CARPATHIAN JOURNAL OF FOOD SCIENCE AND TECHNOLOGY

journal homepage: **http://chimie-biologie.ubm.ro/carpathian_journal/index.html**

ESTIMATING THE SHELF LIFE OF A MAYONNAISE MADE FROM SACHA INCHI (*PLUKENETIA VOLUBILIS* L.) OIL AND DUCK (*ANAS PLATYRHYNCHOS* L.) EGG YOLK

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Article history:
Received
6 January 2018
Accepted
20 October 2018

Keywords:
Emulsion;
Mayonnaise;
Sacha inchi;
Duck egg;
Shelf life

ABSTRACT

Mayonnaise is one of the most industrially produced and consumed food emulsions. Consistent mostly of oil, it is susceptible to deterioration by peroxidation of lipids that is manifested in sensory unpleasant characteristics associated with the chemical species that are produced in this process, which reduce their shelf life. This work studied the shelf life of a mayonnaise made from sacha inchi (*Plukenetia volubilis* L.) oil and duck (*Anas platyrhynchos* L.) egg yolks, using the peroxide value as an indicator. Three storage temperatures (12, 22 and 32 °C) were used to obtain the specific reaction constants (0.112, 0.142 and 0.359 mEq-peroxide·day^{-1}, respectively) to determine the activation energy (41752 J·mol^{-1}) and shelf life for each temperature. The evolution of peroxide value was similar to other mayonnaise formulations.

1. Introduction

Mayonnaise is one of the oil-based products most consumed and produced by the food industry worldwide. Its oily nature makes it susceptible to deterioration by oxidation which is manifested by different compounds of a disagreeable odor. The most commonly used approach to delay rancidity reactions and prolong the shelf life of this product has been the use of synthetic or natural antioxidant compounds (Ghorbani Gorji *et al*., 2016) with great success in most cases except for a deterioration in sensory characteristics when using antioxidants from natural extracts.

Since interest in mayonnaises obtained from oils rich in unsaturated fatty acids has increased (Jacobsen *et al*., 2001; Di Mattia *et al*., 2015), it is necessary to study the effect of different parameters that may affect the product during storage. While light is mostly controlled by packaging, the temperature is usually the ambient temperature in most cases. When mayonnaises formulated with a different lipid profile were investigated, the best analytical tests for early oxidation were the peroxide value and the thiobarbituric acid test (Hsieh and Regenstein, 1992). had also determined that peroxide value is useful in predicting the potential shelf life of mayonnaise. Wills and Cheong (1979) had also determined that peroxide value is useful in predicting the potential shelf life of mayonnaise.

Sacha inchi (*Plukenetia volúbilis* L.) oil has a higher content of polyunsaturated fatty acids than olive and fish oil, and a lower content of saturated fatty acids (Paucar-Menacho *et al*., 2015). Obtained from the cold pressing of the seeds, this oil has an initial peroxide value between 5.2 and 5.6 mEq-peroxide·kg^{-1} oil (Castaño *et al*., 2012).

The aim of this study was to estimate the shelf life of a mayonnaise obtained from sacha inchi oil using duck (*Anas platyrhynchos* L.) egg yolk as an emulsifier. The peroxide value was the variable used to predict shelf life by studying the behavior of its evolution in samples stored at different temperatures.

2. Materials and methods

2.1. Materials

Sacha inchi oil (*Plukenetia volúbilis* L.) was purchased from Empresa Agroindustrias Amazónicas (Lima, Peru) in bottles of 250 ml each. The eggs of duck (*Anas platyrhynchos* L.) were acquired from agricultural breeding areas in the city of Arequipa, Peru. The raw materials were stored refrigerated at 5 °C until use.

2.2. Preparation of the emulsion

The duck egg yolk was pasteurized at 56°C for 5 minutes and mixed with sacha inchi oil at 10500 RPM for 1 minute in a variable speed blender. Emulsification was performed on the same equipment at 12000 RPM for 3 minutes. No antioxidants were used in the formulation.

2.3. Packaging and storage

The mayonnaise samples were packed in 150 x 100 mm aluminum/polyethylene (alupol) bags and 500 grams capacity each, sealed using an electric sealer. The product was stored at three different temperatures for 31 days: 12°C (285.15 K), 22°C (295.15 K) and 32°C (305.15 K), using a laboratory heating oven.

2.4. Determination of peroxide value

Oil extraction from mayonnaise samples was carried out according to the procedure 983.23 described in AOAC (2006). A sample of 15 g was weighed in a 500 mL flask containing 80 mL methanol and 40 mL chloroform. The contents were stirred in a water bath between 45°C and 50°C for 15 min. Then 40 ml of chloroform was added and mixed for 5 minutes. A volume of water of 40 mL was then added and mixed for 1 minute. It was left to stand until the phases were separated and the oily phase was extracted using a pipette to centrifugate the extract at 10500 RPM. The chloroform of the oily extract was evaporated in a water bath.

The method described in ISO (2017) with modifications for determination of the peroxide value was used. A solution of 50 mL of acetic acid: chloroform (3:2 ratio) was added to the extracted and weighed oil sample and the mixture was agitated. Then 0.5 mL of a saturated potassium iodide solution was added, allowed to react for exactly 1 minute and 0.5 mL of starch solution was added. Immediately afterwards 30 mL of distilled water was added. Titration was performed with 0.06 M sodium thiosulfate solution gradually and steadily until the bluish color disappeared. Previously the same procedure was performed using a blank, obtaining a value that was subtracted from the experimental results.

The units of measurement of the peroxide value used were the milliequivalents peroxide per kilogram of oily sample (mEq-peroxide·kg^{-1}). Equation 1 was used to calculate the peroxide value.

$$PV = \frac{1000(V-V_b)\cdot c}{m} \qquad (1)$$

Where PV is the peroxide value (mEq-peroxide·kg^{-1}), V is the volume of sodium thiosulphate solution used for the determination (mL), Vb is the volume of sodium thiosulphate solution used for the blank, c is the concentration of sodium thiosulphate solution and m is the mass (g) of the sample.

2.5. Packaging and storage

Food deterioration has been found to follow zero-order or first-order kinetic models. In foods with a high fat or lipid content, peroxidation reactions predominate, following a behaviour of zero order (Labuza, 1984). The model for the reaction of zero order is presented in Equation 2, according to García Baldizón and Molina Córdoba (2008).

$$-\frac{dX}{dt} = k \qquad (2)$$

Where X is the concentration of the chemical species of interest, k is the specific reaction constant and t is the time. For this work

X was the peroxid value and t is expressed in days.

Since k is time-dependent, the Arrhenius model was used to describe this relationship, according to Equation 3.

$$k = A^{(E_a/RT)} \quad (3)$$

Equation 3 is then cleared to obtain a linear form in Equation 4, where A is the frequency factor, E_a is the activation energy, R is the constant of the ideal gases (8.3143 $J \cdot K^{-1} \cdot mol^{-1}$) and T is the absolute temperature in Kelvin. In this way, the slope of the line allows the activation energy to be determined.

$$\ln(k) = \ln(A) - \frac{E_a}{R} \cdot \frac{1}{T} \quad (4)$$

2.6. Statistical analysis

Simple linear regression analysis and graphs were obtained using the R programming language and environment for statistical computation (R Development Core Team, 2008).

3. Results and discussions

3.1. Evolution of peroxide value

The results of the peroxide value during storage at different temperatures are shown in Table 1. Peroxide values increased over time for all storage temperatures, although at 285.15 K the values seem to stabilize after 17 days so the value of r was relatively low (Table 2) but significant (p-value < 0.05). The highest linearity between peroxide value and storage time was observed at 305.15 K (r^2 = 0.9756). Figures 1, 2 and 3 show the peroxide values for each storage temperature. The plots showed that confidence intervals were narrower as the temperature increased.

The role of stabilizers and antioxidants in decreasing the appearance of oxidation products during mayonnaise storage has been confirmed as very important in other studies. The emulsions obtained with a high percentage of oil rich in polyunsaturated fatty acids and stabilizers with chelating and radical scavenging properties have had very low levels of PV, less than 0.93 mEq peroxides·kg^{-1} oil at 4 weeks of storage (Yesiltas *et al*., 2017). As no antioxidants or stabilizers have been used in this study, peroxide values have been higher.

Table 1. Peroxide values during storage of mayonnaise at different temperatures

Day	Peroxide value (mEq-peroxide·kg^{-1})		
	285.15 K	295.15 K	305.15 K
0	2.91	2.91	2.91
7	4.46	5.08	6.46
17	6.22	6.91	8.18
24	6.28	7.03	12.18
31	6.36	7.50	14.36

Table 2. Correlation matrix (Pearson's correlation coefficients) of peroxide values (PV) and storage time (days)

Variable	Days	PV at 285.15 K	PV at 295.15 K	PV at 305.15 K
Days	1.000	0.920	0.937	0.988
PV at 285.15 K		1.000	0.995	0.887
PV at 295.15 K			1.000	0.913
PV at 305.15 K				1.000

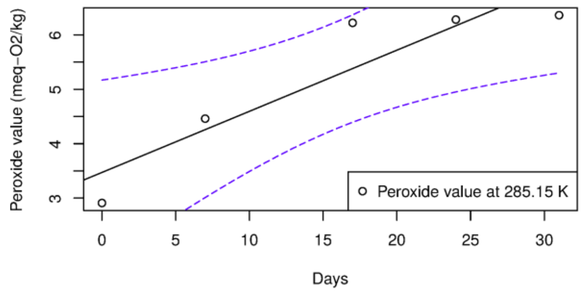

Figure 1. Evolution of mayonnaise peroxide values at 285.15 K (12 °C). Purple lines represent the confidence intervals at 95%.

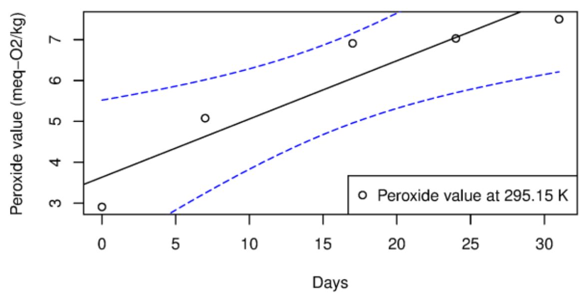

Figure 2. Evolution of mayonnaise peroxide values at 295.15 K (22 °C). Purple lines represent the confidence intervals at 95%.

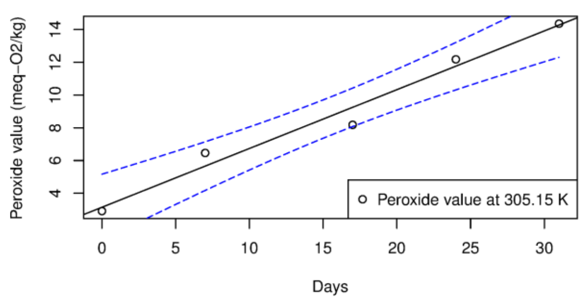

Figure 3. Evolution of mayonnaise peroxide values at 305.15 K (32 °C). Purple lines represent the confidence intervals at 95%.

A mayonnaise-based dressing (the unsaturated fatty acid content was 83.74%), to which a hydrolyzed extract of rapeseed cake was added, had peroxide values of 4.16 to 4.42 mEq-peroxide·kg^{-1} oil which, after 6 weeks of storage at 4 °C, increased to the range of 13.48 to 15.19 mEq-peroxide·kg^{-1} oil, and then decreased by the generation of secondary oxidation products (Kim and Lee, 2017). The authors observed that the peroxide values were significantly lower than those of the control without adding the extract. Our peroxide value results at the same storage temperature were lower at the beginning (Table 1) and would probably have been lower than those reported after 6 weeks considering the projected value. More similar to our initial peroxide values were those reported for mayonnaise mixed with mango using egg yolk and mustard as emulsifiers, which amounted to less than 3.183 mEq-peroxide·kg^{-1} oil (Sethi *et al.*, 2017).

After 35 days of storage at 20 °C, a mayonnaise made from soybean oil (70%) reached a peroxide value of 13.06 mEq-peroide·kg^{-1} oil, from an initial value of 6.6 mEq-peroxide·kg^{-1} oil. At 56 days the value reached 36.8 mEq-peroxide·kg^{-1} oil. The study authors (Phuah *et al.*, 2016) noted that this large increase in peroxide value may have been due to the high percentage of unsaturated fatty acids in soybean oil, although our results at a similar temperature (22°C) with oil also rich in unsaturated fatty acids were lower.

After 5 weeks of storage at 25 °C, another mayonnaise made from soybean oil (70%) had a peroxide value of 9.65 mEq-peroxide·kg^{-1} oil. The mayonnaise samples from the same study (Azhagu Saravana Babu *et al.*, 2016) to which a seed extract of *Cucumis sativus* was added had significantly lower peroxide values. Our results at a similar temperature (22 °C) allowed us to predict that at 35 days (5 weeks) the peroxide value would be 8.62 mEq-peroxide·kg^{-1} oil, which is very close to the reported value.

During storage at 37 °C, mayonnaise samples (78% oil) reached a peroxide value of 7.88 mEq-peroxide·kg^{-1} oil in the third week, and 7.84 mEq-peroxide·kg^{-1} oil in the sixth week (Kwon *et al.*, 2015). The trend of our results at a lower temperature (32 °C, Figure 3) indicates that our samples showed greater oxidation in comparison, although the temperature was lower by 5 °C. At higher storage temperatures (45 °C), it has been reported (Bholah *et al.*, 2015) that samples of mayonnaise from sunflower oil without the addition of an antioxidant extract had a peroxide value of more than 6 mEq-peroxide·kg^{-1} oil, reaching approximately 50 mEq-peroxide·kg^{-1} oil after 15 days. Therefore, it is confirmed that temperature plays a very important role in the spread of auto-oxidation.

3.2. Specific reaction constants and activation energy

The specific reaction constant (k) at 285.15 K was 0.112 mEq-peroxide·kg^{-1}, 0.142 mEq-peroxide·kg^{-1} at 295.15 K and 0.359 mEq-peroxide·kg^{-1} at 305.15 K. It was observed that the k value increases with temperature as expected, remarkably above 22 °C. From the Figure 4 the equation of the regression line (r2 = 0.8832) was ln(k) = 15.307 - 5021.653 · (1/T). Using the slope of this regression line and Equation 4 the activation energy was determined as 41752 J·mol^{-1}.

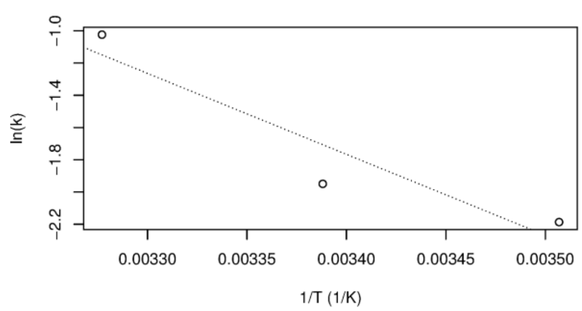

Figure 4. Logarithm of the specific constant of reaction in relation to the inverse of temperature.

It has been suggested that phospholipid peroxidation of mayonnaise is predominantly initiated by radical oxidation (via triplet oxygen) rather than singlet oxygen oxidation throughout the manufacturing and storage process (Kato *et al*., 2017). Unsaturated fatty acids, such as those present in sacha inchi oil, are more susceptible to oxidation due to the low activation energy in the initiation of free radical formation for triplet oxygen auto-oxidation (Min and Boff, 2002). The low activation energy obtained from our results would confirm that peroxidation of the mayonnaise samples was predominantly due to self-oxidation, as the temperature has had an appreciable effect (when greater than 22 °C) and the samples were protected from light by the aluminium/polyethylene container. Temperature has been reported (Yang and Min, 1994) to have little effect on the reaction rate of singlet oxygen oxidation in spite of the low activation energy required (0 - 25120.8 J·mol^{-1}).

3.3. Shelf life

Using the k values and the intercepts from the regression equations obtained to fit the peroxide values for Figures 1, 2 and 3, there was possible to estimate the shelf life considering the limit of 7.96 mEq-peroxide·kg^{-1} oil established sensorially by García Baldizón and Molina Córdoba (2008) for mayonnaise. The relationship was near lineal (Figure 5, r^2 = 0.9685) and the shelf life for the three storage temperatures (12, 22 and 32 °C) as estimated as 40, 30.4 and 12 days respectively, using the same regression equations from Figures 1, 2 and 3.

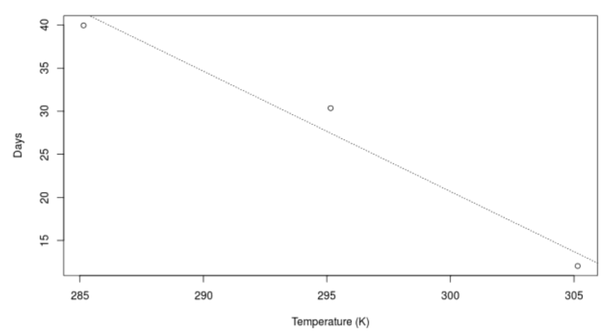

Figure 5. Estimated shelf life for mayonnaise stored at different temperatures.

4. Conclusions

This work estimated the shelf life of a mayonnaise made from sacha inchi oil and duck eggs, using the peroxide value as an indicator. A notable effect of the storage temperature on the peroxide value of the samples was observed during the storage time (31 days). Specific reaction constants (k) increased with temperature and activation energy would allow auto-oxidation in the absence of light due to packaging. The estimated shelf life for storage temperatures of 12, 22 and 32 °C was 40, 30.4 and 12 days respectively.

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Acknowledgment

The authors would like to express their gratitude to BSc. Juan José Alca-Machaca for his support and suggestions of sources to discuss the results.