

SPECTROPHOTOMETRIC AND RHEOLOGICAL STUDIES ON OXIDIZED SOYBEAN OILS

Assis. Lecturer Liviu Cătălin ȘOLEA

PhD. Lecturer Romică CRETU

"Dunarea de Jos" University of Galati

ABSTRACT

This paper presents a rheological and spectrophotometric study of oxidized and non-oxidized soybean oils at 100, 110 and 120°C temperatures. The oxidation periods of time were 5 hours and 10 hours. Changes of the oxidized oil transmittance spectra comparing to non-oxidized oil transmittance spectra were observed, and we emphasized the color differences which appeared following the oxidation phenomena. Meanwhile, an increase of the viscosity while increasing the oxidation parameters was noted. Spectrophotometric and rheological analysis can provide information on the degree of oxidation of vegetable oils.

KEYWORDS: transmittance, viscosity, oxidation, shear rate, soybean oil

1. INTRODUCTION

Until the nineteenth century the most important substances used in lubricants manufacturing were vegetable oils and animal fats. These were compatible to the environment and biodegradable. Materials such as water, vegetable oils, animal fats were successfully used in lubrication. Since 2500 b.C., Egyptians discovered that vegetable oil had been reducing friction if it was applied under the sledge's runners transporting heavy stones for pyramid building. Even in the Greek-Roman period there were used vegetable oils for friction reduction. In the southern European countries there were used poppy and olive oils while in northern regions it was used rapeseed oil for the same purposes [1]. 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 at present based on mineral oils. Owing to low eco-toxicity and biodegradation, these lubricants represent a significant threat for the environment, although these are efficient lubricants with very good tribologic proprieties [2].

Soybean oil is obtained from soy beans originating in China, naturalized in our country in 1931 and currently cultivated on large

surfaces. Oil content of the soybean seeds is 17-20%, and it is obtained by cold pressing or gasoline extraction, the solvent being recovered from the oil by distillation. As in most vegetable oils in soybean oil as well predominates the fatty acid glycerides, with one or more double bonds being in the group of non-siccative oil. Soybean is an extremely valuable crop around the world, and is commonly used as a source of soybean oil. Soybean oil contains 12-15% saturated fatty acids (mostly palmitic) and 85-88% unsaturated fatty acids (mostly oleic, linoleic, and linolenic) [3]. Soybean oil is a food product, but following a 40-50°C hydrogenation it is used in the manufacture of soaps and greases.

Oils rich in unsaturated fatty acids have beneficial nutritional attributes that make them desirable for incorporation into various food, health care, and pharmaceutical products [4]. On the other hand, these oils are also easily oxidized, leading to rancidity and quality deterioration [5], [6].

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 [7].

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 300-1100 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.

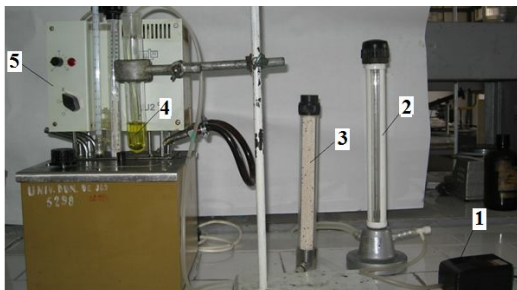


Fig.1. Oxidation equipment

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'Éclairage (CIE), where b* measures the yellowness when is positive, the grayness when zero, and the blueness when negative. In this colour space L* represents the lightness. The a* and b* chromaticity coordinates are independent from L* luminosity. Illumination was performed by C/2° (standard illuminant defined by CIE). Chroma values denote the saturation or purity of color. Hue angle values represent the degree of redness, yellowness, greenness and blueness [8]. Dominant wavelength, λ_d was determined as described according to CIE indications [9], [10].

Forced oxidation behavior research of the oxidized and non-oxidized soybean 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 [11], [12].

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

The transmittance spectra of oxidized soybean oil at 100°C for 5 hours and 10 hours are shown in Figure 2 and 3. It is noted that the shape of the 5 hour oxidized soybean oil transmittance spectrum oxidized soybean oil is similar to the shape of the non-oxidized soybean oil transmittance spectrum, changes occurring in the ultraviolet range only, namely in the range 300-380 nm. In both cases one can observe in the visible a clear fall at 666 nm. This fall is due to the „a” chlorophyll content that is responsible for the positioning of soybean oil regarding trichromatic characteristics (Table 1 ÷ 4), in the second quadrant of the color circle.

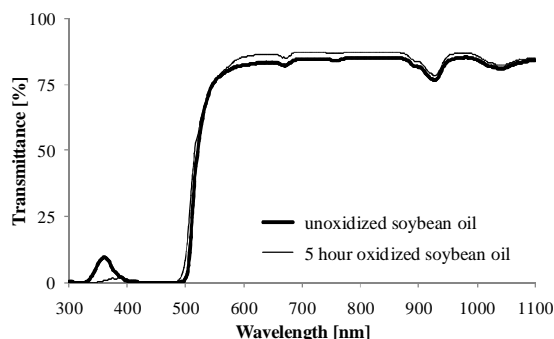


Fig. 2. Soybean oil transmittances oxidized for 5 hours at a temperature of 100°C

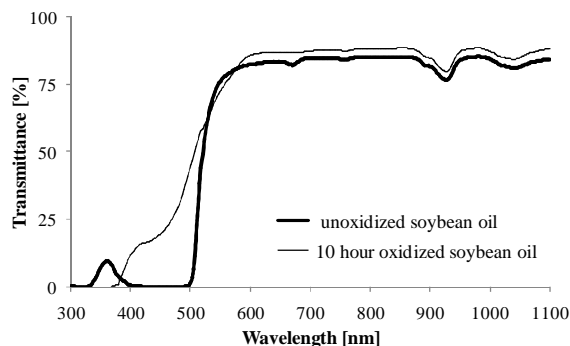


Fig. 3. Soybean oil transmittances oxidized for 10 hours at a temperature of 100°C

From 400 to 666 nm no maximum of absorption was observed, there is a shoulder only at a wavelength of approximately 500 nm for both non-oxidized soybean oil as well as for the 5 hour oxidized one. This can be explained according to [13] as a result of certain pigments destruction (carotenoids for instance) following the industrial process of extraction. In the case of forced oxidation of soybean oil for 10 hours, there is a more pronounced change of the transmittance spectra, with an increase of the transmittance in the range of 362-522 nm.

It also shows the peak for chlorophyll disappears as a result of advanced oxidation. On the other hand, the trichromatic parameters that were determined for 100°C oxidized soybean oil, presented in Tables 1 and 2, certify the presence or absence of pigments belonging to the category of macrocyclic pyrrole colorants.

The experimental results obtained according to color system CIEXYZ / Lighting C/2° lead to components trichromatical coordinates and dominant wavelength in Table 1, determined according to CIE recommendations.

As shown in Table 1, while soybean oil oxidation at a temperature of 100°C, the dominant wavelength is ranging from 576 nm and 573.5 nm, values which correspond to the yellow-orange region in the chromaticity diagram.

Intermediate slight displacement occurs to higher wavelength as a result of partial oxidation. However, oxidation of soybean oil for 5 hours does not seem to lead to a pronounced evolution of trichromatic coordinates. These results are in accordance with color location in the chromaticity diagram by trichromatic coordinates x and y . As expected, the oxidation of soybean oil at 100°C has a deep influence given 10 hours after only, on the trichromatic parameters: L^* , a^* and b^* and, particularly, the parameter b^* which represents the balance of the colors yellow and blue. As indicated by the experimental results, the aggressive oxidation of the studied oil, at this temperature, influences its trichromatic coordinates because absorption, or selective transmission of light with different wavelengths, leads to the changing of X/X_n , Y/Y_n , Z/Z_n color ratio, used in the equations for calculating these chromatic parameters (according to CIELAB color system). As shown in Table 2, the brightness of the studied samples increases and the parameter b^* decreases while the forced oxidation time increases. This variation is due to the fact that with soybean oil oxidation by loss of some pigments, the existing chromophores absorb less light.

Also, the value of the parameter a^* , being too small compared to the b^* parameter, it is clear that the rate of red will tend to subunit values. Chromaticity is colorimetric characteristic determined either by its colorimetric coordinates, or by dominant wavelength and purity. If chroma is the quantitative attribute of color, hue is considered the qualitative attribute.

Chroma decreases with increasing of the oxidation time of soybean oil at 100°C from 151.2 to 55.399. 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 ($90^\circ - 180^\circ$) towards the first quadrant ($0^\circ - 90^\circ$), which is correlated with the variation of the other chromatic parameters.

Increasing the temperature of oxidation from 100°C to 110°C (Figure 4 and 5) is noted in the visible range, significant changes to the shape of transmittance spectrum, for both 5 hour oxidized oil sample and 10 hour oxidized oil sample. This shows that a 10°C temperature increase, under the same experimental conditions, leads to an enhanced oxidation of soybean oil. In Table 3 we point out a larger range of values for the dominant wavelength of 10 hour oxidized soybean oil at 110°C comparing to its values when is 100°C oxidized oil. Also, by locating the position of color in the chromatic diagram (trichromatic coordinates x and y) we deduce sharp color variability of the oil in time.

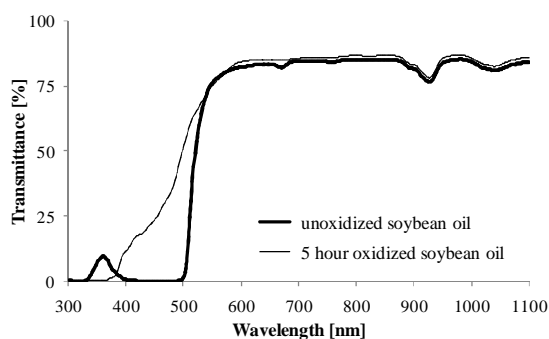


Fig. 4. Soybean oil transmittances oxidized for 5 hours at a temperature of 110°C

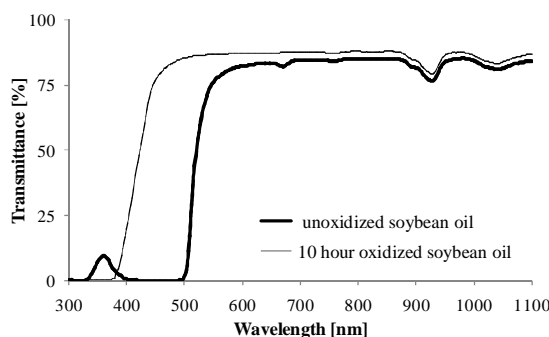


Fig. 5. Soybean oil transmittances oxidized for 10 hours at a temperature of 110°C

Also, the location of soybean oil color is well defined by a^* and b^* parameters (Table 4) in chromaticity diagram. According to this, the color of this oil is also located in quadrant II ($90^\circ - 180^\circ$), as well as for its 100°C oxidation. Also, from the data in Table 4, it is noted the rapid reduction of color

intensity while oxidation, by chroma variation from 151.2 to about 9, while the hue angle increases in the quadrant II to yellow-green hues. On the other hand, these results are expressed by the differences of color calculated for each chromatic parameter analyzed, between the final value (10 hours oxidation time) and the initial one (tabel 5). Trichromatic measurements point out decreases in brightness as compared to non-oxidized oil to both temperatures at which the experiments were carried out ($\Delta L^* = 2.687$ to 110°C and $\Delta L^* = 10.178$ to 130°C). Much sharper turns out to be the b^* parameter variation. Thus, in the soybean oil after 10 hours of oxidation, the degree of yellow drops by about 64% (100°C) and 95% (130°C). In the presence of oxygen, no matter the study temperature is, the color of soybean oil becomes less yellow, meaning the grade of yellow decreases ($-\Delta b^*$). This occurs because following the oxidation process the pigments within the oil disappear while the light corresponding to the blue area from the spectrum is less spread out than the light corresponding to the yellow area. The hue angle vary in a range of values much larger while the soybean oil temperature increasing (tabel 5). As in the case of soybean oil oxidation at 100°C , the analysis of the change in chromatic parameters while oxidation at 110°C , leads to the same conclusions as the information provided by the transmittance spectra regarding the reaction of the oil to oxidation. Viscosities of oxidized and non-oxidized soybean oils were established. The soybean oil was oxidized at the temperatures of 110 and 120°C for 5 or 10 hours. In order to establish the viscosities of these oils, Rheotest 2 equipment was used. Test temperatures for oil samples were settled in the range of 30 - 90°C , from 10 to 10°C , shear rates being within the range of 3.3 - 80 s^{-1} .

In Fig.6 and 7 the variations of 110 and 120°C oxidized soybean oil viscosity depending on the temperature are represented, also the variation of non-oxidized soybean oil viscosity depending on the temperature is shown, when shear rate is 3.3 s^{-1} . Viscosity decreases with temperature, for both test oxidation temperatures. It is noted a slight decrease of the viscosity of 5 hour 110°C oxidized soybean oil compared to non-oxidized oil. Increasing the time for oxidation to 10 hours one can notice an important increase of the oxidized viscosity comparing to non-oxidized viscosity. At the test temperature of 30°C the oxidized oil viscosity increase is 104.1% comparing to soybean non-oxidized oil. At a test temperature of 60°C the viscosity increase is 71.42%

and at a test temperature of 90°C viscosity increase is 50.95% .

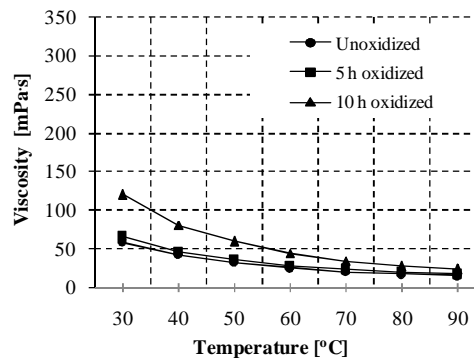


Fig. 6. Variation of viscosity with temperature for oxidized soybean oil at the temperature of 110°C

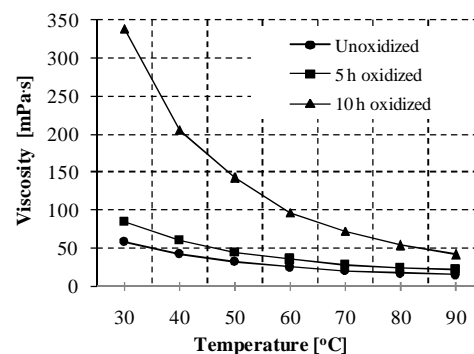


Fig. 7. Variation of viscosity with temperature for oxidized soybean oil at the temperature of 120°C

While increasing the temperature it is noted a viscosity strong increase for 5 hour oxidized soybean and for 10 hour oxidized soybean oil as well. Analyzing the viscosity increases corresponding to a period of time of 10 hour oxidation, at the test temperature of 30°C , the oxidized oil viscosity will increase with 475% comparing to non-oxidized oil viscosity. At the test temperature of 60°C the increase of the viscosity is 280% meanwhile at 90°C test temperature the viscosity increased by 170% . In Fig. 8 and 9 the variations of the viscosity depending on the shear rate for 110 , 120°C oxidized oils were represented, test temperature being 30°C .

Also in this case the viscosity is decreasing with the increase of the shear rate especially when the values of the shear rate are in the range of 3.3 si 18 s^{-1} , this decrease is sharper. Viscosity is increasing when oxidation time and temperature are increasing, an important increase is noted in the case of 10 hour oxidized oil for both oxidation temperatures.

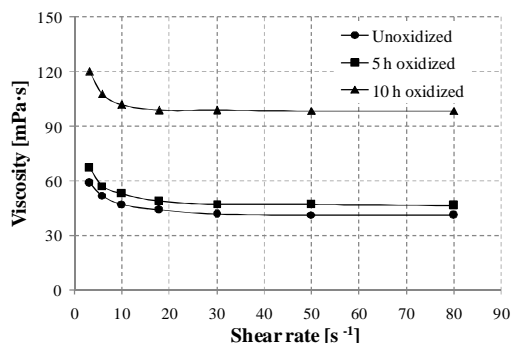


Fig. 8. Variation of viscosity with shear rate for oxidized soybean oil at 110°C

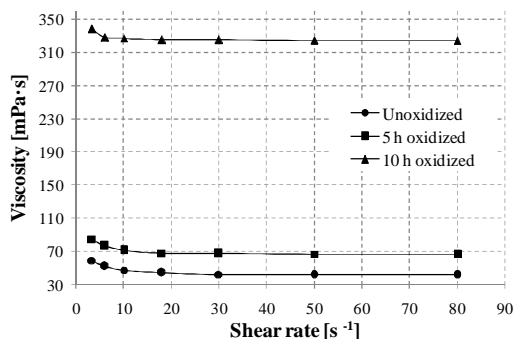


Fig. 9. Variation of viscosity with shear rate for oxidized soybean oil at 120°C

This important increase of the viscosity depending on the temperature and on the variation of the shear rate are due to the fact that following the oxidation of vegetable oils, a lot of chemical products occur such as: hydroperoxides, volatile substances, non-volatile substances, compounds with high molecular weight and fatty acids.

4. CONCLUSIONS

Soybean oil was subjected to a forced oxidation at 100, 110 and 120°C temperatures, exposal time to oxidation being 5 or 10 hours. The samples of soybean oil were subjected to spectrophotometric and rheological analysis.

Changes in the transmittance spectra of oxidized oils compared to non-oxidized spectrum were analyzed. To highlight these changes the occurred chromatic parameters of these oils were compared.

When the oxidation temperature is increasing and the period of time as well, we can notice changes of the transmittance spectra. Similarly when oxidation parameters increase, the color differences between oxidized soybean oil samples increase, too. We determined the variation of viscosity with temperature and shear rate for both oxidized and non-oxidized soybean oil. It is observed a strong increase in viscosity with the increase of temperature and time of oxidation.

The shape and transmittance spectra changes and the increase of viscosity of oxidized oils compared to non-oxidized oil can be explained by the fact that the phenomenon of oxidation of vegetable oils is accompanied by the formation of oxidizing compounds.

Evaluation of viscosity 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 100°C oxidized soybean oil - color system CIEXYZ / illuminant C/2°

Soybean oil	Trichromatic components			Trichromatic coordinates			λ_d [nm]
	X	Z	Z	x	y	z	
Unoxidized	61.628	64.732	0.154	0.487126	0.511657	0.001217	576
5 hours oxidized	62.986	65.899	0.932	0.485191	0.50763	0.007179	577
10 hours oxidized	65.8	70.072	27.18	0.403552	0.429752	0.166695	573.5

Table 2. Chromatic charact. (systems: CIELAB, CIELCH) for 100°C oxidized soybean oils - illuminant C/2°

Soybean oil	Chromatic coordinates			a^*/b^*	$(a^*/b^*)^2$	C^*_{ab}	h_{ab}
	L^*	a^*	b^*				
Unoxidized	84.3452	-4.15075	151.1526	-0.02746	0.000754	151.2096	91.56
5 hours oxidized	84.9448	-3.61199	134.2131	-0.02691	0.000724	134.2617	91.54
10 hours oxidized	87.0321	-6.27641	55.04294	-0.11403	0.013002	55.39963	96.51

Table 3. Experimental results for soybean oils oxidated to 110°C – color system CIEXYZ/illuminant C/2°

Soybean oil	Trichromatic components			Trichromatic coordinates			λ_d [nm]
	X	Z	Z	x	y	z	
Unoxidized	61.628	64.732	0.154	0.487126	0.511657	0.001217	576
5 hour oxidized	66.689	72.32	32.099	0.389749	0.422655	0.187596	573
10 hour oxidized	82.488	86.494	89.842	0.318703	0.334181	0.347116	559

Table 4. Chromatic characteristics (systems: CIELAB, CIELCH) for soybean oils oxidated to 110°C – illuminant C/2°

Soybean oil	Chromatic coordinates			a^*/b^*	$(a^*/b^*)^2$	C^*_{ab}	h_{ab}
	L^*	a^*	b^*				
Unoxidized	84.3452	-4.15075	151.1526	-0.02746	0.000754	151.2096	91.56
5 hour oxidized	88.1221	-9.01166	49.9324	-0.18048	0.032572	50.73909	100.23
10 hour oxidized	94.5231	-4.30284	7.931235	-0.54252	0.294326	9.023244	118.48

Table 5. Experimental values of color differences in the case of soybean oils studied during forced oxidation-illuminant C/2° (non-oxidated – 5 hour forced oxidation, non-oxidated – 10 hour forced oxidation)

Soybean oil	Time [hours]	ΔL^*	Δa^*	Δb^*	ΔC^*_{ab}	Δh_{ab}	ΔE^*_{ab}
Oxidized oil to 100°C	5	0.6	0.54	-16.94	-16.95	0.02	16.96
	10	2.687	-2.1264	-96.107	-95.81	4.95	96.17
Oxidized oil to 110°C	5	3.78	-4.86	-101.22	-100.47	8.67	101.41
	10	10.178	-0.1518	-143.219	-142.187	26.92	143.58

5. REFERENCES

- [1] O. Glavati, L. Glavati, *Lubricating Oils of Plant Origin*, Tribologie + Schmierungstechnik, 42, Jahrgang, nr. 1, 2002, pp. 17-18.
- [2] M. Schneider, P. Smith., *Plant Oil in Total Loss & Potential Loss Applications*, Final Report, 16 May 2002.
- [3] A.P.B. Ribeiro, R. Grimaldi, L.A.Gioielli, *Zero trans fats from soybean oil and fully hydrogenated soybean oil: Physico-chemical properties and food applications*. Food Research International, 42(3), 2009, pp. 401-410.
- [4] D.J. McClements, E.A. Decker, Y. Park, J. Weiss, *Structural design principles for delivery of bioactive components in nutraceuticals and functional foods*. Critical Reviews in Food Science and Nutrition, 49(6), 2009, pp. 577-606.
- [5] B. Chen, A. Han, M. Laguerre, D.J. McClements, E.A. Decker, *Role of reverse micelles on lipid oxidation in bulk oils: impact of phospholipids on antioxidant activity of α -tocopherol and Trolox*. Food and Function, 2(6), 2011, pp.302-309.
- [6] T. Warah, D.J. McClements, E.A. Decker, *Mechanisms of lipid oxidation in food dispersions*. Trends in Food Science & Technology, 22(1), 2011, pp. 3-13.
- [7] I. Stefanescu, C. Calomir, G. Chirita., *On the future of biodegradable vegetable lubricants used for industrial trybosystems*. The Annals of University "Dunarea de Jos" of Galati, Fascicle VIII, 2002, pp. 94-98, ISSN 1221-4590.
- [8] CIE Technical Report., 2004., Colorimetry, 3rd ed., Publication 15:2004, Central Bureau of the CIE, Vienna.
- [9] CIE Technical Report: Improvement to Industrial Colour-Difference Evaluation, 2001.
- [10] CIE Pub. No. 142, 2001, Vienna: Central Bureau of the CIE.
- [11] Gh. Zgherea., *Analize Fizico – Chimice*, Ed. Fd. Universitare "Dunarea de Jos" Galați, 2002, pp. 74-80, 88-94.
- [12] T. Florea., R. Crețu, Gh. Zgherea., *Studiul afinității unor coloranți alimentari față de fracțiile majore ale laptelui*, Buletin de Informare Pentru Industria Laptelui (BIIL), Editura Academica, 19 (2), II, 2004, pp. 86-101.
- [13] A.C. Sancez-Gimeno., A.I. Negueruela., M. Benito., A. Vercet., R. Oria., *Some physical changes in Banjo Aragon extra virgin olive oil during the frying process*, Food Chemistry, No.110, 2008, pp. 654-658.