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SOME PHYSICAL CHANGES IN EXTRA VIRGIN RAPESEED OIL AFTER THE OXIDATION PROCESS

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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 at the transmittance spectra of the oxidized rapeseed oil. Rapeseed oil was oxidized at the temperatures of 110°C, 120°C, 130°C, the periods of time of oxidation being 5 to 10 hours. An increase of viscosity depending on the increase of oxidation temperature and oxidation time is to be noticed. Increasing of the oxidation temperature and the period of oxidation is the cause of the progressing color difference of the oxidized oils compared to non-oxidized rapeseed oil.

KEYWORDS: transmittance, viscosity, oxidation, rapeseed oil

1. INTRODUCTION

At present, approximately 50% of all lubricants sold worldwide end up in the environment via total loss applications, volatility, spills or accidents. More than 95% of these lubricant materials are in nowadays based on mineral oils. Because of low eco-toxicity and biodegradation, these lubricants represent a significant threat for the environment, although these are efficient lubricants with very good tribological proprieties [1].

Due to environmental concerns and because of the law becoming more and more restrictive regarding the environment, a requirement has arisen for lubricants named "friendly" to the environment, with a negative impact as low as possible. In this context, oils obtained from vegetable oils are monitored by the experts in Tribology, their main advantages being relatively inexhaustible source, non-toxicity and biodegradability [2], [3], [4], [5]. The problem is that in addition to these advantages, the disadvantages are also to be taken into account: poor lubricating properties, oxidation instability.

Rapeseed (Brassica oleracea) plant has been grown since the sixteenth century, widly spread both in warmer climates and in the cold climates. Rape is ranked third in the world as a source of vegetable oil following palm oil and soybean oil. Rapeseed oil has a low content of saturated fatty acids (5-10%), a high content of monounsaturated fatty acids being a rich source of antioxidant compounds such as polyphenols, tocopherols, β-carotene, lutein, phytosterols etc.

Physico-chemical properties of rapeseed oil are: indicating active oxygen peroxide = 10 mmol / kg, the mass fraction of moisture and volatile matter = 0.15 to 0.2%, relative density at 20ºC = 0.914 to 0.920, refractive index = 1.465 to 1.467, saponification number = 182-193 mg KOH/g oil, iodine value = 105-126 g I2/100 g [6], [7], [8], [9], [10], [11], [12].

Oxidation of fatty acids, also known under the name of rancid aldehydes, autoxidation or lipid peroxidation, involving radical reactions, is characterized by: lowering the reaction rate of the chemical species which interact with free radicals that occur, massive formation of hydroperoxides (ROOH), yield that exceeds unity, where oxidation takes place under the influence of light, high induction period when substrate is pure.

Oxidation stability of vegetable oils is mainly limited to the double bonds of unsaturated carbon-carbon unsaturated bonds being the cause of many reactions, including the oxidation [13], [14].

Most of the plant oils contain unsaturated fatty acids and are susceptible to oxidation. The higher unsaturation level is more exposed to oxidation than the vegetable oil is [15], [14].

2. EXPERIMENTAL DETAILS

Determination of transmittance spectrum was performed the using a spectrophotometer type T60 produced by PG Instruments Limited (EC), determinations were realized in a range of 300-1100 nm.

To perform forced oxidation process, a system was built in Figure 1. It is composed of 1 - air pump, 2 - air flow meter 3 - air filter, 4 - tube with the sample of oil, 5 - thermostatic bath. For each oxidation test 25 ml of oil were used. The flow rate of air introduced into the oil sample was 20 l/h.

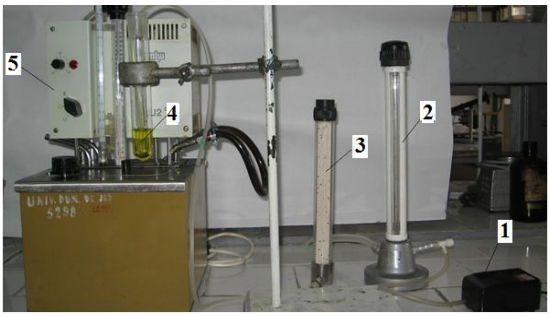

Fig. 1. Oxidation equipment

Also, the samples were measured for colour in the x, y, z or L*, a*, b* and C*, h_{ab} coordinates (CIEXYZ, CIE $L^*a^*b^*$ and CIE $C_{ab}{}^*h_{ab}$ colour systems). CIE L*a*b* scale is recommended by Commission Internationale de l'Eclairage (CIE), where 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 color. Hue angle values (expressed in grades) represent the degree of redness, yellowness, greenness and blueness [16]. Dominant wavelength, λ_d was determined as described according to CIE indications [17], [18]. 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 in the case of oils by determination of the transmittance according to the relations (1):

$$\begin{aligned} X &= 0{,}21 \cdot T_{445} + 0{,}35 \cdot T_{550} + 0{,}42 \cdot T_{625} \\ Y &= 0{,}17 \cdot T_{445} + 0{,}63 \cdot T_{550} + 0{,}20 \cdot T_{625} \\ Z &= 0{,}94 \cdot T_{445} + 0{,}24 \cdot T_{495} \end{aligned} \quad (1)$$

where T is the transmittance measured by the spectrophotometer, when λ is 445, 495, 550 and 625 nm [19], [20].

Viscosity was determined by Rheotest2 system, shear rates ranging between 3.3 and 80 s^{-1}, the test temperatures being between 30 and 90°C.

3. EXPERIMENTAL RESULTS

Oxidizing the rape seed oil at a temperature of 100°C for 5 hours and 10 hours, no changes in shape of the transmittance spectrum were shown. Thus, for evidence of changes in the transmittance spectrum of rapeseed oil shape, this oil was oxidized for 5 hours or 10 hours at 110 ° C and 130°C.

It is noted that the values of rapeseed oil transmittances oxidized for 5 hours and 10 hours at a temperature of 110°C (Fig. 2 and 3) do not change very much relatively to the non-oxidized oil transmittance.

Chromaticity parameters determined for oxidized rapeseed oil at 110°C, shown in Tables 1 and 2, certify the presence or absence of macrocyclic pyrrole pigments dyes category.

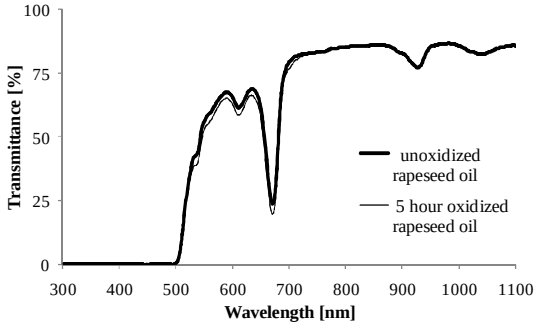

Fig. 2. Rapeseed oil transmittances oxidized for 5 hours at a temperature of 110°C

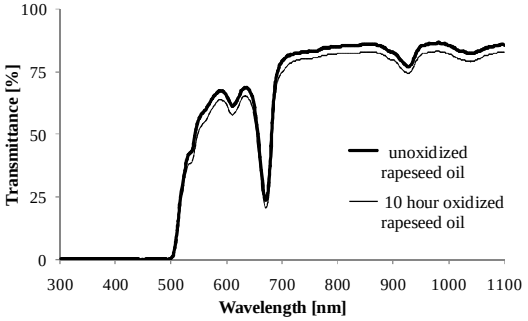

Fig. 3. Rapeseed oil transmittances oxidized for 10 hours at a temperature of 110°C

As shown in Table 1, while rapeseed oil oxidation at a temperature of 110°C, the dominant wavelength is ranging from 577.5 nm and 577.9 nm, values which correspond to the yellow-orange region in the chromaticity diagram. It is noted a very small difference between the dominant wavelength of the o 5 hour oxidized oils and those oxidized for 10 hours. As shown in Table 2, the parameter b* and brightness of the studied samples decrease as forced oxidation time increases. In this context, trichromaticity measurements show a decrease of 3.1% of the brightness comparing to the brightness of unoxidized rapeseed oil (ΔL^* = 2.32 at 110°C). Also, as far as, the value of the parameter a*, which is very small compared to the b* parameter, it is obvious that the rate of red will tend to subunit values.

Chroma decreases with increasing of the oxidation time of rapeseed oil at 110°C from 137.64 to 132.99.

On the other hand, according to the diagram chromaticity CIE 1976 (a*, b*) based on the information in Table 2, the angle of the hue changes depending on the time of oxidation in the second quadrant (90º - 180º) towards the first quadrant (0° - 90°), which is correlated with the variation of the other chromatic parameters. Raising the oxidation of the temperature from 110°C to 130°C, analyzing the spectrum of 5 hour oxidized oil (Fig. 4), the only significant change is observed in the wavelength range between 515 nm and 650 nm.

In the case of 10 hour oxidized oil (Fig. 5) significant changes occur in the range 450 nm - 718 nm.

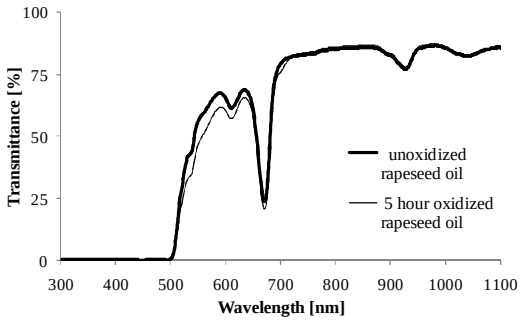

Fig. 4. Rapeseed oil transmittances oxidized for 5 hours at a temperature of 130°C

It is noted a greater range of values for the dominant wavelength of rapeseed oil after 10 hours of oxidation at 130°C, as compared to its value when the oil was oxidized at 110°C (Table 3).

The same observation is highlighted from the location of rapeseed oil color in the color chart through trichromatic coordinates x and y.

The color location of the rapeseed oil is well defined by the parameters a* and b* (Table 4) in the chromaticity diagram. According to this, the color of the oil is also located in quadrant I, as well as for its oxidation at 110°C for 5 and 10 hours.

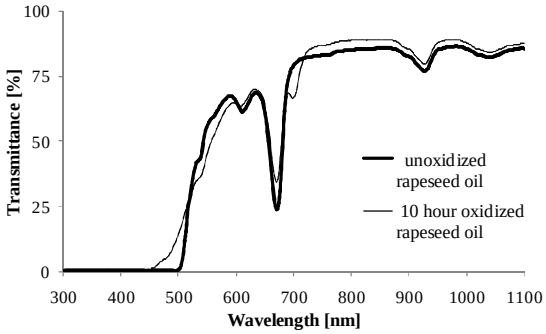

Fig. 5. Rapeseed oil transmittances oxidized for 10 hours at a temperature of 130°C

Also, from the data in Table 4, we notice the rapid decline of color intensity with oxidation, by changing chroma from 137.64 to 92.56.

Meanwhile, hue angle decreases after oxidation to pale yellow. These variations are due to destruction of the present chromophore in oil after oxidation, and also can be attributed to the slight amounts of peroxides resulted.

Based on the results above, color differences for each parameter analyzed were determined, by calculating the differences between the final value (10 hours of oxidation) and initial value (Table 5).

Trichromatic measurements point out decreases in brightness as compared to non-oxidized oil to both temperatures at which the experiments were carried out (ΔL^* = -2.319 to 110°C and ΔL^* = -2.938 to 130°C). Negative values of ΔL^* indicate a decrease in brightness after 5 and 10 hours of oxidation, due to the presence of formed peroxides. Much sharper turns out to be b* parameter variation. Thus, in the rapeseed oil after 10 hours of oxidation, the degree of yellow drops by about 3.5% (110°C) and 32.82% (130ºC). In this context the color difference values (ΔE^*_{ab}) are used in the interpretation of chromatic meanings. According to ΔE^*ab color differences when oils are oxidized at 110°C compared to the oxidized samples and initial samples, become perceptible and small ($\Delta E^*ab < 10$) while in the case of oxidized oils at 130°C they are large ($\Delta E^*ab > 10$).

As in the case of oxidation of rapeseed oil at a temperature of 110°C, the analysis of the change in chromatic parameters to its oxidation at a temperature of 130°C, leads to the same conclusion as the information provided by the

spectra of transmittance, regarding the reaction of the oil while oxidation. The effect of forced oxidation of rapeseed oil was underlined by determining the viscosity of rapeseed oil when non-oxidized and oxidized at 120 and 130°C, oxidation periods being 5 hours and 10 hours.

In this regard, rapeseed oil viscosity determinations were carried out at a temperature of 120°C because at this temperature the experimental results are similar to those obtained at 110°C.

In Figures 6 and 7 there are represented the variations of viscosity with shear rate for rapeseed oxidized oils at a temperature of 120 and 130°C, the test temperature being 30°C.

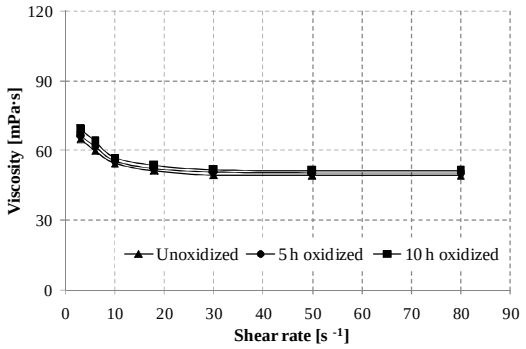

Fig.6. Variation of viscosity with shear rate for oxidized rapeseed oil at 120°C

Viscosity decreases with increasing shear rate, a significant decrease is noticeable in the case of small shear rates (3.3-18s^{-1}). Increasing shear rate viscosity variation is insignificant. This observation is valid for both oxidation temperatures. At the oxidation temperature of 120°C are not observed any significant increases in viscosity while increasing the oxidation time compared to non-oxidized oil. Increasing the oxidation temperature from 120 to 130°C a large increase in 10 hour oxidized oil viscosity is observed comparing to non-oxidized rapeseed oil.

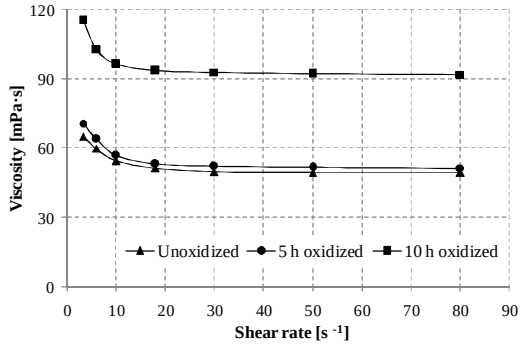

Fig 7. Variation of viscosity with shear rate for oxidized rapeseed oil at 130°C

This increase is explained by the formation of peroxides and hydroperoxides which causes the emergence of nonvolatile compounds (dimers, trimers, and higher molecular weight compounds) [14], a classical representation of an autoxidation mechanism of vegetable oils is shown in Table 6 [21], [22], [23], [14].

Table 6. Autoxidation mechanism of vegetable oils [14]

Stage	The chemical reaction
Initiation	$RH \Rightarrow R^* + H^*$
Propagation	$R^* + O_2 \Rightarrow ROO^*$ $ROO^* + RH \Rightarrow ROOH + R^*$
Branching	$ROOH \Rightarrow RO^* + O^*H$ $RO^* + RH + O_2 \Rightarrow ROH + ROO^*$ $O^*H + RH + O_2 \Rightarrow H_2O + ROO^*$
Termination	$ROO^* + ROO^* \Rightarrow ROOH + O_2$ $ROO^* + R^* \Rightarrow ROOH$ $R^* + R^* \Rightarrow R\text{-}R$

In Figures 8 and 9 it is shown the variation of viscosity with temperature for non-oxidized and oxidized rapeseed oil at 120°C and 130°C for 5 and 10 hours, shear rate 30s^{-1}. Viscosity decreases with increasing temperature for all oil samples for both test periods.

For all analyzed oils it is noted a sharp drop of viscosity in the temperature range between 30 and 60°C.

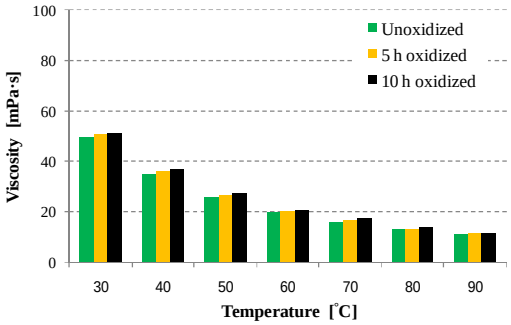

Fig. 8. Variation of viscosity with temperature for oxidized rapeseed oil at the temperature of 120°C

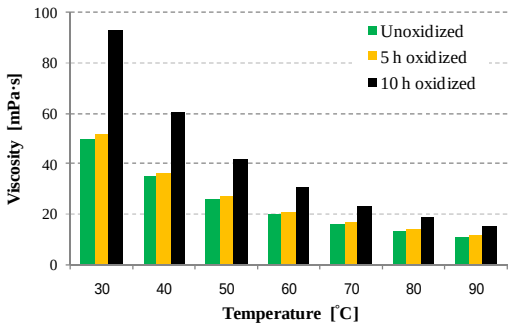

Fig. 9. Variation of viscosity with temperature for oxidized rapeseed oil at the temperature of 130°C

In the case of oxidized oils at 120°C temperature are not observed any significant increases in viscosity comparing to non-oxidized oil. A large increase of viscosity takes place in the case of rapeseed oil if oxidated at a temperature of 130°C for 10 hours as compared to non-oxidized oil. Thus at the test temperature of 30°C oxidized oil viscosity increases by 87.5% compared to non-oxidized rapeseed oil viscosity. At a test temperature of 60°C the viscosity increased by 57.42% and at a temperature of 90°C the viscosity increased by 37.8%.

4. CONCLUSIONS

Using spectrophotometric analysis of oils, oxidized in various conditions, it was found changing of the transmittance spectra and chromatic parameters. Increasing temperature and oxidation period then color differences of oxidized oils comparing to non-oxidized oils, are increasing too.

The analysis of the evolution of viscosity with temperature and shear rate of oxidized oil also shows that this parameter is a measure of oil oxidation. Viscosity decreases with increasing of the temperature and increasing of shear rate. Following viscosity tests it was observed a viscosity increase with increasing of the oxidation temperature and oxidation period of time.

Evaluation of viscosity with temperature and shear rate correlated with the analysis of the transmittance variation, respectively tri-chromatic analysis, shows that these parameters are good indicators of oil oxidation.

Table 1. Experimental results for rapeseed oils oxidized at a temperature of 110ºC - color system CIEXYZ / illuminant C/2º

Rapeseed oil	*Trichromatic components*			*Trichromatic coordinates*			λ_d *[nm]*
	X	*Z*	*Z*	*x*	*y*	*z*	
Unoxidized	47.85	48.97	0.118	0.493615	0.5051	0.00121	577.5
5 hour oxidized	45.66	46.31	0.13	0.495741	0.5028	0.001411	577.8
10 hour oxidized	44.77	45.34	0.13	0.496174	0.5023	0.00144	577.9

Table 2. Chromatic characteristics (systems: CIELAB, CIELCH) for rapeseed oils oxidized at 110°C - illuminant C/2º

Rapeseed oil	*Chromatic coordinates*			a^*/b^*	$(a^*/b^*)^2$	C^*_{ab}	h_{ab}
	L^*	a^*	b^*				
Unoxidized	75.433	-0.385	137.644	-0.00279	0.000008	137.64	90.1603
5 hour oxidized	73.749	0.771	134.084	0.00575	0.000033	134.088	89.5712
10 hour oxidized	73.114	0.995	132.99	0.007484	0.000056	132.994	87.5712

Table 3. Experimental results for rapeseed oils oxidized at a temperature of 130ºC - color system CIEXYZ / illuminant C/2º

Rapeseed oil	*Trichromatic components*			*Trichromatic coordinates*			λ_d *[nm]*
	X	*Z*	*Z*	*x*	*y*	*z*	
Unoxidized	47.8520	48.9720	0.11800	0.493615	0.505168	0.001217	577.5
5 hour oxidized	42.9310	42.2270	0.11800	0.503436	0.495180	0.001384	578
10 hour oxidized	44.9750	44.4010	3.204	0.485796	0.479596	0.034608	578.2

Table 4. Chromatic characteristics (systems: CIELAB, CIELCH) for rapeseed oils oxidized at 130ºC - illuminate C/2°

Rapeseed oil	*Chromatic coordinates*			a^*/b^*	$(a^*/b^*)^2$	C^*_{ab}	h_{ab}
	L^*	a^*	b^*				
Unoxidized	75.433927	-0.38513	137.64465	-0.00279	0.000008	137.64519	90.1603
5 hour oxidized	71.027169	4.621802	130.04679	0.03554	0.001263	130.1289	87.9646
10 hour oxidized	72.495738	4.225183	92.466	0.045694	0.002088	92.56248	87.3837

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

Rapeseed oil	*Time [hours]*	ΔL^*	Δa^*	Δb^*	ΔC^*_{ab}	Δh_{ab}	ΔE^*_{ab}
Oxidized oil to 110ºC	5	-1.68	1.15	-3.56	-3.56	-0.5891	4.1
	10	-2.319	1.381	-4.6545	-4.65133	-2.589	5.38033
Oxidized oil to 130ºC	5	-4.41	5.0	-7.6	-7.52	-2.1957	10.10
	10	-2.938	4.6103	-45.1787	-45.0827	-2.777	45.5082

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