THE INFLUENCE OF WALNUT OIL MOISTURE ON QUALITY

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Abstract: The research presented in this study is an investigation of some of the factors that influence lipid oxidation. A case study on the influence of walnut oil moisture on the storage quality is presented. The quality of nut oil was appreciated by the indices of peroxide and acidity indices. Oil samples with a different moisture content have been stored at different temperatures. The interdependence of the acidity indexes and the storage life of the oil has been evaluated. The regress of walnut oil quality was evaluated by measuring Peroxide Value (PV), Acid Value (AV) et Fats Acidity (FA). All parameters of the quality of the walnut oil were determined in three replicates. It has been found that the acidity of the product in walnut oil with a higher water content has increased approximately 5 to 10 times over two weeks. This was due to the breakdown of triglycerides from walnut oil, which led to the sharply diminishing of its quality.

Key words: walnut oil, peroxide index, acidity, water activity

Introduction

The major constituents of walnut oil are triacylglycerols; free fatty acids, diacylglycerols, monoacylglycerols, sterols, sterol esters, and phosphatides are all present in only minor quantities [12]. The major fatty acids found in walnut oil are oleic (18:1), linoleic (18:2), and linolenic (18:3) acids. Essential linoleic and linolenic fatty acids have a beneficial effect on human health [6]. According to Simopoulos, walnuts are unique because they have a perfect balance of n-6: n-3 PUFA, a ratio of 4:1, which was showed to decrease the incidence of cardiovascular risk [5, 13]. As the results of scientific research [1, 11] show, consumption of walnuts and walnut oil reduces cholesterol in blood due to the increased content of mono- and polyunsaturated fatty acids and vitamin E. Water activity is a critical factor that determines shelf life. The highest ability to promote lipid oxidation in water-in-oil emulsions was shown by linolenic acid, followed by linoleic and oleic acids, indicating that the oxidative capacity increased with increasing degree of unsaturation [16]. Nuts oil is rich in polyunsaturated fatty acids, which are very easily oxidized to improper storage.

The rancidity characterized by deteriorative reactions that affect food fatty acids can be classified according to their nature, as hydrolytic and oxidative. The hydrolytic rancidity occurs by means of lipase enzymes present in the food. The oxidative rancidity can occur enzymatically, in which lipoxygenase enzymes are used, or by non-enzymatic means through autoxidation reactions or photooxidation [4].

The crude oils produced in our country have a free acid content of 1-4% due to the presence of free fatty acids. One of the causes that lead to their occurrence in oil is triglyceride cleavage, which can occur during storage of oilseeds; or in crude oil due to the presence of water traps and improper storage conditions. To obtain edible oils it is necessary to remove the free water [8]. Free fatty acids is the simplest test and indicative of good harvesting and handling processes. FFA are fatty acids which have broken away from oil molecules or triacylglycerols. Their presence indicates that degradation has occurred in the oil through poor handling during processing [7].

This research established the influence of the water-in-oil content on the first phase of the degradation of walnuts oil.

Material and methods

Materials

The study was conducted on autochthonous walnuts R. Moldova, harvest of the year 2017. Walnut oil was obtained by cold pressing. The oil was divided into three equal parts: cold pressed walnut oil; walnut oil, in which 0.5% water was introduced; walnut oil in which 1% water was introduced. The oils were placed in bottles and stored in the refrigerator (+3º C, in dark) and others at +20-22ºC (in dark).
Therefore, 6 samples were obtained and examined:

The sample stored under refrigeration conditions

- ***S 1*** (walnut oil cold pressed);
- ***S 3*** (walnut oil, in which 0.5% water was introduced);
- ***S 5*** (walnut oil in which 1% water was introduced).

The sample stored at room temperature

- ***S 2*** (walnut oil cold pressed);
- ***S 4*** (walnut oil, in which 0.5% water was introduced);
- **S 6** (walnut oil in which 1% water was introduced).

Methods

Peroxide value was determined by official method Cd 8-53 and recommended practices of the American Oil Chemists Society [3]. *Peroxide value* represents the quantity of peroxide who is found in aliment and who have the capacity to liberate in one oxidative process iodine by potassium iodine [9]. It consists of the reaction in darkness of a mixture of oil and chloroform/acetic acid 2:3 (v/v) with a saturated potassium iodide solution. The free iodine released was titrated with a sodium thiosulfate solution until its yellow color disappeared. In this state, 0.5 ml starch solution (1% w/w) was added and titration was continued until the blue. The Peroxide value is expressed in mill equivalents of peroxide oxygen per kilogram of oil and calculated by the following equation:

$$PV = \frac{(V_1 - V_2) \times n}{g} \times 100 \text{ ; (meg/kg oil)} \quad (1)$$

Where:
V_1 = solution volume of sodium thiosulphate used by sample titration, ml;
V_2 = solution volume of sodium thiosulphate used by reference sample titration, ml;
g = quantity of sample, g;
n = solution normality.

Acidity value represents KOH quantity in mg that is necessary for neutralization of free fat acids in one of fat (oil) [10, 14].
AV was determined by the following equation:

$$AV = \frac{28 \times V \times f}{m}; \text{ (mg KOH/g oil)} \quad (2)$$

Where:
V= solution volume of KOH used by titration, ml;

f = 0.8416, solution factor of KOH 0.5 N;
m = sample quantity, g.

FA was determined by the formula:

$$FA = 0.5041 \times AV; \text{ (g oleic acid/100g oil)} \quad (3)$$

Water activity plays an important role in the oxidation of walnuts and walnuts oil in storage. Water activity walnuts and nuts oil was evaluated with the device Novasina Lab Swift-aw.

Results and discussion

The effects of storage temperature and oil moisture content on the oxidative stability of walnut oil have been studied over a 14 days storage period. For this research the walnut oil sample was divided into several samples. Measurement of oil sample degradation parameters was performed each week. In Tables 1 and 2 the values obtained during 2 weeks of storage are entered.

Table 1. *The chemical parameters studied oil samples*

Samples	VP, meqO_2/kg			AV, mg KOH/g oil		
	Retention time, days			*Retention time, days*		
	0	**7**	**14**	**0**	**7**	**14**
	The sample stored under refrigeration conditions					
S 1	1.77±0.01	1.51±0.02	1.38±0.01	0.17±0.02	0.11±0.01	4.92±0.01
S 3	1.74±0.01	0.79±0.01	1.14±0.02	0.15±0.01	0.15±0.01	3.89±0.02
S 5	1.77±0.02	0.40±0.01	1.66±0.01	0.15±0.01	0.15±0.02	3.52±0.02
	The sample stored at room temperature					
S 2	1.77±0.01	0.97	0.94±0.03	0.17±0.01	0.11±0.03	5.05±0.01
S 4	1.74±0.03		0.49±0.01	0.15±0.02	0.27±0.01	5.59±0.02
S 6	1.77±-.01		2.08±0.02	0.15±0.02	0.92±0.01	20.91±0.01

The value of the peroxide (to show the content of the primary oxidation products (peroxides and hydroperoxides) and the acidity of the oil was measured.

Table 2. *Physic chemical parameters studied oil samples*

Samples	a_w			FA, g. oleic acid/100g oil		
	Retention time, days			*Retention time, days*		
	0	**7**	**14**	**0**	**7**	**14**
	The sample stored under refrigeration conditions					
S 1	0.491	0.325	0.306	0,09	0.06	2.46
S 3	0.544	0.418	0.395	0.08	0.08	1.95
S 5	0.531	0.391	0.405	0.08	0.08	1.76
	The sample stored at room temperature					
S 2	0.491	0.463	0.423	0.09	0.06	2.53
S 4	0.544	0.520	0.461	0.08	0.14	2.80
S 6	0.531	0.506	0.472	0.08	0.46	10.46

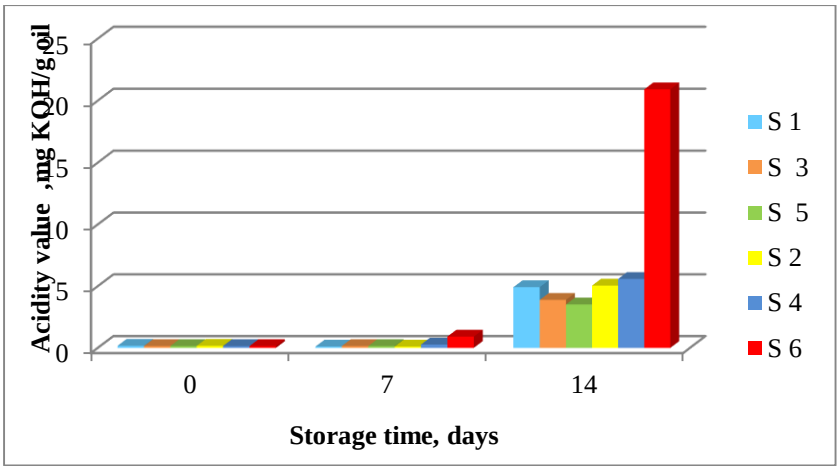

Fig. 1. *The acid values of the oil samples*

The results of the case study show that when stored in oil samples, changes in the peroxide index, acidity and water activity were observed. The most significant changes were the acidity of the oil. Was found that the acidity in vergin oil samples stored in the refrigerator increased from 0.17 to 4.92; in those stored at room temperature the acidity increased to 5.05. The limit value of the acidity index of vegetable oils mentioned in the Technical Regulation "Edible Vegetable Oils" is 4.0 mg KOH/g. However, in oil samples in which 3% water was introduced and stored at room temperature, there was a sudden increase in the acidity index from 0.15 to 20.91. Probably the water introduced into the oil samples interacted with the process of oil degradation. Study [15] indicates that a vegetable oil with an acidity value greater than 14 mg KOH/g is more susceptible to lipase action. The case study has shown that the higher the water content in the oil, the faster the quality of the nut oil. Acid value is an important index of physicochemical property of oil which is used to indicate the quality, age and edibility [2]. Fats must have very low free acidity. When acidity is increased, it denotes a hydrolysis or oil spilling process that refining has not been properly performed [8].

Storage temperature also plays a significant role in the stability of nut oil. High temperature accelerates the action of water on the degradation of nut oil.

It would be of interest for this study to be performed with a higher frequency of fixation of the quality parameters. At the same time, secondary oxidation compounds should be investigated, such as: thiobarbituric value, conjugated dienes, volatile aromatic substances, and fatty acid composition.

Conclusion

It can be concluded that the lipid oxidation of the walnut oil occurred rapidly because of its content of polyunsaturated fatty acids.

There were observed linear correlations between parameters values (Peroxide Value (PV), Acid Value (AV) et Fats Acidity (FA) versus storage time as well as the rate of parameter changes versus temperature and moisture.

The present study has shown that the value of peroxide and the acid value of nut oil are significantly affected by the environmental humidity during walnut storage, water content in nuts, and the oil production method.

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