Comparative Study of the Thermo-Oxidative Stability of Some Electro-insulating Oils

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The simultaneous TG/DTG+DTA thermal analyses have been performed for assessment of thermal stability in air of two fresh mineral oils, a refined sunflower oil, an oil based on synthetic esters and an oil based on natural esters. The results show that the biodegradable vegetal oil exhibits a better thermo-oxidative stability than mineral oils, and, therefore this oil could be a raw material for preparation of environmental friendly oil useful in cooling of electrical equipments. It has been also investigated the effect of long-term operation in electrical transformers upon a mineral oil.

Keywords: transformer oils, mineral oil, vegetable oil, thermal analyses, thermal stability

Worldwide, several billion liters of insulating oil are used in electric equipment for the filling of transformers and during the exploitation of switches, capacitors, cables, etc. [1]. In most of these applications [2, 3] are used oils obtained by fractional distillation of crude oil (mineral oil), with or without added ingredients in order to enhance the thermo-oxidative stability (stabilizers) and to reduce the environment aggressiveness (corrosion inhibitors).

For the power transformers, the insulating oils ensure, on the one hand a uniform electric field lines inside the transformer and on the other hand the transport of heat from the transformer windings towards the environment involved in natural and / or forced cooling of the transformer.

Traditionally, in electro-energy equipment the most widely used insulating fluid is the mineral oil, which is a hydrocarbon fraction obtained by refining crude oil, having in composition [4-6]: paraffins, iso-paraffins, naphthenes, aromatic hydrocarbons, etc. However, some of the substances existing in the mineral oils are toxic and present xenobiotic effect if accidentally reached the ground. Also, by contamination with the oil the surface waters may be hard biodegradable [7].

Although mineral oils have a number of advantages in electrical applications (low dielectric permittivity and electrical conductivity, high dielectric strength and breakdown voltage, acceptable chemical stability and manufacturing costs relatively low), their use in electric equipment presents limitations such as: ignition point relatively low (approx. 130°C), limited compatibility with seals and / or other materials with which they come into contact during operation [2], soil and water pollution in case of accidental leaks or spillages [7]. In this way, taking account of sustainable development at global level the researches aimed to replace mineral oils with synthetic and / or natural (vegetable) ester oils for electrical applications [3, 5, 6, 8, 9].

Vegetable oils are esters of fatty acids and, in principle, following the appropriate processing could be used in cooling of electric installations. They have advantages that are obtained from environmentally friendly renewable resources [6].

In practice, it has been verified that vegetable ester oils ensure a durability and safety in operation of cellulose-based insulation systems (paper, cotton etc.) higher than mineral oils [1]. During exploitation in an insulating system the constituents of mineral oils degrade cellulose structure, and the degradation products (CO, CO_2, H_2O, H_2, CH_4, furans) substantially reduce the performance [1, 9]. Unlike conventional mineral oils, vegetable ester oils contain triglycerides, which hydrolyze with water presents in traces (humidity) resulting glycerol and fatty acids. The last compounds react with the OH groups of cellulose in order to form ester cellulose with high dielectric stability [8].

It has been shown experimentally that under influence of the electric field of 50 Hz frequency, the growth and multiplication of filamentous mold *Aspergillus niger* is faster [10], because the oil is a carbon, source for mold. This can increase the risk of degradation of electrical insulating materials together with bio-corrosion of metallic materials [11-15].

The durability and the reliability of the electrical insulating oils used in electric installations are determined by their physicochemical stability, respectively ignition point, evaporation losses, resistance to thermo-oxidation, etc. It is also important for the oil used to be environmentally friendly, on the one hand to be obtained by raw materials and technologies with minimum negative impact to environment and on the other hand to be readily biodegradable by natural microbial flora (bacteria and molds).

According to the arguments presented above, the comparative study on the oxidative stability of mineral oil, vegetable oil and oils based on natural and synthetic esters is highly desirable and this is the main objective in this paper. We intended to present the thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) results that will be comparatively commented.

Experimental part

Investigated oils

A number of sorts of oil were investigated and labeled as in the followings:

(A) mineral oils: Swedish oil *Nytro Taurus* (A1), non-additive Hungarian *TO 30.01* (A2) and three exhausted non-additive transformer oils *TR 30* (A3, A4 and A5). The last *TR 30* oils were recovered from various transformers and operating time: 400 kVA and 34 years (A3), 1000 kVA and 27 years (A4) and 630 kVA and 30 years (A5), respectively; (B) a refined edible sunflower oil; (C) a Canadian oil based on synthetic esters - *Luminol TRi 205 L*; (D) a transformer biodegradable oil based on natural esters - *BIOTEMP.* All oils were used as purchased without purification.

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The thermal analysis of oil samples was performed with a TG/DTG+DTA Analyzer equipment produced by Netzsch – Germany. The experiments were carried out in synthetic air atmosphere (99.999% purity), with a gas flow rate of 30 cm^3 min^{-1}, under non-isothermal linear regime, at heating rate of 10 K min^{-1}. All measurements were made by heating the oil samples from the room temperature (RT) to 700^0 C into Pt-Rh crucibles. The experimental results were processed using the dedicated Proteus Software, from Netzsch - Germany. XRF chemical analyses were also performed using an equipment S8 TIGER from Bruker.

Result and discussions

The thermal stability is presented and discussed for each class of the investigated oils.

Mineral oils

The results of thermal analysis of new sorts of mineral oils A1 and A2 are shown in figures 1 and 2. The obtained data for the exhausted oils A3, A4 and A5 were represented in figures 3 and 4 and they exhibit similar TG, DTG and DTA curves with A2 oil. These results are in agreement with those reported in literature for other sorts of mineral oils [16, 17].

As can be seen from figures 1 and 2, the TG, DTG and DTA curves show a full thermal stability of all samples up to 90^{0}C. At temperatures higher than 90^{0}C, the TG, DTG and DTA results reveal the following transitional stages: degassing accompanied by an endothermic effect (process DEG, noted by I in figs. 1 and 2), a low temperature oxidation (LTO) and a high temperature oxidation (HTO). DEG and LTO occur in the temperature range from room temperature (RT) to 320^{0}C, while HTO occurs in the temperature range 320^{0}C – 600^{0}C. We noticed that some gaseous compounds were evolved in all these processes. DEG process is overlapped with the endothermic distillation of oil, noted with II in figures 1 and 2. The process II is followed by some exothermic processes with formation of gaseous compounds. In comparison with LTO, HTO process exhibits a lower mass loss. The characteristic parameters of non-isothermal thermo-oxidation of the investigated mineral oils are listed in table 1.

The comparison of the results obtained for the new mineral oils A1 and A2 shows that: (1) the oil A1 exhibits a more complex LTO; (2) there are low differences among the mass losses of these oils in the temperature ranges RT – 320^{0}C and 320^{0}C – 600^{0}C; (3) for LTO and process III, the oil A1 exhibits lower values of the temperatures corresponding to DTG minimum and DTA maximum.

The exhausted oils A3, A4 and A5 have been obtained by using oil A2 in some transformers in the conditions mentioned in Experimental section of this paper. These oils have a similar thermal behavior, but with different values of characteristic parameters of thermo-oxidation. This is illustrated in figures 3 and 4, in which the changes in LTO stage are presented. These changes consist in values of the temperatures corresponding to the mass loss of 10% (T_{10}), the DTG minimum ($T_m(DTG)$) and the DTA maximum ($T_m(DTA)$), as the result of long-time operating of oil A2 in electrical transformers. One notes that the long duration of operation in different electrical transformers has determined the decreasing of the values of these

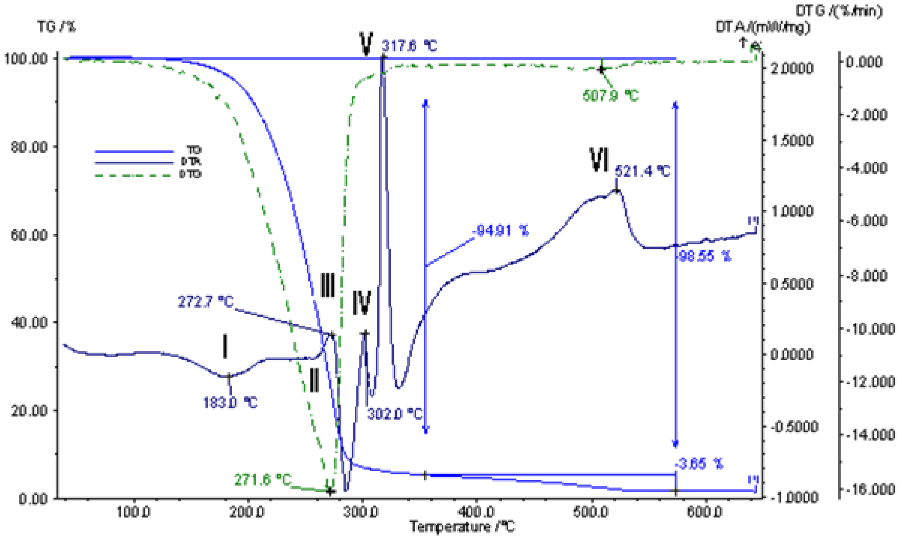

Fig. 1. TG, DTG and DTA curves corresponding to oil A1

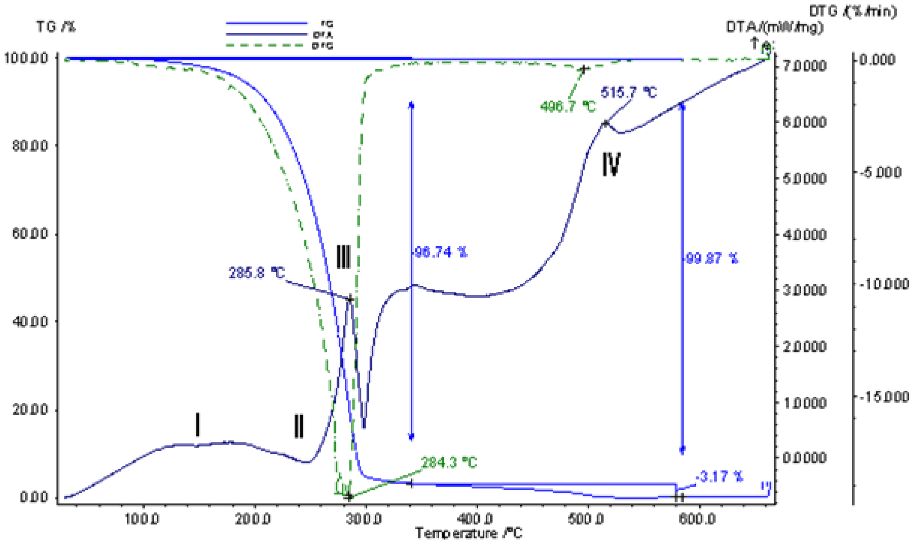

Fig. 2. TG, DTG and DTA curves corresponding to oil A2

Table 1

CHARACTERISTIC PARAMETERS OF NON-ISOTHERMAL THERMO-OXIDATION OF INVESTIGATED MINERAL OILS

Oil	ΔT [^{0}C]	Process	T_m(DTA) [^{0}C]	T_m(DTG) [^{0}C]	Thermal effect	%Δm [%]
A1	RT – 320.0^{0}C	I	183.0	-	endothermic	–94.91*
		II	260.0	-	endothermic	
		III	272.7	271.6	exothermic	
		IV	302.0	-	exothermic	
		V	317.6	-	exothermic	
	320.0^{0}C - 600.0^{0}C	VI	521.4	507.9	exothermic	–3.65
A2	RT – 320.0^{0}C	I	158.0	-	endothermic	–96.74*
		II	250.0	-	endothermic	
		III	286.8	284.3	exothermic	
	320.0^{0}C-600.0^{0}C	IV	515.7	496.7	exothermic	–3.17
A3	RT – 320.0^{0}C	I	160.0	-	endothermic	–96.46*
		II	240.0	-	endothermic	
		III	283.0	278.3	exothermic	
	320.0^{0}C-600.0^{0}C	IV	516.6	508.7	exothermic	–3.24
A4	RT – 320.0^{0}C	I	160.0	-	endothermic	–96.45*
		II	240.0	-	endothermic	
		III	282.6	280.2	exothermic	
	320.0^{0}C-600.0^{0}C	IV	526.0	513.1	exothermic	–3.41
A5	RT – 320.0^{0}C	I	160.0	-	endothermic	–96.15*
		II	238.0	-	endothermic	
		III	274.3	271.8	exothermic	
	320.0^{0}C-600.0^{0}C	IV	525.2	502.3	exothermic	–2.66

ΔT = temperature range; RT = room temperature; T_m(DTA) = temperature corresponding to minimum or maximum of DTA peak; T_m(DTG) = temperature corresponding to minimum of DTG peak; * mass loss in the temperature range RT – 320^{0}C

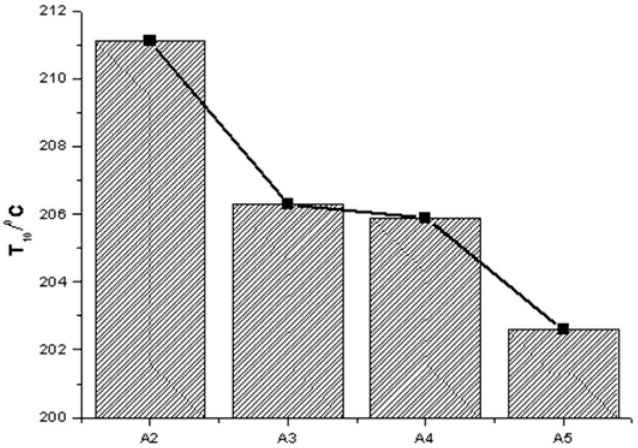

Fig. 3. The change of T_{10} of oil A2 after long-time operation in electrical transformers; A3 (34 years); A4 (27 years); A5 (30 years)

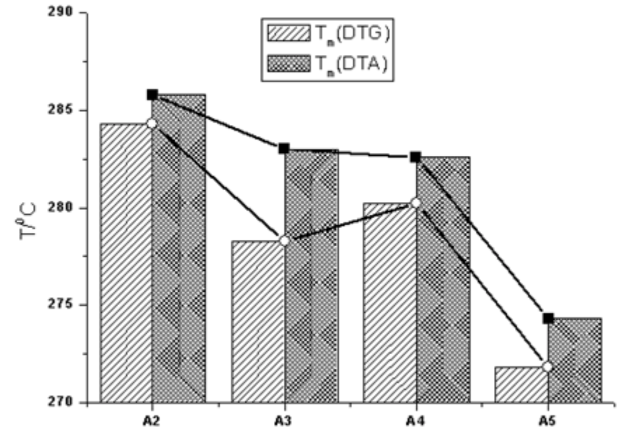

Fig. 4. The changes of T_m(DTG) and T_m(DTA) by operating of oil A2 in electrical transformers; A3 (34 years); A4 (27 years); A5 (30 years)

parameters. In other words, the exhausted oils exhibit lower thermo-oxidative stabilities than the fresh oil A2. This could be explained by the complex degradation processes of oil that occur by its operation in electrical transformers during 27 – 34 years.

We consider that the stability of transformer oil is affected by several complex processes occurring in dielectric medium under action of heat and high voltage. The most important process of deterioration is thermo-oxidation that leads to formation of gaseous compounds (volatile hydrocarbons, carbon monoxide, carbon dioxide), liquid compounds (alcohols, aldehydes, ketones, acids, resins, water) and solid compounds (asphalts and carbenes) [18]. FTIR analyses performed by Degeratu et al. [17] for fresh and degraded transformer oil TO 30.01 show that this oil used for 4.5 years also contains unsaturated compounds (in general compounds containing double bonds). Our determinations performed by X-ray fluorescence spectroscopy (XRF) show that the sulfur content of fresh oil A2 increases from 0.04% to 0.14 – 0.15% by its operating in electrical transformers. This increase is due to absorption of sulfur from rubber seals of transformer during the use of oil. The existence of carbon double bonds and sulfur in exhausted oil leads to increase its cross-linking degree and, consequently, to increase of number of sites reactive in oxidation. The process is similar with the thermo-oxidative reactivity increase of polymer materials with the increasing substitution obtained by cross-linking [19]. This explains why the temperature of thermo-oxidation for A3, A4 and A5 oils is shifted at lower values after operating in electrical transformers.

Refined edible oil (oil B)

The oil B is a refined vegetable oil produced from sunflower seeds, containing mostly triacylglycerols (more than 98 wt% [20]).

The results of thermal analysis of the investigated refined edible oil (oil B) are shown in figure 5. We observed that the obtained TG and DTG curves are similar to those recently reported for some vegetable oils by Dos Santos Politi et al. [21].

As can be seen from figure 5, the thermo-oxidation of oil B occurs in five stages, noted by I – V in this figure. In the first stage (I), alkyl radicals are formed and then react with oxygen to form solid hydroperoxides. This reaction, which occurs together with a small increase of sample mass (0.07 wt%), is directly related to the degree of unsaturation of fatty products. The atmospheric oxygen interacts with C-H bond from the allylic position (site C-H bonds adjacent to double bond), and the resulting hydroperoxides are susceptible to cross-linking reactions (fig. 6). This stage is

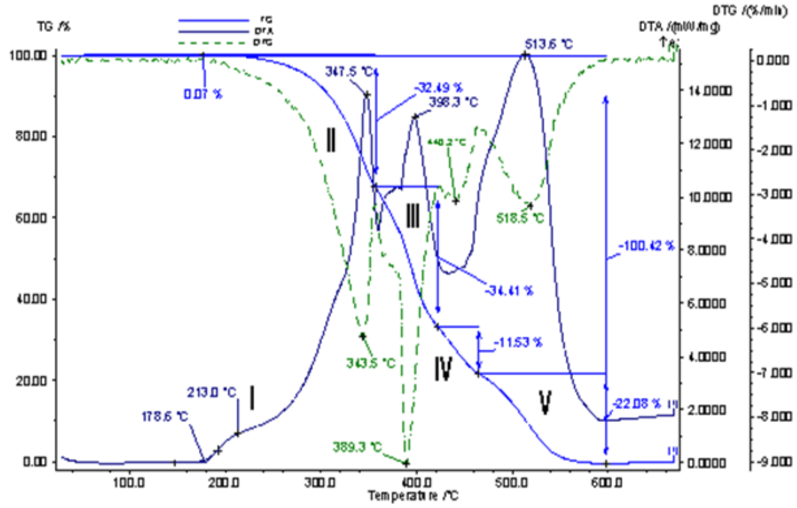

Fig. 5. TG, DTG and DTA curves corresponding to oil B

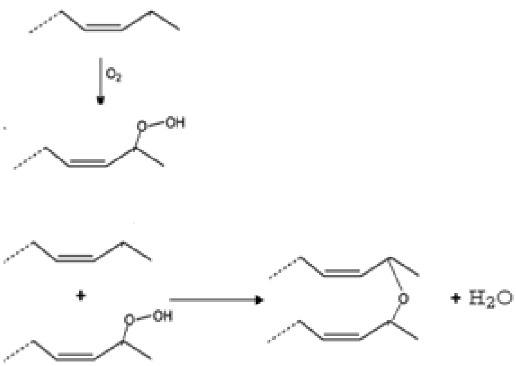

Fig. 6. The mechanism of stage I of thermo-oxidation of vegetable oil

Table 2

CHARACTERISTIC PARAMETERS OF NON-ISOTHERMAL THERMO-OXIDATION OF OILS B, C AND D

Oil	ΔT [⁰C]	Process	T_m(DTA) [⁰C]	T_m(DTG) [⁰C]	Thermal effect	%Δm [%]
B	178.6-≈242.0	I	213.0	-	exothermic	+0.07
	≈242.0-342.0	II	347.5	342.5	exothermic	-32.49
	342.0-420.8	III	398.3	389.3	exothermic	-34.41
	420.8-460.3	IV	435.0	440.2	endothermic	-11.53
	460.3-600.0	V	513.6	518.5	exothermic	-22.08
C	170.0-433.0	I	289.4	283.4	exothermic	-97.11*
		II	306.7	-	exothermic	
		III	336.9	-	exothermic	
	433.0-540.0	IV	507.5	500.0	exothermic	-2.69
D	212.0-260.0	I	249.4	244.3	exothermic	-4.19
	260.0-≈360.0	II	299.7 321.4	331.0 350.0	exothermic	-40.43
	≈360.0-398.0	III	375.9	373.0	exothermic	-16.80
	398.0-429.0	IV	420.2	418.0	exothermic	-15.33
	429.0-583.0	V	480.3 518.0	517.1	exothermic	-22.83

The meaning of ΔT, T_m(DTA) and T_m(DTG) are given at the bottom of table 1.
* mass loss in the temperature range 170.0 – 433.0⁰C

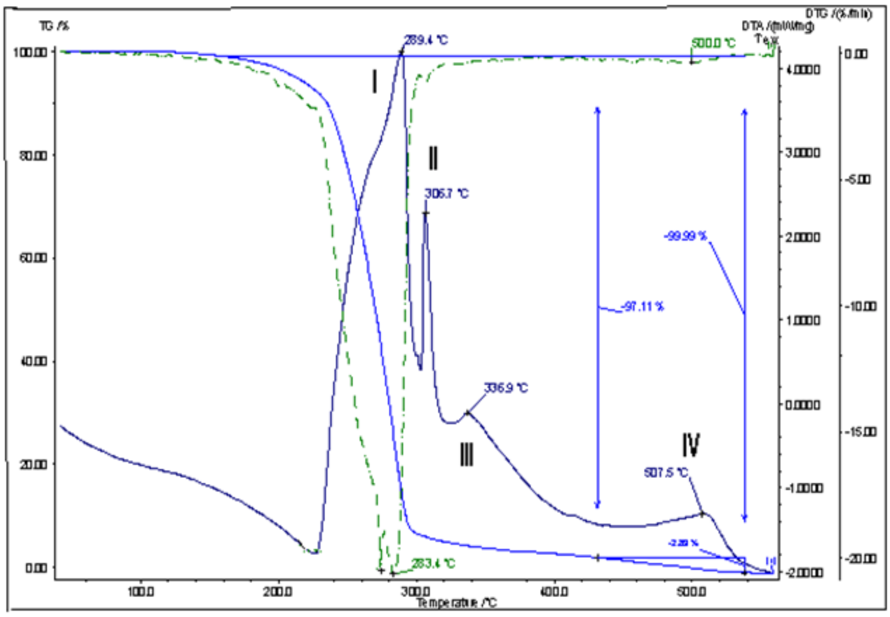

Fig. 7. TG, DTG and DTA curves corresponding to oil C

followed by other four stages of thermo-oxidation with formation with gaseous compounds (stages noted by II – V in fig. 5). The characteristic parameters of non-isothermal thermo-oxidation of oil B are listed in table 2. According to these results, the oil B is stable until 179⁰C limiting temperature.

Oil based on synthetic esters (oil C)

Figure 7 shows the results obtained by thermal analysis in air atmosphere of oil C. It can be seen that the thermo-oxidation of this oil occurs in four stages, noted by I – IV, which are accompanied by formation of gaseous compounds. The characteristic parameters of these stages are also listed in table 2. According to these results, the oil

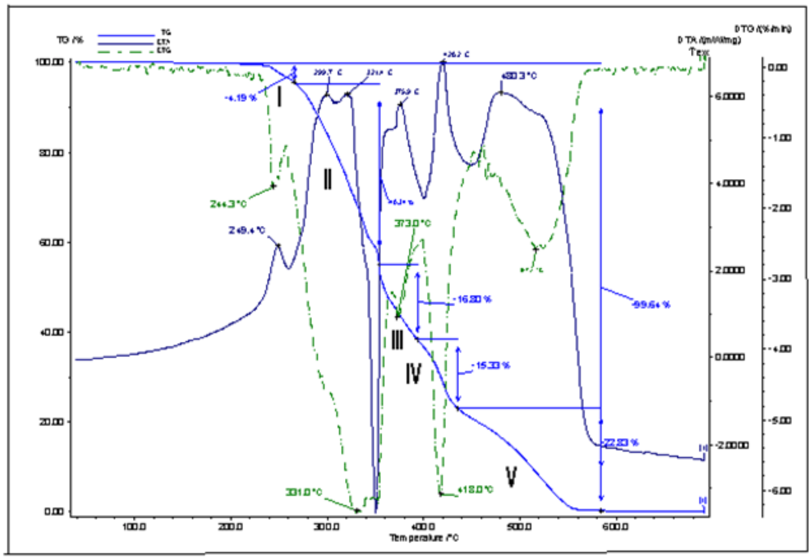

Fig. 8. TG, DTG and DTA curves corresponding to oil D

C is stable until 170^{0}C which is an allowed limiting temperature.

Oil based on natural esters (oil D)

TG, DTG and DTA curves corresponding to oil D are presented in figure 8. It was obtained that the following successive processes occur at the progressive heating of oil D in air: an initial exothermic process with formation of liquid compounds (probably hydroperoxides) followed by their decomposition and/or thermo-oxidation, noted by I in figure 8, and successive four exothermic processes with formation of gaseous compounds, noted by II – V in figure 8. The characteristic parameters of these stages are also listed in table 2. According to these results, we can stated that the oil C is stable until 234^{0}C.

Conclusions

The simultaneous TG/DTG + DTA thermal investigation was successfully used for assessment the thermal stabilities in air of the following oils: a new oil - *Nytro Taurus*, a new oil - *TO 30.01*, a refined edible sunflower oil, an oil based on synthetic esters - *Luminol Tri 205 L* and an oil based on natural esters - *BIOTEMP*. The onset temperature of the first process during thermo-oxidation was considered as characteristic stability temperature. For the investigated oils the following values of stability temperature were obtained: 90^{0}C for mineral oils *Nytro Taurus* and *TO 30.01*; 179^{0}C for refined edible sunflower oil; 170^{0}C for oil based on synthetic esters - *Luminol Tri 205 L*; 234^{0}C for oil based on natural esters – *BIOTEMP*, respectively.

One notes that the biodegradable refined edible sunflower oil exhibits a thermo-oxidative stability substantially greater than the mineral oils used in present in electrical transformers. Therefore, it seems to be possible obtained by purification of any vegetable environmental friendly oil and it may be useful in electrical equipments.

The simultaneous TG/DTG + DTA technique was also used for assessment of the changes of thermal properties for the mineral oil *TO 30.01* as a result of its operating in some electrical transformers. It was observed that the thermo-oxidative stability of the exhausted mineral oil is lower than of the fresh oil. This was explained by the cross-linking process occurring during after long period of the use of this oil.

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