformers," High Voltage Engineering and Application (ICHVE), 2014 International Conference on, Poznan, 2014, pp. 1-4. Doi: 10.1109/ICHVE.2014.7035468

[3] Hussin, N., Aslan, N. H. M., Jamil, M. K. M., Isa, M., & Hamid, H. A. (2016). “The effect of antioxidants on the performance of vegetable oil in high voltage applications.” ARPN Journal of Engineering and Applied Sciences, 11(8), 5060-5065. Retrieved from www.scopus.com

[4] S. Tenbohlen and M. Koch, "Aging Performance and Moisture Solubility of Vegetable Oils for Power Transformers," in IEEE Transactions on Power Delivery, vol. 25, no. 2, pp. 825-830, April 2010. Doi: 10.1109/TPWRD.2009.2034747