Comparative TG/DTG/DTA+FTIR Studies Concerning the Stability of Some Mineral and Vegetable Electro-Insulating Fluids

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Thermal TG/DTG/DTA analysis coupled with FTIR spectroscopy was applied to some sorts of mineral and vegetable oils used in electrical equipment. On heating in inert atmosphere, it was observed that the mineral oils vaporize, while the vegetable oils undergo hydrolysis, yielding fatty acids as main volatiles, as indicated by FTIR. In synthetic air, the FTIR spectra of gaseous products confirm the presence of similar oxidation products, both for mineral and vegetable oils. The TG results indicated that the vegetable-based oils exhibit a substantially higher thermal stability than the mineral oils. The presence or absence of anti-oxidant inhibitors in these oils greatly influences the onset of the oxidation process in air environment factor, as results from the DTA results.

Keywords: mineral oils, vegetable oils, thermal stability, thermal analysis, TG/DTG/DTA, FTIR

Worldwide significant quantities (hundreds of thousands of tons) of insulating fluids are used in electrical equipment (transformers, reactance's, cables, etc.). In the electrical applications, the mineral oils obtained by the fractional distillation of crude oil [1, 2] are traditionally used. Mineral oils in electrical applications have functional features and acceptable costs. However, there are some limitations, such as: they contain toxic compounds, which are hardly biodegradable [3-5] (accidental discharges seriously affect the environment [6, 7], pollute air, soil and surface waters with persistent organic pollutants [8, 9]) have a relatively low flammability point (below 140 °C) and under the action of thermal stress decompose into flammable gases (H_2, CH_4, C_2H_4, C_2H_6) [10-14]. This latter aspect leads to increases the risk of explosions and fires [13, 15]. Flammable gases degrade electro insulating paper with furans formation [16-20]. These toxic products (the furans) contain compounds with sulfur which corrode copper and copper sulphide in suspension which affects paper/oil insulations [21-27].

Numerous recent researches address the issue of replacing mineral oils by electro insulating fluids based on natural esters (vegetable oils). These appropriately selected and treated, electro insulating fluids can successfully replace mineral oils in electrical applications [2, 3, 14, 15, 25 - 33]. In this context, the aim of the paper consists in the comparative study of the thermal behavior in both oxidant and inert environment of some mineral and vegetable oils for electrical applications.

Experimental part

In order to assess the thermal behavior both in the oxidant environment (synthetic air) and in the inert environment (argon), two commercial types of mineral oil have been investigated, ***Oil 1*** [34] and ***Oil 2*** [35]; a commercial sort of vegetable transformer oil, ***Oil 3*** [36] and an experimental type of pure vegetable oil, with high content in dehydrated oleic ester (over 75 %), ***Oil 4*** [31, 37].

The FTIR measurements were performed by applying a thin layer of the analysed oils on KBr pellets and recording FTIR spectra in the 250"4000 cm^{-1} range using a Bruker TENSOR 27 FTIR spectrometer.

The TG/DTG/DTA + FTIR measurements were performed on a Netzsch STA 409 PC thermal analyzer coupled to a Bruker Tensor 27 FTIR spectrometer equipped with a TG-IR gas cell. Samples weighing approximately 20 mg were placed in Pt-Rh crucibles and heated in synthetic air or argon flow (100 mL min^{-1}, purity 99.999 %), from room temperature to 700 °C, at a heating rate of 10 °C min^{-1}. The experimental data were processed using Proteus software, Netzsch - Germany. The FTIR spectra were collected continuously during measurements in the wavenumber range of 650-4000 cm^{-1} at a resolution of 4 cm^{-1}. Assignment of FTIR bands was performed using the public NIST database [38].

Results and discussions

FTIR measurements

The FTIR spectra of the studied oils are in agreement with their chemical composition.

Thus, the spectra of mineral ***Oil 1*** and ***Oil 2*** show the characteristic bands of CH_3-and -CH_2- groups: the strong ν_{C-H} bands in the 2800-3000 cm^{-1} range and the medium d_{C-H} bands at ~1377 and ~1460 cm^{-1}, corresponding to CH_3-and -CH_2-groups, respectively.

The spectra for vegetable oils ***Oil 3*** and ***Oil 4*** show, besides the above-mentioned bands, a strong band at 1747 cm^{-1} and a medium one at ~1163 cm^{-1} attributable to the $\nu_{C=O}$ and ν_{C-O} of the carboxylic ester, respectively, confirming the triglyceride structure. Also, the band at ~3005 cm^{-1} ($\nu_{=C-H}$) suggests the presence of C-H groups linked to double bonds.

Comments

By comparing mineral with vegetable oils some differences are noticeable. The strongest bands are evidenced in the 2080-3010 cm^{-1} region, where a group of three, respectively four peaks can be considered as fingerprints for the two types of oils. The stretching methylene vibrations in long aliphatic chains appear usually at 2855-2955 cm^{-1}. However, the most intensive band appears in between this doublet, at 2925 cm^{-1}, and can be assessed to a less mobile CH_2 groups from polyols like glycerine. The smallest, but yet distinct band at 3005 cm^{-1}

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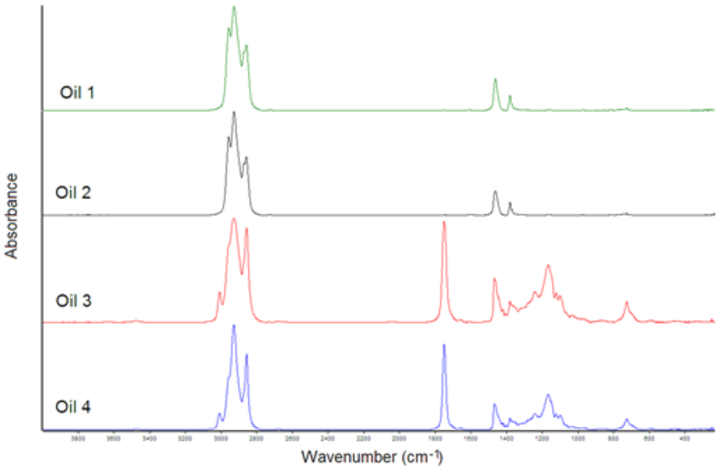

Fig. 1. FTIR spectra of the investigated oil samples

can be assessed to CH_3- terminal groups or to C-H linked to double bonds. Another major difference between the two types of oils is given by the very intensive band at 1747 cm^{-1} existent in vegetable oils, assessed to carbonyl groups from esters, accompanied by a series of bands in the region 1100-1466 cm^{-1} due to several oxygen containing compounds.

TG/DTG/DTA+FTIR measurements

Argon

The prevalent process occurring on heating ***Oil 1*** and ***Oil 2*** in an inert atmosphere is the vaporization of their components, which starts at above 120°C and ends at about 300-320°C (figs. 2 and 3). This is confirmed by the fact that the main bands appearing in the FTIR spectra of the evolved

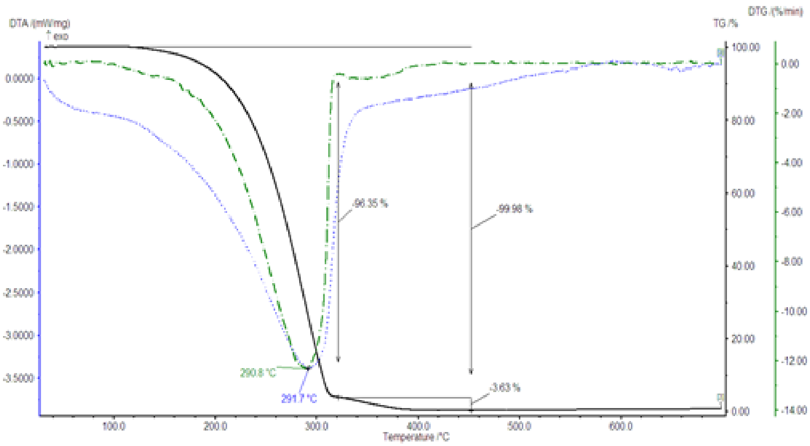

Fig. 2. TG, DTG and DTA curves for oil sample, **Oil 1** in argon.

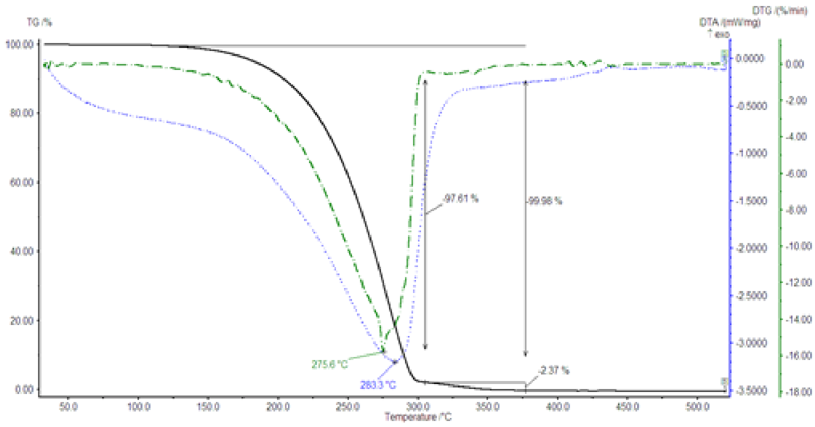

Fig. 3. TG, DTG and DTA curves for oil sample, **Oil 2** in argon

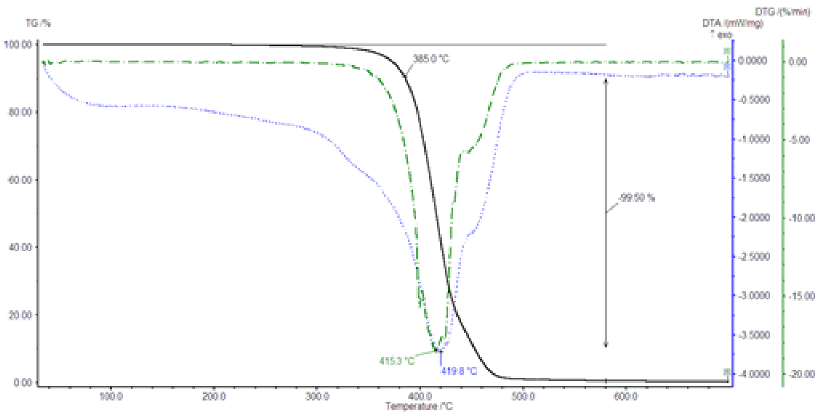

Fig. 4. TG, DTG and DTA curves for oil sample, **Oil 3** in argon.

gases (fig. 6) resemble those of initial oils, slightly shifted due to their presence as gas instead of liquid. This step is characterized by a very large mass decrease, a single DTG peak, and a strong endothermic effect. At higher temperatures, a slight mass loss step is observed (2-4 %), most probably indicating the decomposition/evaporation of low-volatile components.

In the case of vegetable oils ***Oil 3*** and ***Oil 4***, an almost total mass loss is observed between 350 and 500°C, characterized by single DTG peaks at 415.3 and 427.8°C, respectively, and by endothermic effects (figs. 4 and 5). The main products identified in the FTIR spectra (fig. 6) are fatty acids (exact identification is difficult due to similarity of their gaseous FTIR spectra), suggesting that a hydrolysis of the initial triglyceride has occurred. Also, small amounts of CO_2, H_2O and CO were detected, indicating partial decomposition reactions.

Air

The thermal analysis results of mineral oils are shown in figures 7 and 8 and exhibit similar TG, DTG and DTA curves. These results are in agreement with those reported in literature for other sorts of mineral oils [32, 39]. As can be seen from figures, the TG, DTG and DTA curves show a thermal stability of these samples up to about 100°C. At further heating, a significant mass loss is observed (~94 %), ending at slightly above 300°C.

From FTIR data, it can be noticed that the onset of the mass loss is due to the evaporation of oils, (FTIR spectra are similar to those observed in argon), while DTA data show an endothermic effect corresponding to this process. At temperatures above 200°C, an exothermic effect seen in DTA curve indicates the onset of a low temperature oxidation (LTO). This effect is weak for ***Oil 2*** (most probably due to the additives that inhibit oxidation) and significant for ***Oil 1***.

The FTIR spectra recorded in this temperature region show the presence of CO_2, CO, water vapor, carboxylic and carboxylic compounds, methanol, confirming the occurrence of oxidation reactions (fig. 11).

A small mass loss step is then observed in the 350–500°C regions, also characterized by a strong exothermic effect in the DTA curve, indicative of high temperature oxidation (HTO). In the FTIR spectra, the bands of CO_2 are ... agreement with the oxidative reactions.

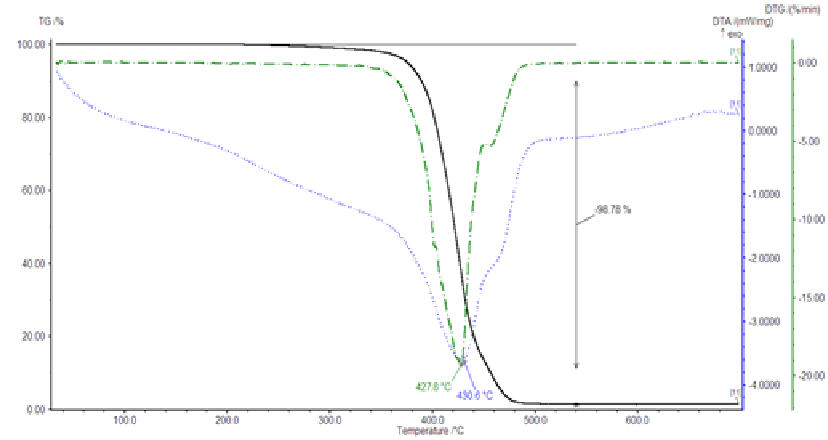

Fig. 5. TG, DTG and DTA curves for oil sample, **Oil 4** in argon.

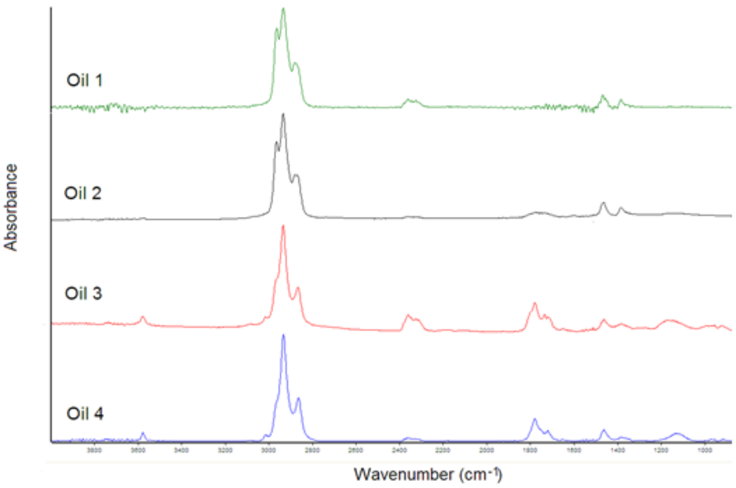

Fig. 6. FTIR spectra of volatile products from the studied oils, in argon atmosphere

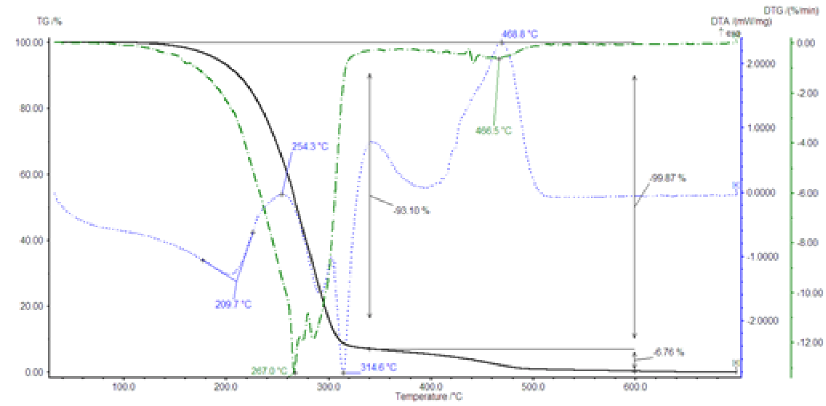

Fig. 7. TG, DTG and DTA curves for oil sample, **Oil 1** in air.

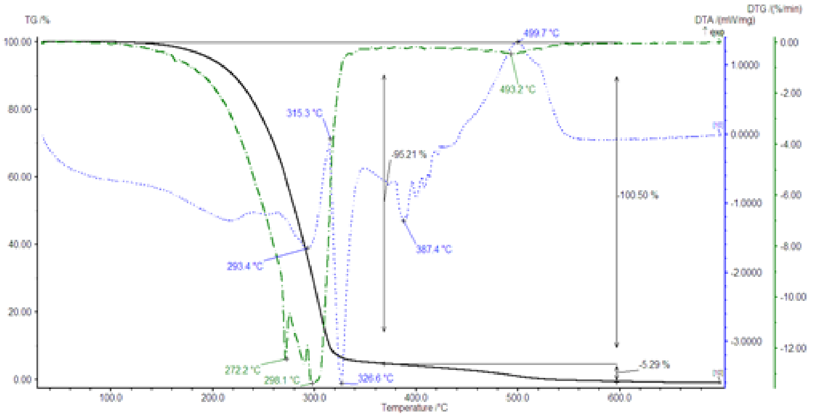

Fig. 8. TG, DTG and DTA curves for oil sample, **Oil 2** in air.

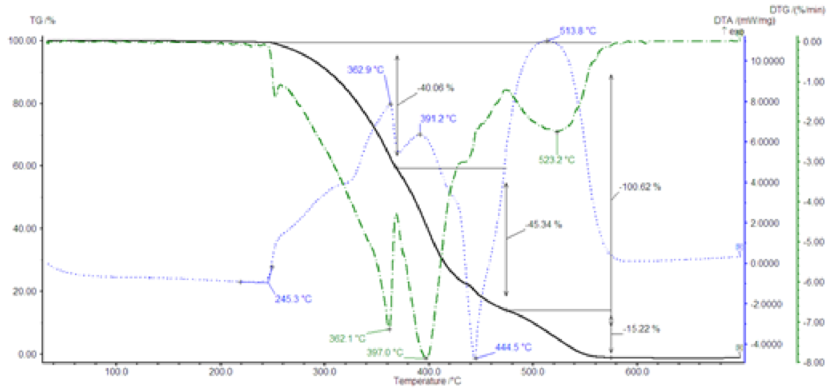

Fig. 9. TG, DTG and DTA curves for oil sample, **Oil 3** in air.

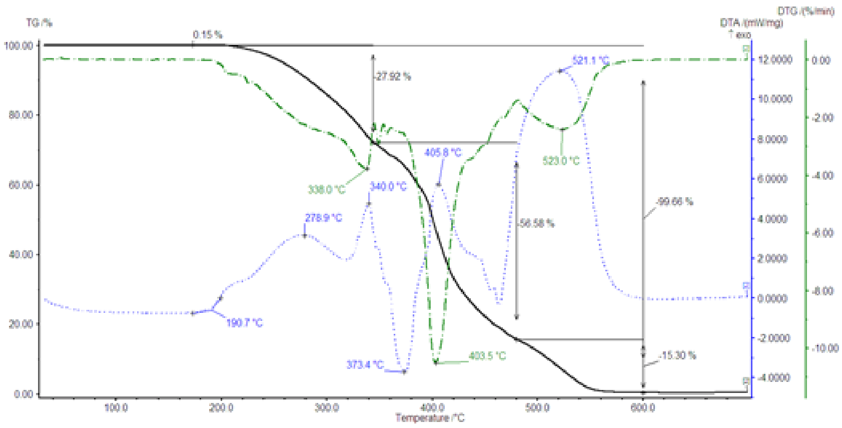

Fig. 10. TG, DTG and DTA curves for oil sample, **Oil 4** in air.

The TG, DTG and DTA curves corresponding to ***Oil 3*** are presented in figure 9. The oil is stable up to 245°C, as no mass change is observed in this region.

Above this temperature, the mass starts to decrease, while in the DTA curve the onset of a strong exothermic effect is observed, suggesting the occurrence of a thermo-oxidative decomposition.

Although this vegetable oil contains double bonds, no typical mass gain due to addition of oxygen is noted. This can be due to the presence of anti-oxidation inhibitors. During several decomposition/oxidation processes that follow, the FTIR bands are similar to those observed for ***Oil 1*** and ***Oil 4*** (fig. 11), as well as to those found for other vegetable oils [40]. A total mass loss is complete at about 580°C.

On heating the ***Oil 4*** up to about 200°C, a slight mass gain (0.15 %) is observed (fig. 10), due to the addition of oxygen and formation of hydro peroxides at reactive carbon positions adjacent to double bonds [41]. On further heating above 200°C, the mass loss starts, together with the onset of exothermic reaction (oxidation) observed at 190.7°C. The almost total mass loss is complex and is characterized, as the ***Oil 3***, by several DTG and DTA peaks and similar volatile products (fig. 11).

The last process at above 500°C is highly exothermic, most probably due to the combustion of carbonaceous residues, as high amounts of CO_2 only are observed in the FTIR spectra corresponding to this temperature region.

The thermo-oxidative stability of the studied oils in air can be evaluated and compared based on two parameters: the onset temperature of oxidation measured by DTA, T_{onset} (DTA), and the temperature corresponding to a 10 % mass loss, T_{10} (air).

For inert atmosphere, a corresponding T_{10} (Ar) can be assessed. Comparing the first parameter, one notes that ***Oil 3*** has the highest stability (T_{onset} (DTA) = 245°C), which can be assigned to anti-oxidation inhibitors, followed by ***Oil 2*** (T_{onset} (DTA) = 217°C) and ***Oil 1*** (T_{onset} (DTA) = 210 °C) (fig. 12).

The ***Oil 4*** has the lowest thermo-oxidative stability (T_{onset} (DTA) = 191°C), as it contains no anti-oxidation inhibitors. Concerning the T_{10} parameter, both in air and in argon, it is obvious that the vegetable-based oil show a far better stability than the mineral-based oils (fig. 12). It is interesting to note that for ***Oil 3*** and ***Oil 4***, the T_{10} (Ar) values in argon (385 and 389°C, respectively) are much higher than the values observed in air atmosphere (T_{10} (air) = 304 and 283°C, respectively). This indicates that in inert, oxidative-

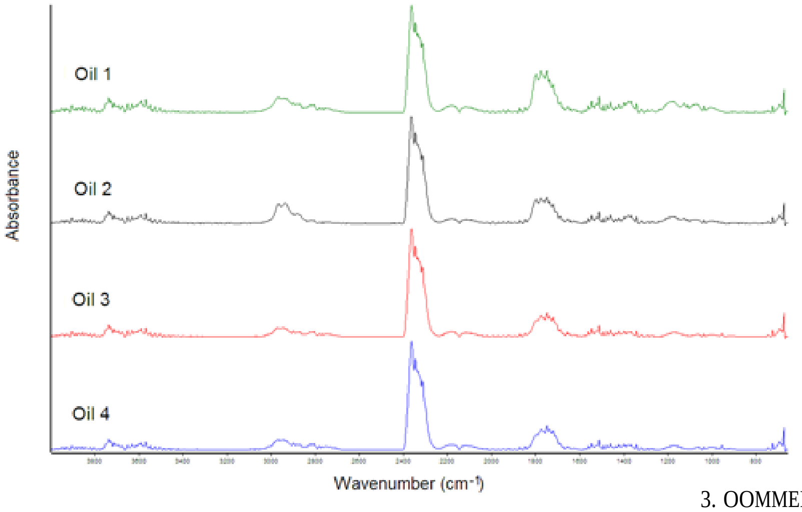

Fig. 11. FTIR spectra of volatile products from the studied oils, in air atmosphere

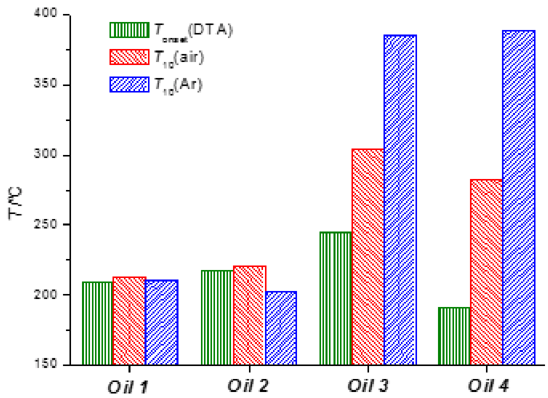

Fig. 12. The values of T_{onset} (DTA), T_{10} (air) and T_{10} (Ar) for the studied oil samples

free gaseous environment the vegetable oils have an exceptional thermal stability.

Conclusions

Thermal analysis coupled with FTIR was applied to some sorts of mineral and vegetable oils. Monitoring the volatiles that are released, both in inert (argon) and oxidative (synthetic air) atmosphere, some insights concerning the processes occurring during the heating of these oils were gained.

Thus, on heating in inert atmosphere, the mineral oils vaporize, while the vegetable oils undergo hydrolysis, yielding fatty acids as main volatiles. In air, the FTIR spectra of gaseous products released from both mineral and vegetable oils are similar, showing the presence of oxidation products. Based on the TG results, namely the T_{10} parameter, both in air and in argon, it is confirmed that the vegetable-based oils exhibit a substantially higher thermal stability than the mineral oils used in electrical transformers.

However, it is observed that the presence or absence of anti-oxidation inhibitors in these oils greatly influence the onset of oxidation process in air environment, as indicated by the T_{onset} (DTA) parameter.

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