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EFFECT OF OXIDATION ON SPECTROPHOTOMETRIC AND RHEOLOGICAL PARAMETERS OF CORN OIL

Liviu Cătălin ŞOLEA, Romică CREŢU
“Dunărea de Jos” University of Galaţi, 111, Domnească Street, 800201, Galaţi, Romania
email: liviu.solea@yahoo.com

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 corn oil. Corn oil was oxidized of the temperatures of 100°C, 110°C, 120°C, the periods of time of oxidation being 5 to 10 hours. An increase of the 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 comparing to non-oxidized corn oil.

KEYWORDS: transmittance, corn oil, viscosity, shear rate

1. Introduction

Vegetable oils are composed to an extent of 98-99% by fatty acids whose characteristics vary according to the number of carbon atoms, the number of double bonds between carbon atoms and position of these bonds in the fatty acid molecule.

Groups of fatty acids are:

-saturated acids (no double bonds) - myristic acid, palmitic, stearic and so on;

-monounsaturated acids (only one double bond) - oleic acid, erucic acid;

-polyunsaturated acids (with more double bonds) - linoleic acid, linolenic acid;

-fatty species (radicals containing hydroxy, epoxy, etc.).

The most important fatty acids contained in vegetable oils are: oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), palmitic acid (C16:0) and stearic acid (C18:0)

Research has shown that oils with a high content of oleic acid (high oleic) are significantly more stable than those with a low content of oleic acid. Oils with long links between carbon atoms indicate a low friction and a low wear compared to oils which have short links between carbon atoms. Oils containing saturated compounds have improved stability to oxidation at high temperature and high pressure compared to the oils containing unsaturated compounds. Free fatty acids have a high degree of polarization and will have a slight reaction with metallic surfaces, forming a layer of adsorption [1], [2].

Corn oil is obtained from corn germs containing 20-30% oil and remaining from degerminating of corn for maize or from starch production, ethyl alcohol, etc. Refined corn germ oil has superior sensory properties, high content in essential fatty acids, being included in the group of dietary product because it helps to reduce cholesterol in the blood, it also has a low free acidity (maximum 0.3% oleic acid) and a low water content.

2. Experimental details

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

Viscosity was determined by Rheotest 2 system, shear rates ranging between 3.3 and 80s^{-1}, the test temperatures being between 30 and 90°C.

In a first stage we determined the transmittance spectra for non-oxidated corn oil then this oil has been undergone a forced oxidation process to different temperatures and periods of time of oxidation so as to establish the transmittance spectra. Corn oil was oxidized to 100°C and 110°C temperatures, the periods of oxidation time being 5 hours and 10 hours.

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.

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 Commission Internationale de l'Eclairage (CIE), were b* measures the yellowness when is positive, the grayness when zero, and the blueness when negative. In this colour space L* represents the lightness.

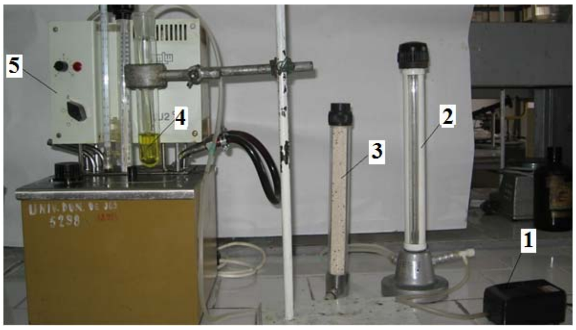

***Fig. 1.** Oxidation equipment*

Illumination was performed by C/2^o (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 in the case of oils by determination of the transmittance according to the relations:

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

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

3. Experimental results

Corn oil was oxidized at the temperatures of 100ºC and 110ºC for 5 or 10 hours. Transmittance spectra of corn oil oxidized at a temperature of 100ºC for 5 and 10 hours are shown in Figures 2 and 3.

It is noted that the transmittance values of 5 or 10 hour oxidized corn oil are not too much changed compared to the transmittance values of non-oxidized oil. Important changes occur for the range of wavelengths between 490nm and 590nm. On the other hand trichromatic parameters established for 100ºC oxidized corn oil, presented in the Tables 1 and 2, certify the presence or absence of the pigments from the macrocyclic pyrrole colorants category.

According to the data from the Table 1, while 100ºC corn oil oxidation, the dominant wavelength vary between 576.5nm and 579.5nm, values that are corresponding to the yellow-orange area in chromatic diagram.

It is noted a slight difference between the dominant wavelength of 5 hour oxidized oils and 10 hour oxidized oils. Oil oxidation can influence the trichromatic parameters beginning with a period of exposal of 5 hours.

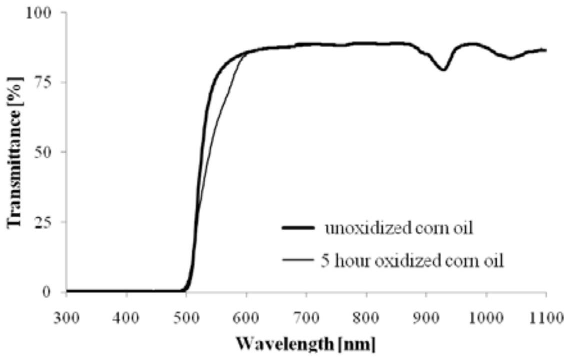

***Fig. 2**. Transmittances of unoxidized and oxidized corn oils for 5 hour at a temperature of 100°C*

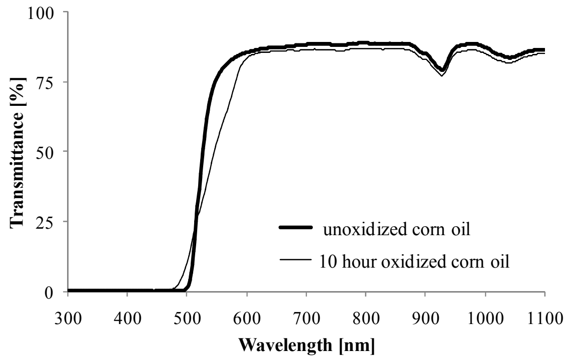

***Fig. 3**. Transmittances of unoxidized and oxidized corn oils for 10 hour at a temperature of 100°C*

As shown in Table 2, the parameter b* and brightness of the studied samples decrease as the time of forced oxidation increases. Thus, the trichromatic measurements show a decrease of 8.66% of the brightness compared to non-oxidized corn oil (ΔL^* = -7.35 on 100ºC), probably due to the chromophores destroyed by the effect of the oxygen. Also, the value of the parameter a^* is very small compared to the b^*

parameter, it is clear that the rate of red will tend to subunit values. Chroma, another trichromatic parameter, decreases with increasing of the time of oxidation for the corn oil at 100°C, from 150.41 to 111.95. On the other hand, according to the CIE 1976 (a^*, b^*) chromaticity diagram carried out according to the data from Table 1, the hue angle h_{ab} vary with the time of oxidation from 5 to 10 hours, in quadrant I (0-90 °) to lighter shades of yellow, which is correlated with variation of the other chromatic parameters, in order to elucidate the color change of corn oil during the oxidation. We notice the hue angle migration from the second quadrant of the chromaticity diagram (corresponding to the position of non-oxidized oil color) to the first quadrant (corresponding to oxidized oil).

Increasing the oxidation temperature from 100ºC to 110ºC (Fig. 4 and 5), it is noted that, in the visible area, there are important changes of the transmittance spectra, for 5 hour oxidized oil sample or for 10 hour oxidized oil sample as well. This thing shows that a 10ºC temperature increase, in the same experimental conditions, lead to a sharp oxidation of the corn oil.

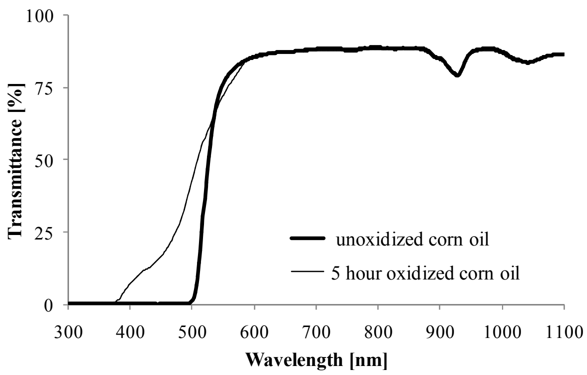

Fig. 4. *Transmittances of unoxidized and oxidized corn oils for 5 hour at a temperature of 110°C*

From Table 3 it is revealed a larger range of values for dominant wavelength of corn oil after 10 hours of oxidation, at 110ºC, compared to its values when the oil was oxidized at 100ºC (Table 1). Also, by color position location in chromatic diagram (trichromatic coordinates *x* şi *y*), we deduce the pronounced variability of the oil color in time. Also, corn oil color localization is well defined by the parameters a^* and b^* (Table 4).

According to these the color of this oil is localized in the quadrant II (90º - 180º), unlike the case when the oil is oxidized at 100ºC. Also, from the data in Table 4 it is revealed a rapid decrease of the color intensity while oxidation, by the variation of chroma from 150.41 to about 9. Meanwhile the angle hue is increasing in the quadrant II up to shades of yellow-green.

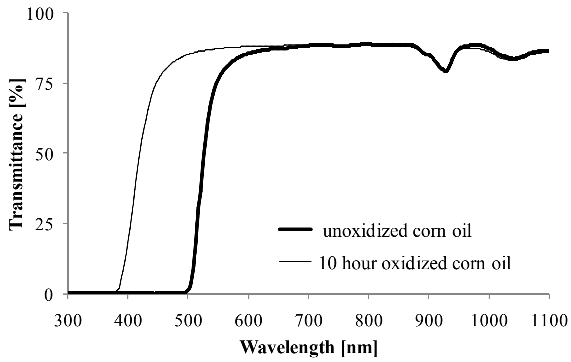

Fig. 5. *Transmittances of unoxidized and oxidized corn oils for 10 hour at a temperature of 110°C*

Based on the results above we determined the differences of color for each chromatic parameter analyzed, by calculating the color difference between the recorded values during 10 hour and 5 hour oxidation and the initial one (Table 5). Trichromatic measurements show an increase of brightness as compared to non-oxidized oil, to both periods of oxidation time for which the experiments were performed, ΔL^* = 2.03 after 5 hour oxidation time, or ΔL^* = 9.94 after 10 hour oxidation time at 110°C. This is due to the fact that even after 5 hour oxidation time are some of the oil pigments are destroyed, in 10 hour oxidation time peroxides and hydroperoxides are both formed in the stage of oxidation phenomena propagation.

Much sharper turns out to be b^* parameter variation by its decrease comparing to the initial sample. Thus, in corn oil case, the degree of yellow is decreasing with about 25.8% (100ºC) and 94.35% (110ºC). In the presence of oxygen, no matter the study temperature might be, the corn oil becomes a little yellow, meaning the grade of yellow is decreasing ($-\Delta b^*$). This occurs because, as a consequence of oxidation, oil pigments disappear, and the light corresponding to the blue area in the spectrum is less distributed than that corresponding to the yellow area (leading to a decrease of the yellow degree).

The hue angle (tonality angle) vary in a range of values much wider the oxidation temperature for corn oil increases (Table 5). As in the case of 100ºC oxidation of the corn oil, the analysis of the chromatic parameters at 110ºC oxidation, leads to the same conclusions as information provided by the transmittance spectra regarding oil oxidation reaction. Further on, using Rheotest 2 equipment, we determined the viscosities of oxidized corn oil and non-oxidized corn oil as well. In the graphs shown in Figures 6 and 7 there are represented the temperature variation with shear rate, for non-oxidized corn oil and oxidized corn oil at a temperature of 110°C and 120°C, the period of oxidation time being 5 and 10 hours respectively.

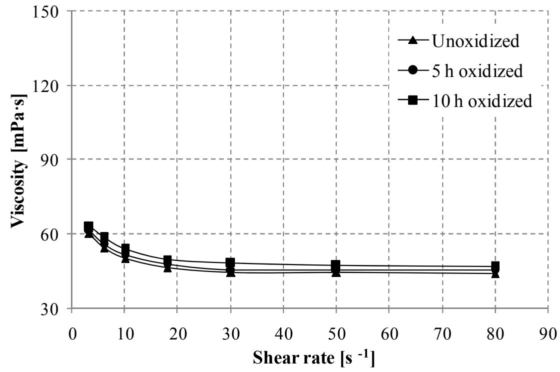

Fig.6. *Variation of viscosity with shear rate, for the unoxidized and oxidized corn oil at the temperature of 110°C*

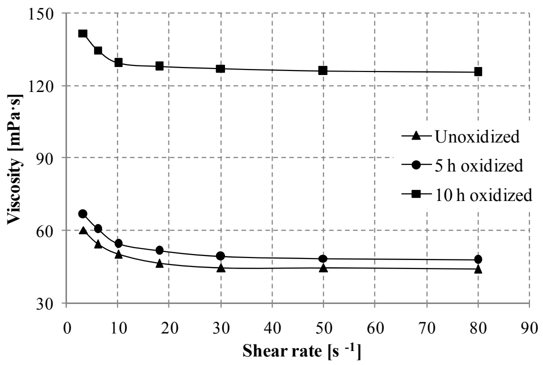

Fig.7. *Variation of viscosity with shear rate, for the unoxidized and oxidized corn oil at the temperature of 120°C*

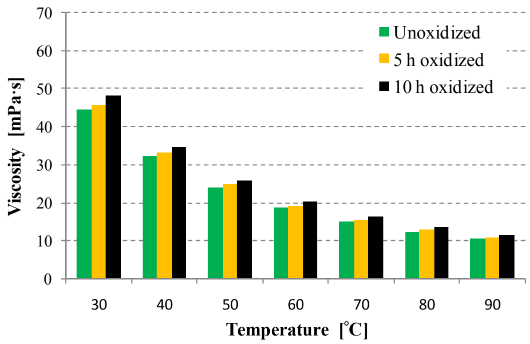

Fig. 8. *Variation of viscosity with temperature, for the unoxidized and oxidized corn oil at the temperature of 110°C*

Viscosity decreases with the shear rate for both oxidation temperature values, meanwhile one can notice a high increase of viscosity for the oil that was oxidized for 10 hours at a temperature of 120°C.

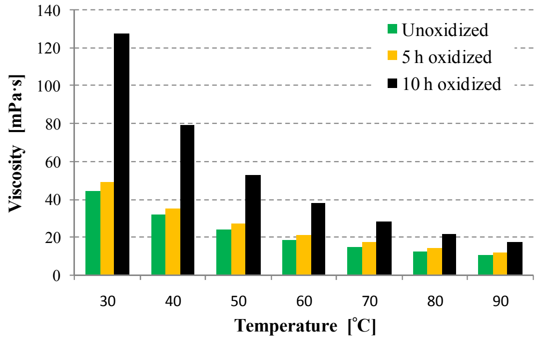

Fig. 9. *Variation of viscosity with temperature, for the unoxidized and oxidized corn oil at the temperature of 120°C*

In Figures 8 and 9 we represented the variation of viscosity with temperature for non-oxidized corn oil and for corn oil that was oxidized at 110°C and 120°C for 5 hours and 10 hours respectively. Viscosity is decreasing with temperature for all oil samples in both cases of temperature and periods of testing time.

It is noted a sharp increase of the viscosity for 10 hours oxidized oil at the temperature of 120°C. Thus for a testing temperature of 30°C it is recorded an increase of the viscosity with 187.16% compared to non-oxidized oil viscosity, in the case of recorded testing temperature the increase is 104.17%, the percentage increase observed for 90°C testing temperature is 66.67%. The percentage increase of oxidized oil at a temperature of 120°C for 10 hours decreases with the increase of testing temperature.

4. Conclusions

Using spectrophotometer analysis of corn oil, oxidized in various conditions, it was found that the transmittance spectra and chromatic parameters are changing. The color differences of oxidized oils compared to non-oxidized oils, increase with the temperature and the period of time of oxidation.

Analysis of viscosity evolution with temperature and shear rate for corn oils also show that this parameter is an indicator of oil oxidation. Viscosity decreases with increase of the temperature and shear rate.

Following these viscosity tests we noticed an increase of viscosity with the increase of oxidation temperature and the period of time for oxidation.

Viscosity evaluation with temperature and shear rate, correlated with oxidized oils transmittance variation analysis, respectively trichromatic analysis shows that these parameters are good indicators of oil oxidation.

Table 1. *Experimental results for corn oils oxidized at a temperature of 100ºC*

Corn oil	Trichromatic components			Trichromatic coordinates			λ_d [nm]
	X	Z	Z	x	y	z	
Unoxidized	63.245	65.666	0.19	0.4898	0.5086	0.0014	576.5
5 hours oxidized	57.456	55.249	0.43	0.5078	0.4883	0.0038	579
10 hours oxidized	54.831	52.327	1.798	0.5032	0.4802	0.0165	579.5

Table 2. *Chromatic characteristics (systems: CIELAB, CIELCH) for corn oils oxidized at 100°C*

Corn oil	Chromatic coordinates			a^*/b^*	$(a^*/b^*)^2$	C^*_{ab}	h_{ab}
	L^*	a^*	b^*				
Unoxidized	84.825	-2.507	150.395	-0.01668	0.0002	150.416	90.95
5 hours oxidized	79.18	8.2005	133.334	0.06150	0.00378	133.586	86.48
10 hours oxidized	77.475	9.0922	111.582	0.08148	0.0066	111.952	84.91

Table 3. *Experimental results for corn oils oxidized at a temperature of 110ºC*

Corn oil	Trichromatic components			Trichromatic coordinates			λ_d [nm]
	X	Z	Z	x	y	z	
Unoxidized	63.245	65.666	0.19	0.4898	0.5086	0.00147	576.5
5 hours oxidized	65.247	69.703	23.81	0.4109	0.4390	0.1499	574
10 hours oxidized	83.08	87.057	89.63	0.31982	0.33513	0.34504	564

Table 4. *Chromatic characteristics (systems: CIELAB, CIELCH) for corn oils oxidized at 110°C*

Corn oil	Chromatic coordinates			a^*/b^*	$(a^*/b^*)^2$	C^*_{ab}	h_{ab}
	L^*	a^*	b^*				
Unoxidized	84.825	-2.5079	150.395	-0.0166	0.00027	150.416	90.955
5 hours oxidized	86.851	-6.7254	60.0226	-0.11205	0.01255	60.3982	96.393
10 hours oxidized	94.762	-4.2072	8.48755	-0.4956	0.24570	9.47306	116.367

Table 5. *Experimental values of color differences when studied corn oils during forced oxidation*

Corn oil	Time [hours]	ΔL^*	Δa^*	Δb^*	ΔC^*_{ab}	Δh_{ab}	ΔE^*_{ab}
Oxidized oil to 100ºC	5	-5.64	10.71	-17.06	20.92	-4.475	20.92
	10	-7.349	11.61	-38.82	-38.47	-6.037	41.172
Oxidized oil to 110°C	5	2.03	-4.21	-90.37	-90.02	5.438	90.49
	10	9.94	-1.699	-141.91	-140.95	25.412	142.261

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