OXIDATION STABILITY OF NON INHIBITED VEGETABLE TRANSFORMER LIQUIDS

Ernesto DIESTRE
Repsol – Spain
ediestrer@repsol.com

Jesús IZCARA
Ormazabal CT – Spain
jih@ormazabal.com

Francisco SANZ
Fundación Gómez Pardo - Spain
alub.lpp.minas@upm.es

ABSTRACT

Mineral oils have been used for decades as transformer fluids because of their excellent dielectric properties and availability. In the last decade vegetable transformer liquids have been introduced in the market. Vegetable transformer fluids show higher fire point than mineral oil and produce less smoke and less heat in case of fire contributing positively to reduce the risk of personal and property damage. Furthermore, vegetable transformer liquids are readily biodegradable fluids and induce very low toxicity levels against aquatic organisms like fish, algae or daphnia. This work presents the development and oxidation stability of non inhibited highly stable vegetable transformer fluids based on low unsaturated fatty acid distribution and high natural antioxidants concentration. The vegetable transformer fluid described in this work does not contain added antioxidants including synthetic antioxidants, therefore enhancing the biodegradability and toxicity properties of the final product.

INTRODUCTION

Oxidation stability in transformer fluids is a critical parameter that must contribute to extend the life of the transformer over 40 years. Oxidation stability in most vegetable transformer fluids must be improved by adding synthetic antioxidant additives. The oxidation process occurs via a free radical mechanism where synthetic antioxidants act as radical scavengers breaking the propagation step of the process.

Oxidation stability in vegetable oils depends on fatty acids distribution, the refining process and the presence of natural antioxidants.

It is well known that the oxidation stability of vegetable oils decreases as the unsaturation of the fatty acids increases. As an example, oxidation stability of oleic acid (1 double bond) is reported 10 times greater than oxidation stability of linoleic acid (2 double bonds) which is 2 times more stable than linolenic acid (3 double bonds).

Oxidation stability of vegetable oils also depends on the refining process of the oil. The refining process consists of several steps that reduce the concentration of free fatty acids, waxes, metals, colouring pigments and odours but also contribute to the reduction of the concentration of natural antioxidants as tocopherols.

In this work the development process of a non inhibited vegetable oil based transformer fluid is described and oxidation stability according to Rancimat is reported.

MATERIALS AND METHODS

Raw materials

Two vegetable oil based transformer fluids were used in this study. One of them (F) was a commercial transformer fluid that contained added synthetic antioxidants. The other fluid (BIOELECTRA) was based on a high oleic vegetable oil that does not contain added antioxidants. A naphthenic mineral oil was used as a reference for fire safety tests.

Sample characterization

Viscosity

Viscosity at 40º C and 100º C was determined according to ASTM D445 standard.

Acidity

Acidity was measured according to ASTM D974 standard.

Water content

Water content was measured in accordance with IEC 60814.

Dielectric dissipation factor

Dielectric dissipation factor at 90º C was measured in accordance with IEC 61620.

Breakdown voltage

Breakdown voltage of unused transformer liquids was determined in accordance with IEC 60156.

Synthetic antioxidants

BHT and BHA were measured using high performance liquid chromatography (HPLC) with UV detection.

Natural antioxidants

Tocopherols were measured by HPLC according to IUPAC 2432.

Fatty acids composition

Fatty acids composition was measured according to EN ISO 5508 and EN ISO 5509.

Oxidation stability

A Metrohm Rancimat model 743 (Herisau, Switzerland) was used. The tests were carried out in triplicate at temperatures of 373, 383 and 423 K with 2,5 g of oil samples at an airflow rate of 10 L/h. The glassware, electrodes, vessels and tube were cleaned to avoid any contamination. For each temperature, eight samples were placed in the equipment randomized on their position in the heating block. The induction times were calculated automatically by apparatus software with precision of 2 decimal places. 3 measurements were taken for both oils at each temperature and the averages were determined. The maximal deviation from mean value was less than 1%.

Another set of experiments at the same temperatures was performed in the presence of copper as oxidation catalyst. Copper is the most common material used in electrical transformers´ windings and oxidative stability testing in the presence of copper is of paramount importance in order to predict the behaviour of the oil in the field. Copper was accommodated in the measuring vessels maintaining the same oil/copper surface ratio used in IEC 61125 C standard.

The kinetic rate constant was taken as the inverse of the induction time (k, h–1) for each temperature. The natural logarithm of the rate constant was plotted vs. the absolute temperature.

RESULTS AND DISCUSSION

Transformer fluid development

The main objective was the development of a biodegradable, highly renewable, high fire point transformer fluid. All these requirements could only be met by using vegetable oils as base stock for the transformer fluid. Some vegetable oils were evaluated and those containing high oleic acid concentration showed the most appropriate balance between pour point and oxidation stability.

The vegetable oil selected as base stock contains more than 80 % oleic acid and less than 10 % linoleic and linolenic acids. The typical fatty acids distribution of the selected oil is shown in Table 1.

Once the base oil has been selected a common route in the development of vegetable oil based transformer fluids is the addition of synthetic antioxidants in order to improve oxidative stability. On one hand this route enhances stability of poorly stable vegetable oils but on the other hand it could have a negative impact on fundamental characteristics of natural oils as biodegradability or acute aquatic toxicity.

Table 1. Fatty acids distribution of high oleic oil

Fatty acids (%)	High oleic oil
C 14:0	0.04
C 16:0	3.96
C 16:1	0.11
C 18:0	3.66
C 18:1	81.27
C 18:2	8.93
C 18:3	0.11
C 20:0	0.32
C 20:1	0.26
C 22:0	1.01
C 24:0	0.32

In order to avoid such negative effects synthetic antioxidants were not used in the development of BIOELECTRA transformer fluid.

In order to assure an adequate resistance against aging, the selected base stock contained less than 10 % linoleic and linolenic acids. Furthermore tocopherols, known as natural antioxidants, were present at a concentration higher than 700 ppm mainly as α-tocopherol. Tocopherols are phenolic antioxidants comprising a mixture of four tocopherol homologues (α, β, γ, and δ). They appear naturally in fats and oils and avoid oil degradation by reacting with free radicals.

Tocopherol concentration greatly depends on the nature of the vegetable oil selected. Moreover not only total concentration but also individual tocopherol concentration plays an important role on oxidation stability. A comparison of the antioxidant activity of the tocopherol homologues in soybean oil concluded that α-tocopherol was 3–5 times more active than γ-tocopherol and 16–32 times more active than δ-tocopherol [1]. A similar conclusion is shown in [2] quoting tests on foodstuffs that demonstrate that the antioxidant activity of tocopherols increases in the sequence γ, δ, β, α-tocopherol

The total concentration of tocopherols in commercial oils depends not only on the nature of the vegetable oil but also on the processing steps and the conditions used to refine the oils. However, the relative amounts of the individual tocopherols do not change significantly with processing [3].

Murat Tasan and Mehmet Demirci [4] studied the loss of total and individual tocopherols of sunflower oils at different stages of industrial chemical and physical refining processes. The average losses of total tocopherol content during the physical refining process were found to be 35.5%. The deodorization stage of the physical refining process caused greatest overall reduction (average 24.6%) in total tocopherol content. Similar results are reported by Roland Verhé [5] with a reduction of total tocopherol content during deodorization in the range of 25-35%.

Tocopherols content is a critical parameter in BIOELECTRA transformer fluid as this fluid does not contain added antioxidants. The vegetable oil selected possesses a high quantity of α-tocopherol and the deodorization step has been adjusted in order to preserve tocopherols in the oil.

The high oleic content oil is refined, bleached and deodorized and no further processing is applied to the oil. BIOELECTRA characteristics are shown in Table 2.

Environmental and fire safety

BIOELECTRA was tested for biodegradability according to OECD 301 B. Professional environmental scientists widely agree that biodegradability higher than 60% in 28 days under OECD 301 B predicts a rapid and ultimate biodegradation of the product in the environment. Biodegradation of BIOELECTRA is greater than 85% (Figure 1).

Algal growth inhibition test (OECD 201), daphnia sp., inhibition of mobility test (OECD 202) and fish, acute toxicity test (OECD 203) were also tested. At a loading ratio of 1000 mg/l BIOELECTRA gives no acute toxicity towards algae, daphnia or fish.

BIOELECTRA as a “high fire point” fluid has a K2 fire hazard classification according to IEC 61100. BIOELECTRA and a mineral naphthenic oil were tested using a calorimetric cone for heat release rate (HRR) and smoke production rate (SPR) according to ISO 5660-1.

The results regarding fire safety are shown in Table 3 where both heat release rate and smoke production rate are 50 % reduced when BIOELECTRA is burnt instead of a naphthenic oil. Both parameters are of paramount importance in case of fire and are directly related to the personal and property damage that a fire may cause.

Smoke produced during oil combustion was tested for opacity and toxicity. The first parameter is evaluated according to NF X 10 702 and the second one to NF X 70-100. According to NF 16101, the combination of these two parameters gives the “smoke value” which ranks oils from F0 to F5, being FO the safer class and F5 the most risky class.

According to NF 16101 BIOELECTRA is classified as F1 and naphthenic oil as F3.

Table 2. BIOELECTRA characteristics

Characteristic	Standard	Result
Kinematic viscosity @ 40º C (mm^2/s)	ASTM D445	39.2
Kinematic viscosity @ 100º C (mm^2/s)	ASTM D445	8.5
Acidity (mg KOH/g)	ASTM D974	0.055
Water content (ppm)	IEC 60814	100
Breakdown voltage (kV)	IEC 60156	65
Dielectric dissipation factor @ 90º C, 50 Hz	IEC 61620	0.03
Electric conductivity @ 25º C (pS/m)	ASTM D 2624	3

Figure 1. Biodegradation of BIOELECTRA

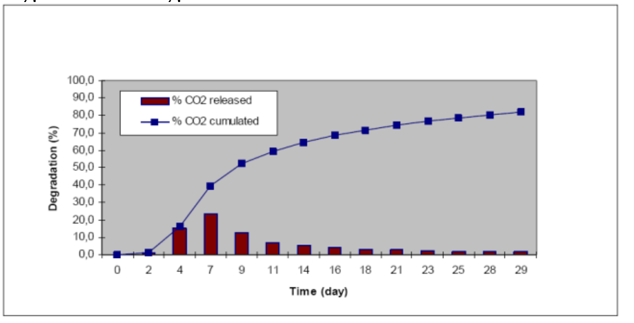


Table 3. Fire safety

	BIOELECTRA	Naphthenic oil
HRR (kW/m^2)	705	1578
SPR (m^2/s)	0.0612	0.1162

Oxidation stability

The natural logarithm of the oxidation kinetic rate constant were plotted vs. the absolute temperature. As shown in Figure 2, despite the absence of added antioxidants the oxidative stability of BIOELECTRA is better than the stability of F oil. The kinetic rate constants for BIOELECTRA were lower over the whole range of temperatures and the slopes of the lines generated by regressing ln (k) vs. the absolute temperature indicate a lower increase in kinetic rate constant as temperature increases.

Similar results were found when copper was used as an oxidation catalyst as it is depicted in Figure 3. Copper increases kinetic rate constants for both fluids at the whole range of temperatures but again BIOELECTRA shows lower values than F oil.

These results demonstrate that the addition of antioxidants, including synthetic antioxidants, is not compulsory in order to obtain a vegetable oil based transformer fluid showing adequate oxidation stability.

In this case, the proper selection of the base oil, the right amount of non added natural antioxidants and the adjustment of the refining process have led to a transformer fluid that has been tested successfully for more than three years in distribution transformers.

Figure 2. Oxidation stability without copper

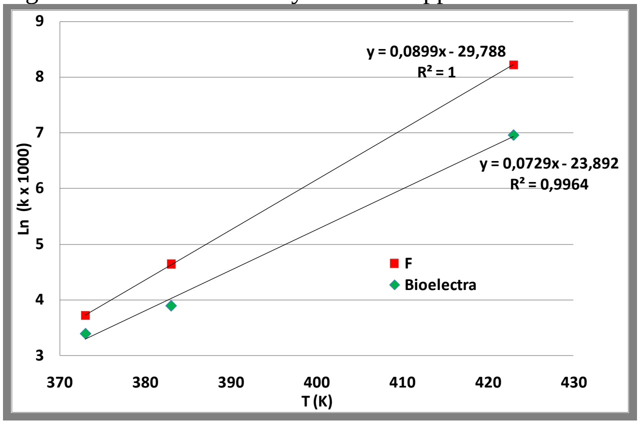
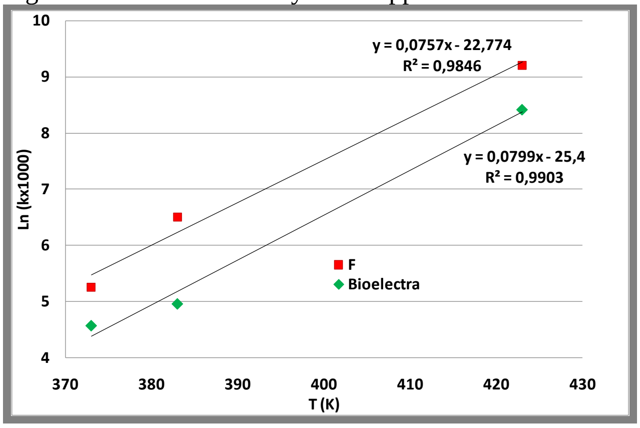


Figure 3. Oxidation stability with copper



ACKNOWLEDGMENTS

The authors wish like to thank CDTI for funding this work through the Program INGENIO 2010.

REFERENCES

[1] J.C. Evansa, D.R. Kodalia, and P.B. Addisb, 2002, "Optimal Tocopherol Concentrations to Inhibit Soybean Oil Oxidation", *JAOCS* vol. 79, 47–51.

[2] T. Hodisan, D. Casoni, M. S. Beldean-Galea, and C. Cimpoiu, 2008, "Identification and Quantification of Tocopherols in Vegetable Oils by Thin-Layer Chromatography", *Journal of Planar Chromatography* vol. 3, 213–215.

[3] Jung, M.Y., S.H. Yoon, and D.B. Min, 1989, "Effects of Processing Steps on the Contents of Minor Compounds and Oxidation of Soybean Oil", J. *Am. Oil Chem. Soc.* vol. 66, 118–120.

[4] M. Tasan and M. Demirci, 2005, "Total and individual tocopherol contents of sunflower oil at different steps of refining", *Eur Food Res Technol.* vol. 220, 251–254.

[5] R. Verhé; T. Verleyen, V. Van Hoed and W. De Greyt, 2006, "Influence of Refining of vegetable Oils on Minor Components", *Journal of Oil Palm Research*, 168-179.