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STUDY ON PEROXIDE VALUES FOR DIFFERENT OILS AND FACTORS AFFECTING THE QUALITY OF SUNFLOWER OIL

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Abstract

The aim of this paper is to evaluate the peroxide value (PV) of different alimentary oils, as well as to determinate the number of yeasts and molds that develops in this oils. Fungi value is an indicator that ensure the sanitation of samples. Also for refined sun flower oil, the oxidation rate of the samples exposed to daylight or kept in darkness was followed for 60 days. PV exceeds the maximum recommended value of 10 meq/kg after 45 days for sunflower oil exposed to daylight. The samples stored in the dark reached the value of 8.68 mEq/kg at the end of the investigation period. Oxidative rate of used refined sunflower oil subjected to frying temperatures (170^{0}C) was motorized during heat treatment, finding a rapid increase in PV at 18.32 meq/kg after 60 minutes.

***Key words**: alimentary oils, oxidative deterioration, peroxide value*

INTRODUCTION

Oxidation of fats and oils is an important indicator for performance and shelf life of oils (Marina et al., 2013). The oxidation process is complex, dependent on the light intensity and temperature. In the first stage is formed hydro peroxides, peroxides, and then polymers of peroxides (Lupea, 2004).
The PV is applicable for monitoring the formation of peroxides in the early stages of oxidation. However, the accuracy of the method is questionable since the results are depending on the process used, on the temperature at which the determinations are made. During oxidation the PV may reach a maximum and then decreases (Abramovic et al., 2005). Recommended limits that have been set for the quality oils are: PV less than 3 when the oil leaves the factory, less than 5 after the bottle it's open and less than 10 in use. Generally, the values are substantially lower than that. PV is used only in the case of oil that is not rancid.
The reason why it might be possible like the PV to have low level and still to have a rancid oil is because, in reality, in oil are more degraded compounds than results during the decomposition, which is not seen in the respective index values. Various volatile oxidation products are compounds that contribute to the taste and odor of edible oils.
The quality of the oils, inclusive physic-chemical parameters as the PV, were regulated by Romanian Decree no. 454/917/22 form 2001 (D. 454; 917; 22/2001), but the Decree no. 10/2013 repeal the most of the parameters that have a role in characterization of the oils.
Also, section 2 of Codex Standards for Fats and Oils from Vegetable Sources - Codex Standard for Named Vegetable Oils, show the quality characteristics for PV in refined oils that are up to 10 milliequivalents of active oxygen/kg oil, and for cold pressed and virgin oils being up to 15 milliequivalents of active oxygen/kg oil (CODEX-STAN 210 - 1999).
Variations of PV can arise from different factors such as the degree of unsaturation of the fatty acids present in the particular oil, storage, exposure to light, and the content of metals or other compounds that may catalyze the oxidation processes (Choe and Min, 2006).

Also, during the frying process of the fats and oils form a large number of volatile and nonvolatile compounds given by the various types of chemical reactions that occur and cause changes in the structure of fats and oils (Drum and Spanier, 1991). Other studies show that for different oils subjected to different frying temperatures in many cases (except Seasons corn oil, Season canola, Kausar banaspati, Dalda Groundnut) the PV value was constant after 130°C (Kaleem et al., 2015).

In this context, the aim of this study was to determine the PV for different alimentary oil and also for refined sun flower oil using the storage conditions: exposed to daylight or kept in darkness, time period 60 days. Another sample was subjected to frying temperatures (170^0C) 60 minutes and lipid oxidation was monitored.

MATERIALS AND METHODS

In the experiment it was studied:

- The oxidation rate after 30 days from production for ten edible oils (cold pressed: walnut oil, milk thistle, linseed, poppy, hempseed, mustard, pumpkin, sesame, almond, rafinated: sunflower oil) by determining the PV,
- The oxidation rate of edible and used sunflower oil, by tracking the variation of PV in time, in the following conditions:

1. Exposed to daylight (the oil samples exposed to daylight, at room temperature were placed approximately 1 m from the window and were not exposed to direct sunlight. The intensity of light in the room depended on the weather conditions in Alba Iulia, Romania) and preserved to dark in dark glass bottles, at room temperature, for 60 days;
2. Heat treated (170°C) for 60 minutes. In 200 ml sunflower oil were fried 20 g potatoes and 20 g of degassed chicken meat. The temperature is maintained constant at 170°C. The potatoes and the meat are changed from 10 to 10 minutes and oil samples shall be taken in the same time frame. The frying process lasts for 60 minutes. The oil samples were cooling at ambient temperature and the PV was determinate.

<u>*PV determination*</u> (AOAC 965.33). 5.00 ± 0.05 g of oil was dissolved with 30 ml CH_3COOH-$CHCl_3$. 0.5 ml saturated KI solution and 30 ml H_2O was added. The mixture was titrated with 0.1N $Na_2S_2O_3$ until yellow is almost gone. 0.5 ml 1% starch solution was added and titration continued until the light blue colour discharged. Peroxide value (meq O_2/kg of oil) = S x N x 1000/g sample, where S=ml $Na_2S_2O_3$ (blank corrected) and N=normality $Na_2S_2O_3$ solution.

<u>*Yeasts and molds (YM)*</u> (SR ISO 21527-2: 2009). Three Petri plates with Dichloran 18% glycerol agar (DG18) medium were used for each tested samples. With a sterile pipette, the plates were inoculated with 1 ml of test sample (dilution 10-1). The liquid was spread over the agar surface using a sterile spreader until the liquid was completely absorbed. In the next step, the plates were incubated aerobically with lids up at 25°C + 1°C. After three, four and five days, the yeasts and molds colonies were counted. If the developing of colonies was not observed in this period, incubation will be extended to seven days.

RESULTS AND DISCUSSIONS

For ten types of oil samples, the values of the PV, yeasts and molds, are presented comparative in the Table 1.

Table 1. The PV and the number of yeasts and molds for different types of oils

Type of seeds oil	YM, cfu/g	PV, meq/g
Walnut *(Nux)*	5×10^2	0.27
Milk thistle *(Silybum marianum)*	< 10	0.17
Flax *(Linum)*	< 10	0.24
Poppy *(Papaver somniferum)*	1 x 10	0.97
Hemp *(Cannabis sativa)*	1.4 x 10	3.19
Mustard *(Sinapis alba)*	< 10	1.60
Pumpkin *(Cucurbita maxima)*	6 x 10	4.99
Sesame *(Sesamum indicum)*	1 x 10	1,80
Almonds *(Prunus dulcis)*	2.1 x 10	1.00
Sunflower *(Helianthus annuus)*	< 10	1.18

The number of yeasts and molds in edibles oils is maximum 1×10^2 cfu/g, according to Romanian Decree nr. 27/2011, regarding the approval of the microbiology and hygiene criteria's applying to edibles products, others then those mentioned in the Regulation (CE) no. 2.073/2005 regarding the microbiological criteria's for edible products. The number of yeasts and molds value that develops in this oils is an indicator that ensure the sanitation of samples.

For the *sunflower oil exposed to daylight and kept to dark*, the results are presented in figure 1.

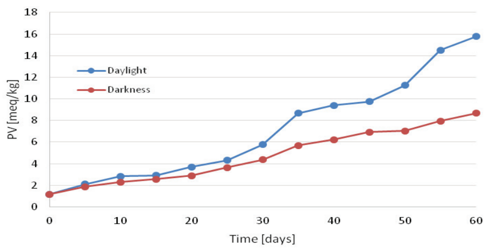

Figure 1. The comparative representation of the variation of the peroxide value for the sunflower oil exposed to daylight and kept to dark.

It can be notice that the value of the PV is fluctuating progressive in time for the sunflower oil samples, however if they are kept to dark or exposed to daylight. The value of the peroxide parameter exceeds 10 meq/kg only after 45 days for the daylight exposed sunflower oil. For the samples kept to dark the PV sets a small amount of variations relatively to the daylight exposed samples.

The sunflower oil examined in the present study, showed large variations in PV between exposure on daylight and darkness after 60 days up to 7.09 meq/kg.

In the heat treated samples were fried low fat food of animal and no animal origin (chicken meat and potatoes).

It was determinate the PV for an hour at 10 minutes time intervals. The results are presented in the in figure 2.

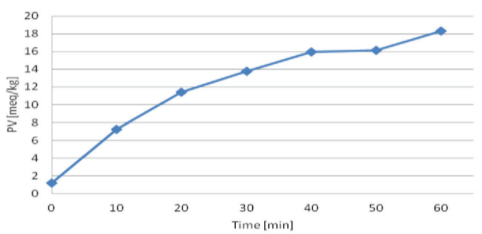

Figure 2. The representation of the variation of the PV for the used sunflower oil – heat treated

Vegetable oils are a cooking medium in food industry. In this study it is found that the heating of the sunflower oil causes the increase of the PV from the beginning of cooking to 18.32 meq/kg after 60 min.

For the heat treated oil the changes are more significant, detectable even sensorial, as follows the PV increases in short time over 10 meq/kg.

Generally, the oxidation rate increase with the temperature. While the temperature is increasing, the changes of the partial pressure of the oxygen had less influence on the reaction rate of oxidation, because the oxygen is becoming less soluble in lipids and water.

Statistical analysis

In order to study the evolution of oil's PV during storage at room conditions, in daylight or in darkness, a two-degree polynomial model was proposed:

$$PV = c_0 + c_1 \cdot t + c_2 \cdot t^2 \qquad (1)$$

where:

PV - peroxide value, [meq/kg];

t – time, [min],

c_0, c_1, c_2 – model coefficients.

The same equation was used to investigate the influence of heat on PV of sunflower oil.

The software used to determine those parameters was Matlab R2008b (version 7.7.0.741). The goodness of model was first evaluated graphically and then the Pearson correlation coefficient (r) and the root mean square deviation (RMSD) were calculated.

The results of models and the experimental data are presented in figures 3 and 4. The model parameters and the values of statistical indicators are presented in table 2.

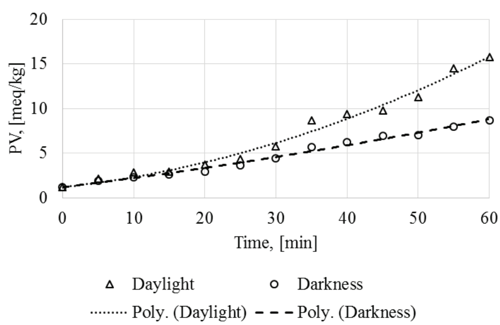

Figure 3. Experimental data (markers) and models results (lines) for evolution in time of oil peroxide values after storage in daylight and in darkness

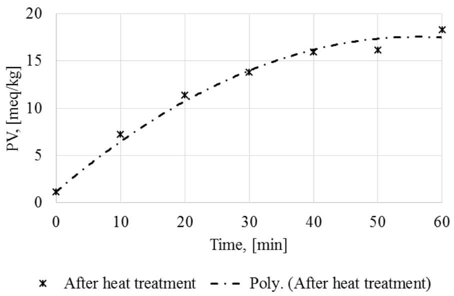

Figure 4 . Experimental data (markers) and model results (lines) for evolution in time of oil peroxide values during heat treatment

Table 2. Parameters of mathematical models and the values of statistical indicators

Studied	Model parameters			r^a	$RMSD^b$
	c_0	c_1	c_2		
Daylight	1.18	0.0874	0.0026	0.9920	0.3433
Darkness	1.18	0.0983	0.0005	0.9934	0.0776
Heat treatment	1.18	0.5816	-0.0052	0.9932	0.4641

[a]pearson correlation coefficient; [b]the root mean square deviation

The good values of the Pearson correlation coefficient and of root mean square deviation indicate that the models describes very well the phenomena that took place in sunflower oil during time as a result of storage factors. Statistical equations obtained are valid on the range of values studied.

CONCLUSIONS

The study is inquiring the PV for nine types of cold pressed oils walnut oil, milk thistle, linseed, poppy, hempseed, mustard, pumpkin, sesame, almond and refined oil, sunflower oil.
The effect of storage conditions on oxidation expressed as PV versus time of storage was also followed. The PV increase in time, however if the oil is daylight exposed or kept to darkness.
The variation of the PV is smaller for the samples kept to darkness, comparative to those exposed to daylight.
The temperature has the highest influence on the oxidization of the sunflower oil, thus the used oil presents a high level of oxidative degradation in the PV which increases to 18.32 meq/kg in 60 minutes.

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