Biochemical Changes During Red Peppers Preservation Process as a Function of Water Activity

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Dehydrated products may change during storage due to their chemical composition or factors of the environment. The main factor in maintaining the quality of dehydrated products is compliance with a maximum moisture content of the product. The water sorption isotherm is used to determine the amount of water that is absorbed until the product becomes unacceptable. On the sorption isotherm is a point called monolayer (m_0), which represents the optimal moisture content responsible for a maximum storage stability. The water sorption isotherm of red peppers can be determined by equilibrating samples at a constant temperature of 25°C over saturated salt solutions. The equilibrium moisture content, m, can be determined using the method of desiccators and then applying the GAB (Guggenheim – Anderson – du Boer) equation to calculate monolayer. Qualitative indexes of oil extracted from red peppers whose monolayer value were 0.026 g water/g red pepper show lower values compared to samples whose values of monolayer were 0.015 water/g red peppers respectively 0.050g water/g red peppers.

Key-words: red peppers, water activity, monolayer, lipid oxidation

Vegetables are the most important sources of bioactive principles in human diet.

Red peppers are rich in nutrients being an important source of vitamin A and vitamin C and also in polyphenolics compounds which act as antioxidants.

The red peppers are used in fresh form, preserved form and also in dried form to meet the domestic needs during the period between two harvesting stages.

The fresh red peppers quality is limited by the life processes that occur during storage in different conditions.

A good part of red peppers are dried to be consumed outside the harvest season and to avoid quantitative losses.

Red peppers by dehydration maintain its nutritional value, taste and smell and the volume and weight become smaller.

Dehydration products may change during storage due to their chemical composition or factors of the environment. These changes are caused by physical, chemical or biochemical processes[1].

The main factor in maintaining the quality of dehydrated products is compliance with a maximum moisture content of the product. Microorganisms can not used bond water retained in fine capillary tubes of porous dehydrated products.

The physical binding of water occurs by decreasing the vapor pressure at the surface of product.

Compared to the vapor pressure of water from the environment, the product can be found in three cases:

-the pressure of water in the sample is decreased compared to vapor pressure of pure water;

-the pressure of water in the sample is increased compared to vapor pressure of pure water;

-when pressures are reaching an equilibrium, the equilibrium relative humidity (φ) is expressed by the following equation:

$\varphi = (p/p_o) \cdot 100$ where p is the pressure of water in the sample and p_0 is the vapor pressure of pure water. The ratio p/p_0 is called water activity (a_w).

The plot of equilibrium moisture content and water activity at constant temperature is called a water sorption isotherm[2-17].

The water sorption isotherm is used to determine the amount of water that is absorbed or desorbed until the product becomes unacceptable.

On this isotherm are an point called monolayer being the optimal moisture content for maximum storage stability of the food [2]. Also at the monolayer moisture content, theoretically all polar groups have adsorbed one molecule of water vapor. It is at or just above this point where chemical compounds begin to dissolve, diffuse or to react in the aqueous phase.

The monolayer, m_0, can be determined from more than 200 equations. The most used equations for foods are Guggenheim – Anderson – du Boer (GAB), Brunauer – Emmet – Teller (BET), Henderson, Caurie, Smith, Oswin, Halsey, Iglesias – Chirife [4, 5 ,7, 8, 14 - 16].

$$m = \frac{m_0 \cdot K_b \cdot C \cdot a_w}{(1 - K_b \cdot a_w)(1 - K_b \cdot a_w + K_b \cdot C \cdot a_w)} \quad \text{GAB}$$

$$m = A\left[\frac{a_w}{1 - a_w}\right]^B \quad \text{Oswin}$$

$$m = \frac{m_0 \cdot C \cdot a_w}{(1 - a_w)(1 + (C - 1)\, a_w)} \quad \text{BET}$$

$$m = \left(\frac{A}{\ln(1/a_w)}\right)^{1/B} \quad \text{Halsey}$$

$$m = 0{,}01\left[\frac{-\log(1 - a_w)}{10^f}\right]^{1/n} \quad \text{Henderson}$$

$$m = A + B\frac{a_w}{(1 - a_w)} \quad \text{Iglesia - Chirife}$$

$$m = \exp\left[a_w \cdot \ln(V) - \frac{1}{4{,}5 \cdot m_s}\right] \quad \text{Caurie}$$

$$m = B + A \cdot \log(1 - a_w) \quad \text{Smith}$$

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The monolayer of red peppers can be determined using GAB equation:

$$m = \frac{m_0 . K_b . C . a_w}{(1 - K_b . a_w)(1 - K_b . a_w + K_b . C . a_w)}$$

where:

m is the equilibrium moisture content, g water/g red peppers;

m_0 is the monolayer (the optimal moisture), g water/g red peppers;

a_w – water activity;

k_b – correcting constant, 0.998 [15,18];

C – Guggenheim constant, 13.264 [15,18].

Experimental part

Water sorption isotherms were determined for red peppers samples whose moisture was below and above the monolayer value.

The equilibrium moisture content, m, can be determined using the method of desiccators and to calculate the monolayer, m_0, were applied the GAB equation[2,10,11].

Water sorption isotherm were determined by placing the red peppers samples in desiccators containing saturated salt solutions, table 1.

Salt solutions should present a liquid layer above the crystals.

Table 1

WATER ACTIVITY OF SATURATED SALT SOLUTION AT A TEMPERATURE OF 25°C

No.	Salt	Water activity, t = 25°C
1.	LiCl	0,112
2.	$MgCl_2$	0,326
3.	K_2CO_3	0,431
4.	$Mg(NO_3)_2$	0,527
5.	NaCl	0,754
6.	KCl	0,843

The desiccators were stored for 3 weeks at a constant temperature of 25°C and the water activity of saturated salt solutions is varying from 0.1 to 0.9.

Sample are dehydrated by drying for 4 h at 60°C in a vacuum oven. "Zero" water content can be obtained for dehydrated red peppers kept over P_2O_5 in a desiccator for 7 days.

The weighings of samples were done to the tenth of a milligram in a Precisa XB 120 A analytical balance, before and after placing samples in desiccators.

There aformed 3 sets of samples as a function of water activity to determine the biochemical changes that might happened during the storage of red pepers (lipid oxidation):

-red peppers with a value of monolayer of 0.015 g water/g red peppers;

-red peppers with a value of monolayer of 0.026 g water/g red peppers;

-red peppers with a value of monolayer of 0.050 g water/g red peppers.

The samples were packed in plastic pouches laminated with aluminium foil and stored at room temperature for 12 months. Daily we measured temperature resulting an average temperature of 25°C. Once a month oil were extracted in a Soxhlet apparatus using petroleum ether as a solvent, the length of extraction being 10 h [19].

To study the influence of water activity on lipids were determined the following indexes:

-the peroxide index by a potentiometric titration Hara-Totani[20] allowed to determine very low amounts of hydroperoxides (20 nano equivalents) formed by lipid autooxidation;

-acidity index is expressed as mg KOH/g oil;

-refraction index was determined with Abbe refractometer.

The equilibrium moisture content is calculated as follows:

$$m = (w_2 - w_1) / w_1 \text{ ; g water/g dry red peppers}$$

were:

w_1- the weight of red peppers at the beginning of experiment, g;

w_2 - the weight of red peppers after 21 days, g.

Results and discussions

The results are shown in figure 1.

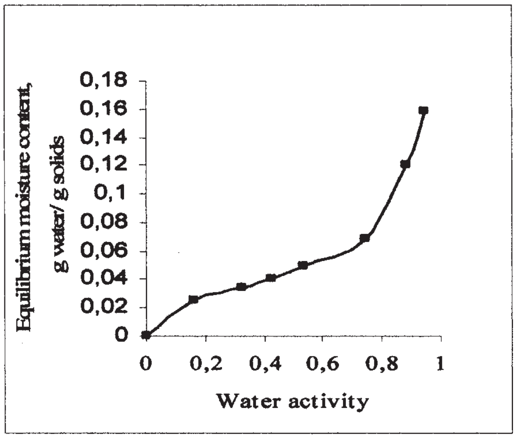

Fig. 1. Water sorption isotherm for red peppers

The value of calculated monolayer for red peppers is 0.026 g water/ dry red peppers.

Labuza[21] showed in a stability map that is a correlation between moisture content and water activity and also between water activity and microorganisms growth, lipid oxidation, enzymatic and nonenzymatic reactions(fig. 2).

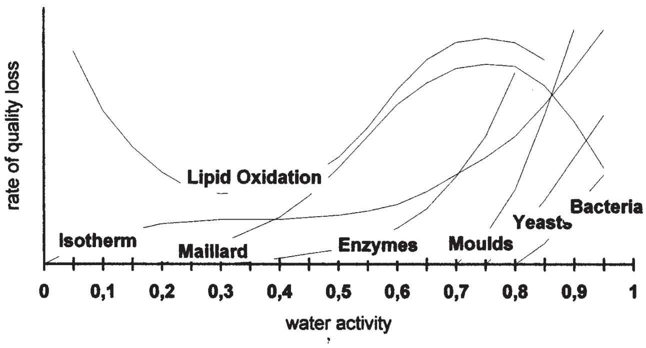

Fig. 2. Water Activity – Stability Map (adapted from Labuza)

In the stability map, lipids have a maximum stability when water activity ranged between 0.2 to 0.4, is enhanced below the value of 0.2 of water activity respectively for a range of 0.4 to 0.75 and when water activity is ranged between 0.75 to 0.85 the stability is low[14].

Microorganisms grow in a large domain of water activity ranged between 0.7 to 0.95. Moulds grow in a domain of water activity which ranged between 0.7 to 0.87, yeast at a domain between 0.75 to 0.94 and bacterias at a domain between 0.8 to 0.95.

In figure 3 are presented the values of peroxides for oil extracted from red peppers and in table 2 are presented the refraction and acidity values.

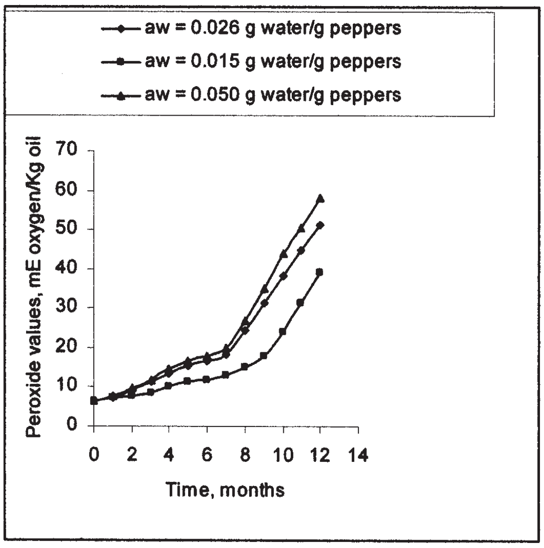

Fig. 3.Peroxides values of oil extracted from red peppers

Table 2

VALUES OF ACIDITY AND REFRACTION INDEXES FOR OIL EXTRACTED FROM RED PEPPERS

Time, months	Red peppers, monolayer value 0,015 g water / g red peppers		Red peppers, monolayer value 0,026 g water / g red peppers		Red peppers, monolayer value 0,050 g water / g red peppers	
	Acidity value, mg KOH/g oil	Refraction value	Acidity value, mg KOH/g oil	Refraction value	Acidity value, mg KOH/g oil	Refraction value
0	0,11	1,4461	0,11	1,4461	0,11	1,4461
2	0,14	1,4669	0,12	1,4663	0,13	1,4671
4	0,18	1,4672	0,15	1,4669	0,21	1,4692
6	0,23	1,4683	0,19	1,4674	0,31	1,4710
8	0,32	1,4687	0,28	1,4680	0,48	1,4791
10	0,40	1,4691	0,34	1,4687	0,57	1,4800
12	0,72	1,4710	0,55	1,4695	0,90	1,4899

The results showed that oil extracted from red peppers whose monolayer is 0.026 g water/g red peppers had lower values of peroxide, refraction and acidity indexes after 12 months of storage compared to oil extracted from red peppers whose monolayer was 0.015 g water/g red peppers respectively 0,050g water/g red peppers.

The oil extracted from red peppers whose monolayer was 0.015g water/g red peppers had lower values of peroxides, refraction and acidity indexes after 12 months of storage compared to red peppers whose monolayer was 0.050g water/g red peppers.

Conclusions

The value of water activity obtained for red peppers samples are found in the stability map in the area where lipids had a maximum stability. The reactions of quality loss of red peppers are due to the composition of lipids in saturated fatty acids (capric acid, lauric acid, miristic acid, palmitic acid, stearic acid) and unsaturated fatty acids (oleic acid, linoleic acid, linolenic acid) during red peppers storage.

An increase moisture of red peppers between 0.026g water/g dry solids and to 0.045g water/g dry solids is responsible for water mobility followed by dissolving of chemical compounds.

Disolved compounds bound molecules of water through van der Waals bounds.

An increase moisture up to 0.045g water/g dry solids assure enough amounts of water to bound the compounds of red peppers which are dissolved remaining a low quantity of water in free form.

This form of water is responsible for free radicals formation and also in blocking the reactivity of peroxides by stabilization of some of them thanks to solvation process.

If moisture content is higer than 0.045g water/g dry red peppers the rate of quality loss of lipids are increased.

A decrease moisture below 0.026g water/g dry red peppers is responsible for dissolving of a low quantity of chemical compounds and for a partial solvation of free radicals. Red peppers samples whose moisture in bellow monolayer are responsible to more formation of peroxides with a consequence on peroxides break-down followed by changes in food quality.

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