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STUDIES ON THE EFFECTS OF OLIVE OIL OXIDATION

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ABSTRACT

The aim of this study is the viscosity’s evolution depending on the temperature and the shear rate and the analysis of the transmittance spectra of the oxidized olive oil. Oxidation of olive oil is a process that leads to the degradation of the sensorial qualities (color) and generates compounds such as peroxides and aldehydes. Studies performed in order to determine olive oil transmittance have shown that this method can be successfully used for the analysis of vegetable oils oxidation, oils that are going to be used as lubricants in food industry. Olive oil oxidation becomes more obvious by determination of trichromatic parameters. Thus it has been proved that by using this method, conclusive results regarding olive oil oxidation are obtained.

KEYWORDS: viscosity, transmittance, oxidation, olive oil

1. Introduction

Recently, lubricants based on vegetable oil which are biodegradable are bit by bit reducing the field application of mineral oil. Biodegradable lubricants will be used more as they are less damageable and toxic to the environment. This will be an important factor in the agriculture and food industry where there are possibilities of lubricant leakage [1].

A high percentage of at least 65% of 16 to 22 carbon fatty acids is required in order for the base oil to provide adequate lubrication. Longer chain fatty acid sources are preferred to provide longevity to the oil. Preferred sources of long chain fatty acids are from members of Cruciferae family, Compositae family and Leguminosae family. Common oilseeds in these families are: canola, rapeseed, crambe, sunflower, safflower, flax, and soybean. Other sources of the base oil include cotton, corn, olive, peanut and other common oils. Each base oil has unique functionality and lubricant formulations will vary depending upon base oil used, [2].

Vegetal oil oxidation is initiated by formation of free radicals. Free radicals can easily be formed from the removal of a hydrogen atom from the methylene group next to a double bond. Free radicals rapidly react with oxygen to form a peroxy radical. The peroxy radical can then attack another lipid molecule to remove a hydrogen atom to form a hydroperoxide and another free radical, propagating the oxidation process. The vegetable oil autooxidation mechanism presented here is a simplification of a complex series of reactions. The process is further complicated by variations in conditions, such as ultraviolet rays, temperature, pressure and oxygen availability, or by the presence of other compounds, such as antioxidants, chelating agents and metals. Metals, for example, act as a catalyst for the oxidation of vegetable oils speeding up degradation and the production of free radicals [3].

2. Experimental Details

The olive oil that was tested here had been purchased from a local store. This oil, according to the information provided by the analysis performed within Expur Slobozia labs, presents this compsition: 12.6% palmitic acid (C16:0), 79.3% oleic acid (C18:1), 4.7% linoleic acid (C18:2), 0.8% linolenic acid (C18:3), 0.4% arahidic acid (C20:0), 1.2% palmitoleic acid (C16:1) and very little percentage of heptadecanoic acid (C17:0), behenic acid (C22:0) and erucic acid (C22:1), as well. Transmittance spectrum determination was performed using a T60 spectrophotometer, produced by PG Instruments Limited (C.E.), the determinations were performed for the range of 300-1100nm. In order to reach a forced oxidation process, the equipment in Figure 1 was used. That is composed of 1-air pump, 2-air flowmeter, 3- air filter, 4-oil sample tube, 5-thermostatic bath. For every test oxidation 25 ml of oil were used. The flow rate of air introduced into the oil sample was 20 L/h.

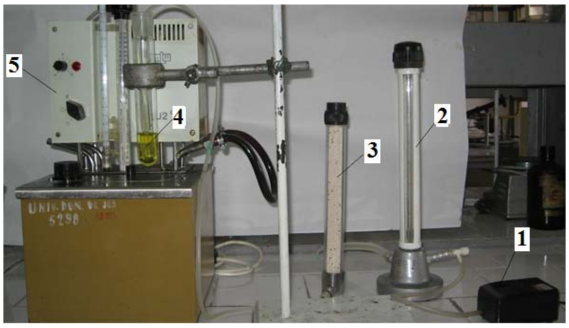

***Fig. 1.** Oxidation equipment*

Also, the samples were measured for colour in the x, y, z or L*, a*, b* and C*, h_{ab} coordinates (CIEXYZ, CIEL a*b* and CIEC$_{ab}$*h$_{ab}$ colour systems). CIE L*a*b* scale is recommended by the Commission Internationale de l'Eclairage (CIE), were b* measures the yellowness when it is positive, the grayness when zero, and the blueness when negative. In this colour space L* represents the lightness. Illumination was performed by C/2° (standard illuminant defined by CIE).

Chroma values denote the saturation or purity of colour. Hue angle values (exprimate in grade) represent the degree of redness, yellowness, greenness and blueness [4].

Dominant wavelength, λ_d was determined as described according to CIE indications [5], [6]. Forced oxidation behavior research of the oxidized and non-oxidized rapeseed oils give us qualitative and quantitative estimations regarding their efficiency in use as lubricants. Trichromatic values are obtained according to Tristimulus Colorimetry method, in the case of oils by determination of the transmittance according to the relations:

$$X = 0.21 \cdot T_{445} + 0.35 \cdot T_{550} + 0.42 \cdot T_{625}$$
$$Y = 0.17 \cdot T_{445} + 0.63 \cdot T_{550} + 0.20 \cdot T_{625} \qquad (1)$$
$$Z = 0.94 \cdot T_{445} + 0.24 \cdot T_{495}$$

where T is the transmittance measured by the spectrophotometer, when λ is 445, 495, 550 and 625nm [7], [8].

3. Experimental Results

Oxidizing the olive oil at a temperature of 100°C for 5hours and 10hours, no changes in shape of the transmittance spectrum were shown. Thus, for evidence of changes in the transmittance spectrum of olive oil shape, this oil was oxidized for 5hours or 10hours at 110ºC and 130ºC (Figure 2 and 3). The shape of spectrum for non-oxidized olive oil is similar to that presented by other authors in the specific literature [9] for other varieties of olive oil.

In Figure 2 and 3 it is noted that the spectra shapes of olive oxidized oil at 100ºC for 5 or 10 hours, weren't changed too much compared to reference oil.

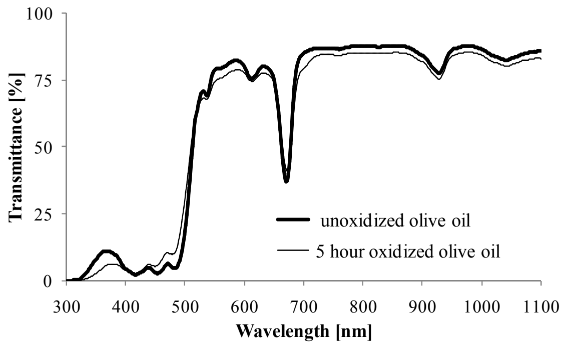

***Fig. 2.** Transmittances of unoxidized and oxidized olive oils for 5 hour at a temperature of 110°C*

By comparing the absorpsion spectra of olive oil while oxidation, there are highlighted its hypochromic displacements between 450nm and 470nm respectively up to 662nm and hypochromic displacements to 520nm and 640nm.

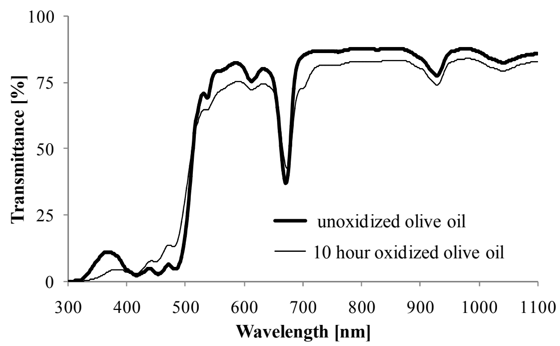

***Fig. 3**. Transmittances of unoxidized and oxidized olive oils for 10 hours at a temperature of 110°C*

It was also performed the study of olive behaviour during oxidation, regarding the evolution of cromatic parameters at variations of oxidation temperature, using different color systems.

Thus, in Tables 1 and 2 there are shown the experimental results related to olive oil oxidation at the temperature of 110ºC for different oxidation periods of time. Olive oil color parameters, shown in these tabels are given by *X, Y, Z* tristimulus values or by *x*, *y*, *z* trichromatic coordonates.

Trichromatic measurements are highlightning a decrease of luminosity by 2.65% comparing to unoxidized olive oil (ΔL^* = -2.272 at 110ºC). On the other hand, vegetable oils also have their own aromatic systems which make the particular being eventually present even after tough treatements. Meanwhile it is to be taken into account that color intensity varies similarly to the variation of luminosity. It is also noted that this color variation of 110ºC oxidized olive oil is sustained by the hue angle too, presenting a more restricted value range.

Increasing the oxidation temperature from 110ºC to 130ºC, important changes of transmittance occur, for olive oils that were oxidized for 5 or 10hours (Fig.4 and 5).

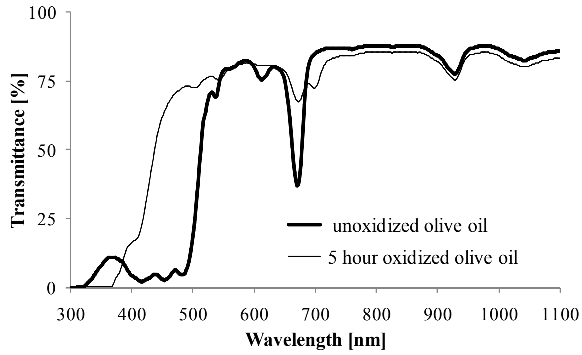

Fig. 4. *Transmittances of unoxidized and oxidized olive oils for 5 hour at a temperature of 130°C*

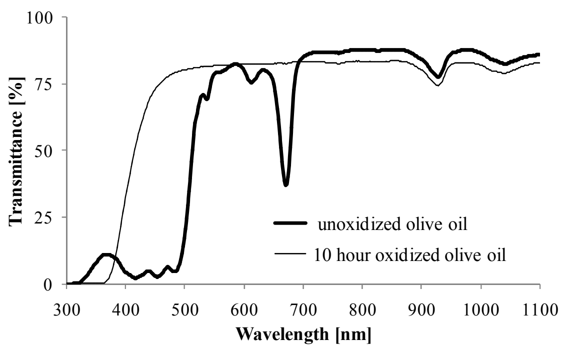

Fig. 5. *Transmittances of unoxidized and oxidized olive oils for 10 hour at a temperature of 130°C*

It is noted the oxidized oil spectra displacement to ultraviolet range. At the same time it is revealed an important decrease, even the disappearing of initial spectrum peaks corresponding to unoxidized olive oil, after an oxidation period of time of 5 or 10hours, at 130ºC temperature. As a result of oxidation, the peaks related to the presence of carotenoids and those related to chlorophyll as well disappear, due to the destruction of the pigments responsible for the color of oil.

Table 3 presents trichromatic compounds and coordinates, respectively the dominant wavelengths determined by the latter, for 130ºC oxidized olive oil. It is noted that oxidation process leads to displacements of the dominant wavelength, which is decreasing with oxidation time, from 575nm to 559.5nm. The experimental data also show a close connection between chromatic parameters as the luminosity, displacement from red to yellow, chroma and tonality angle and oxidation temperature/time.

In the case of 130ºC oxidation too, the yellow rate and chroma are the parameters which prevail for a comparative evaluation of olive oil behaviour (Table 4). After a period of time of 10 hour oxidation it is noted a slight increase (about 8%) of luminosity, which is in accordance with the information that other authors have previously shown [9].

At the same time, color differences that were presented in Table 5 are corresponding to the information provided by the measured parameters.

According to the data presented in Table 5 it is highlighted that the luminosity of 110ºC oxidized oil for 5 or 10 hours, is decreasing. This aspect is the result of the minus sign of the luminosity value differences. Meanwhile, the luminosity of 130ºC oxidized oil for 5 or 10 hours, is increasing. This aspect is the result of the positive values of the luminosity differences values.

The same variations are noticed regarding other important trichromatic parameters differences, as the yellow grade or chroma. It should be specified that these variations occur, in addition for the case of olive oil oxidized at 130°C. In the case of the latter we can notive that after a maximum period of time of oxidation, under the experimental conditions, the difference of the yellow grade is wider compared to that obtained in the case of 110ºC oxidized oil. This is due to the destruction of the most of the chromophores present in the original oil.

Color differences expressed by L^*, b^* and C^*_{ab} parameters are also supported by the hue angle h_{ab} . The values for h_{ab} differences for oxidized oil at 110ºC and the oxidized oil at 130ºC as well, after 5 and 10 hour oxidation time period, are positive in all cases. This result shows that the position of olive oil color being subject of this experiment is moving within the same quadrant in chromatic circle, counter clockwise, towards the hues of yellow green. This occurs due to the fact that during forced oxidation hydroperoxides are formed too because of the composition of olive oil containing just a little quantity of polyunsaturated acids (the quantity of linolenic acid is 0.8% while the studied olive oil contains 4.7% linoleic acid).

The color difference is very important considering the cumulated contribution of chromatic parameters. In this context, the data in Table 5 show large and even very large differences in the color of olive oil that occur during its oxidation, expressed by parameter ΔE^*_{ab} (ΔE^*_{ab}>10). According to enshrined data in literature and industrial practice [5], [10], the values of the color differences are used for chromatic significance interpretation. It is accepted in standards that if $\Delta E^*_{ab} < 0.2$ then the difference of color is not perceivable; by visualisation it is hardly noticed if $0.2 < \Delta E^*_{ab} < 0.5$, but it becomes perceivable if $\Delta E^*_{ab} = 0.5 – 1.5$, and easily to be observed when $\Delta E^*_{ab} = 1.5 – 3.0$. In literature [10] it is mentioned that the differences of color when $\Delta E^* < 10$ are considered slight differences, and the color difference for $\Delta E^* > 10$ are considered big differences.

In Figure 6 and 7, the variations of viscosity with shear rate are represented, for olive oils oxidized at 120 and 130°C, testing temperature being 30°C.

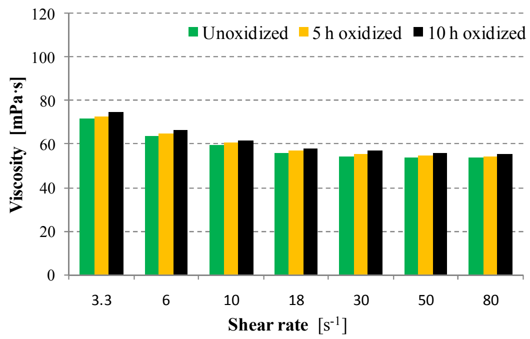

Fig.6. *Variation of viscosity with shear rate, for the unoxidized and oxidized olive oil at the temperature of 120°C*

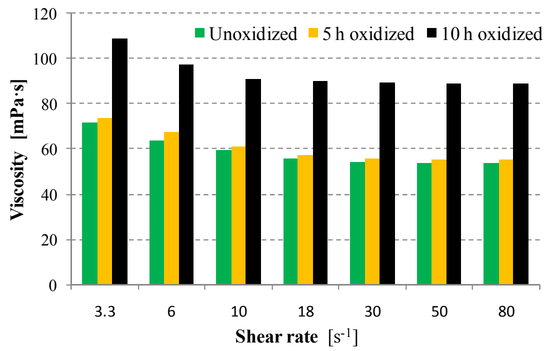

Fig.7. *Variation of viscosity with shear rate, for the unoxidized and oxidized olive oil at the temperature of 130°C*

Viscosity decreases with shear rate increase but this decrease is sharper when the values of the shear rate are in the range of 3.3 to $18s^{-1}$. Viscosity increases with oxidation temperature increase and the increase of oxidation period of time, important increases are observed in the case of oil that was oxidized for 10 hours at a temperature of 130°C.

In Figure 8 and 9 there are represented the variations of the viscosity with the temperature for olive oil that was oxidized at 120 and 130°C, and the variation of viscosity depending on the temperature for non-oxidized olive oil as well, at a shear rate of de $3.3s^{-1}$. Viscosity is decreasing when temperature is increasing, the same situation for both oxidation temperatures. It is noted a slight increase of the olive oil viscosity when oxidized at a temperature of 120°C for 5hours and 10hours compared to non-oxidized olive oil.

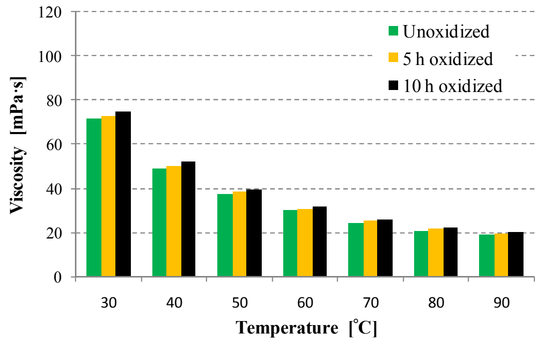

Fig. 8*. Variation of viscosity with temperature, for the unoxidized and oxidized olive oil at the temperature of 120°C*

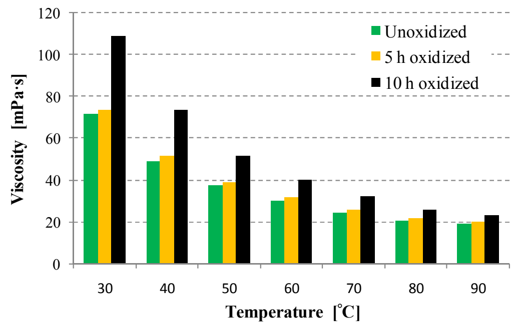

Fig. 9. *Variation of viscosity with temperature, for the unoxidized and oxidized olive oil at the temperature of 130°C*

When oxidation temperature is increasing one can notice a sharp increase of the viscosity for olive oil that was oxidized for 10 hours. Analyzing viscosity increases corresponding to the 10 hour oxidation period of time, at a testing temperature of 30°C, the viscosity of the oxidized olive oil increases by 51.51% compared to the viscosity of non-oxidized olive oil. At a 60°C testing temperature, the viscosity increase is 32.35% and at a temperature of 90°C the viscosity increased by 22.36%.

These significant increases in both viscosity variation with temperature and the variation with shear rate may be due to the fact that after oxidation of vegetable oils some chemical compounds could result, such as hydroperoxides, volatile substances, non-volatile substances, high weight molecular compounds and fatty acids.

4. Conclusions

Oxidation of olive oil is a process that leads to the degradation of the sensorial qualities (color) and generates compounds such as peroxides and aldehydes.

Some aspects regarding olive oil oxidation were clarified, for different temperatures and differend periods of time, usings pectrophotometric data analysis and Tristimulus Colorimetry method.

Studies performed in order to determinate olive oil transmittance showed that this method can be successfully used for the analysis of vegetable oils oxidation, oils that are going to be used as lubricants in food industry. Olive oil oxidation becomes more obvious by determination of trichromatic parameters. Thus it has been proved that by using this method, conclusive results regarding olive oil oxidation are obtained.

Viscosity variations with temperature and shear rate were determined both for oxidized and non-oxidized olive oils. A strong increase of the olive oil viscosity is observed, when olive oil was oxidized at a temperature of 130°C and for 10 hour period of time of oxidation. The increase of the viscosity represents an indicator of vegetable oil oxidation. Using these two methods, olive oil use parameters could be optimized at the industrial level.

***Table 1**. Experimental results for olive oils oxidized at a temperature of 110ºC*

Olive oil	*Trichromatic components*			*Trichromatic coordinates*			*λ_d [nm]*
	X	*Z*	*Z*	*x*	*y*	*z*	
Unoxidized	61.642	67.215	6.232	0.45631	0.49756	0.04613	575
5 hours oxidized	59.43	65.808	10.34	0.43834	0.48538	0.07626	574.5
10 hours oxidized	57.026	62.806	12.879	0.42969	0.47325	0.09704	574.2

***Table 2**. Chromatic characteristics for olive oils oxidized at 110°C - illuminant C/2º*

Olive oil	*Chromatic coordinates*			*a^*/b^**	*$(a^*/b^*)^2$*	*C^*_{ab}*	*h_{ab}*
	L^*	*a^**	*b^**				
Unoxidized	85.61242	-9.5804	100.1562	-0.0956	0.009151	100.6134	95.46
5 hours oxidized	84.89814	-11.688	85.12887	-0.1373	0.018853	85.92757	97.81
10 hours oxidized	83.34022	-10.7599	75.69697	-0.1421	0.020205	76.45787	98.09

***Table 3.** Experimental results for olive oils oxidized at a temperature of 130ºC*

Olive oil	*Trichromatic components*			*Trichromatic coordinates*			*λ_d [nm]*
	X	*Z*	*Z*	*x*	*y*	*z*	
Unoxidized	61.642	67.215	6.232	0.456307	0.497561	0.046133	575
5 hours oxidized	72.912	77.103	71.57	0.329048	0.347961	0.322991	562
10 hours oxidized	78.134	81.517	85.986	0.318087	0.33186	0.350053	559.5

***Table 4**. Chromatic characteristics for olive oils oxidized at 130ºC- illuminant C/2º*

Olive oil	*Chromatic coordinates*			*a^*/b^**	*$(a^*/b^*)^2$*	*C^*_{ab}*	*h_{ab}*
	L^*	*a^**	*b^**				
Unoxidized	85.61242	-9.5804	100.1562	-0.0957	0.00915	100.6134	95.46
5 hours oxidized	90.36901	-5.4215	14.09896	-0.3845	0.147869	15.10544	111.03
10 hours oxidized	92.36127	-3.4411	6.854868	-0.502	0.251991	7.670076	116.66

Table 5. *Experimental values of color differences when studied olive oils during forced oxidation - illuminant C/2º (unoxidized – 5 hour forced oxidation, unoxidized – 10 hour forced oxidation)*

Olive oil	*Time [hours]*	ΔL^*	Δa^*	Δb^*	ΔC^*_{ab}	Δh_{ab}	ΔE^*_{ab}
Oxidized oil to 110ºC	5	-0.72	-2.1	-15.03	-14.69	2.35	15.19
	10	-2.272	-1.179	-24.46	-24.16	2.63	24.59
Oxidized oil to 130°C	5	4.75	4.16	-86.06	-85.51	15.57	86.29
	10	6.748	6.1394	-93.31	-92.95	21.2	93.75

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