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Research Article

Kinetic Modeling of Deterioration of Strawberry (*Fragaria x ananassa* Duch cv. Albion) Grown in Cumbal (Colombia)

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Abstract: The effect of packing and temperature on the strawberry (*Fragaria x ananassa* Duch cv. Albion) was studied by kinetic modeling of degradation since this fruit is a highly perishable, it has a high respiratory rate and low mechanical resistance being prone to bruising and microbial attack during postharvest and shelf life. For this reason, the physicochemical quality of the product must be known and assured through the mathematical model of deterioration kinetics. We used a completely random categorical design with two study factors: temperature (4°C, 18°C and 30°C) and packaging Polyethylene Terephthalate (PET) and expanded polystyrene-plastic film (polyethylene and polypropylene)). We used the integral method to determine degradation kinetics, with measurements on days 1, 2, 4, 7, 9, 11, 15 and 17. The best fit for degradation kinetics was pH in PET packaging, which follows a one order reaction and kinetic constants of (0.0380±0.0036, 0.0348±0.0041 and 0.0199±0.0012) /day. Finally, when evaluating the treatments, T5 (PET-4°C) was obtained as the best treatment and, starting from the Arrhenius equation, an activation energy of 32.14 kJ/mol. In conclusion, the estimated useful life of the Albion strawberry at different storage temperatures was modeled by the equation: Useful life = 10-0.0115T + 1.1938 (T in °C).

Keywords: Activation energy, Arrhenius, packaging, pH, temperature, useful life

INTRODUCTION

The strawberry has a high commercial potential, due to its sensory attributes and to its active principles that provide health benefits (Soria, 2010). However, the strawberry has not acquired the degree of expected importance, due to its high respiratory rate that makes it a very perishable fruit (Restrepo and Aristizabal, 2010).

The strawberry undergoes unfavorable changes in its physicochemical properties, which decreases its quality and affects its commercialization (Schestribatov and Dolgov, 2005).

Determination of the useful life of the strawberry is of great importance for its production, storage and transport; thereby ensuring to final consumers that the food purchased maintains all its characteristics (García *et al*., 2011). The useful life of the fruits depends on the significant differences that they have in the time, the reason why the mathematical models are used to relate the changes in their quality.

These models provide objective ways to determine the limits of the useful life of the food, taking into account the different mechanisms of deterioration and a correct analysis of the results (Salinas *et al*., 2007). One of the models most used to know the shelf life of a product is the determination of the deterioration kinetics (García *et al*., 2011). The temperature strongly influences all the physiological processes catalyzed by enzymes; increases in it generate exponential increases in respiration. For this reason, modeling of the Arrhenius type usually adjusts well to the behavior of fruits stored at different temperatures (Fonseca *et al*., 2002). The knowledge of the reaction order that deteriorates the food is the primary factor for the selection of the packaging to minimize the changes that degrade the product (Giraldo, 1993).

The above mentioned shows the need to perform different studies that allow the physicochemical characterization of Albion variety strawberry. These studies will serve as a basis for the handling of the product in fresh, since they play a significant role to achieve an excellent presentation and conservation, allowing to define the most appropriate management of the product during the post-harvest periods. Also, the

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knowledge of the behavior of the physicochemical properties in the storage to different conditions and the use of various packaging materials, allow establishing the optimum conditions for transport, shelf life and consumption time (García Mogollón *et al*., 2010).

The objective of the research was to model the degradation kinetics of the strawberry. For this purpose, the physicochemical variables involved in the quality of the fruit subjected to different storage conditions were analyzed, which can be easily replicated and used by the farmers. The most appropriate treatment while preserving the organoleptic characteristics was determined.

MATERIALS AND METHODS

The strawberry samples used from the Albion variety come from the Tasmag (Cumbal, Nariño), with a maturity status of 3 and 4 (ICONTEC, 1997).

The tests were carried out in the laboratory of research on conservation and quality of food of the University of Nariño, at Torobajo (Pasto, Nariño), at the height of 2527 meters above sea level, with an average temperature of 18°C and relative humidity of 70%. The strawberries were washed and disinfected by spraying using sodium hypochlorite (2.5%) at 50ppm (Restrepo and Aristizabal, 2010).

The packaging of the strawberries was carried out in two types of containers, 170±5 g of sample was packed in each one with three replicates for each treatment, whose conditions are in Table 1.

The determination of the strawberry color was carried out using a Konica Minolta CM5 spectrophotometer, taking into account a measuring area of 30 mm and a viewing angle of 10° illuminant D 65, with transverse reading on the top of the fruit. The measurement of strawberry firmness was carried out using a Lloyd LS1 texturometer, using Nexygen plus software for data reading. The calculation of the percentage of weight loss was carried out by the gravimetric method (ICONTEC, 2002).

On the other hand, the acidity measure (g citric acid/100 g) was carried out according to NTC 4103 (ICONTEC, 1997). The determination of TSS (total soluble solids) expressed in °Brix was carried out using a Brixco 3030 table refractometer (ICONTEC, 1999); and the pH measurement according to the AOAC standard (AOAC, 1990).

Experimental design: We performed a completely random categorical experimental design with three replicates and two study factors, with factor A being the temperature and factor B the package.

As for the data analysis, the procedure of Analysis of Variance (ANOVA) and test of comparison of means with the proof of Fisher's LSD to a 95% of reliability was carried out by the program Statgraphics Centurión XVI.I.

Table 1: Identification of treatments

Treatment	Temperature (°C)	Packing
T1	30	Polyethylene terephthalate
T2	30	Expanded polystyrene - Plastic film
T3	18*	Polyethylene terephthalate
T4	18*	Expanded polystyrene - Plastic film
T5	4	Polyethylene terephthalate
T6	4	Expanded polystyrene - Plastic film

*Average ambient temperature in the Pasto City

Mathematical modeling: The expression for loss of food quality is represented by a mathematical equation, as follows:

$$\frac{dQ}{dt} = kQ^n \tag{1}$$

where,
Q = The quality factor measured
t = Time
k = A rate constant which depends on temperature and packing
n = A power factor called the order of the reaction
dQ/dt = The rate of change of Q with time

A negative sign is used if the deterioration is a loss of Q and a positive sign if it is for production of an undesirable end-product (Yan *et al*., 2007).

From the previous one the integral method, represented by the following equations of order zero and one respectively was used:

$$\pm Q = Q_0 - kt \tag{2}$$

$$ln\frac{Q}{Q_0} = kt \tag{3}$$

where,
Q_0 = Initial value of the quality attribute
Q = Attribute value at time t
K = Apparent reaction constant (slope)
T = Time

Therefore, we evaluated the goodness of the fit of the model for the calculation of the kinetics of deterioration with Eq. (4) and (5), also with the coefficient of determination (R^2) and the standard deviation:

$$RMSE = \left[\frac{\sum_{i=1}^{n}(C_{Cal} - C_{exp})_n^2}{n}\right]^{0.5} \tag{4}$$

$$E\% = \frac{\sum_{i=1}^{n}\frac{|(C_{Cal} - C_{exp})n|}{C_{exp}}}{n} \times 100 \tag{5}$$

where,
C_{cal} : Calculated value
C_{exp} : Probative value
n : The number of determinations

Table 2: Physicochemical properties of Albion variety strawberry

Physicochemical parameter	Initial value*	Units
Maturity index	6.070 ± 0.183	(TSS % C.A)
Color parameter b*	16.631 ± 1.470	Without units
Firmness	8.327 ± 0.867	Newton (N)
Pulp content	0	%
pH	3.110 ± 0.056	Without units

* Average values (n = 3) ± standard deviation

Table 3: Kinetic parameters and goodness of fit of the exponential model

				Goodness of fit	
Treatment*	pH kinetic constant K(1/day)**	R^2	Reaction order	RMSE	E%
T1	0.0348 ± 0.0041^{bc}	0.9321	Order 1	0.128	3.014
T2	0.0465 ± 0.0061^{c}	0.9737		0.118	2.152
T3	0.0380 ± 0.0036^{b}	0.9631		0.116	2.741
T4	0.0670 ± 0.0081^{d}	0.9866		0.339	4.743
T5	0.0200 ± 0.0011^{a}	0.9742		0.115	2.716
T6	0.0228 ± 0.0012^{a}	0.9858		0.1	1.48

* T1 = 30°C in PET, T2 = 30°C in expanded polystyrene packing, T3 = 18°C in PET, T4 = 18°C in expanded polystyrene packing, T5 = 4°C in PET, T6 = 4°C in expanded polystyrene packing; ** Mean values (n = 3) ± standard deviation; Uncommon letters indicate significant differences between the means, according to Fisher's LSD test at 95% confidence

The effect of temperature on the reaction rate constant was evaluated with the Arrhenius equation Eq. (6), calculating the activation energy:

$$K = K_0 exp^{\frac{-Ea}{RT}} \quad (6)$$

where,

K = The rate constant of the reaction
K_0 = The constant of the Arrhenius equation
Ea = The activation energy

RESULTS AND DISCUSSION

The physicochemical properties of Albion variety strawberry used in the present study are in Table 2.

Determination of the useful life: the adjustment quality for each variable was evaluated taking into account the coefficient of determination (R2), the square Root of the Mean Square Error (RMSE) and the average percentage error (E%), according to the Eq. (4) and (5).

Different authors cited by Brousse *et al*. (2014), mentioned that a good fit is indicated when they have an R2 greater than 0.85 E% <10% and RMSE values <0.3, meaning that the prognostic values are very close to the real values (Cerón *et al*., 2016). According to the adjustment of the experimental data, the variable with the highest correlation was the pH with values of R2, E% and RMSE lower and, therefore, is the parameter used to determine the Arrhenius equation.

Salinas *et al*. (2007) and Ibarz and Garza (2004) show that pH is one of the most critical characteristics of fruits and vegetables concerning quality and consumer acceptability. The variation of the pH in the food generates a drastic reduction of the survival of the microorganisms, besides the alkalinization of the cellular interior leads to the loss of transport of nutrients.

Kinetics of deterioration according to pH: The values of the kinetic constants in Table 3 indicate that the treatments have statistically significant differences (p<0.05), except the treatments T5 and T6 whose kinetic constants were lower at a temperature of 4°C in the two containers. Therefore, low cooling temperatures delay the maturation processes and the useful life of the fruit is more significant.

In the T5 treatment, the pH remained relatively low (Fig. 1 and 2) without the presence of fungi for a longer time (17 days). While in the T6 treatment to 4°C, there was a slight presence of fungi on day 15. Therefore, the fruit retains its characteristics at a temperature of 4°C in the PET package. The presence of fungi, the transformation of sugars into organic acids and the ripening process of the strawberry, influence the pH value (Medina, 2006).

Figure 1 and 2 show the quality loss that occurs in treatments T2 and T4. In these procedures, H * ions are part of the formation of substrates such as sucrose and glucose, so that their concentration in the vacuolar level decreases during the last stages of maturation and as a consequence, there is a slight increase in pH (Álvarez-Herrera *et al*., 2009).

During the time of storage, the pH of the strawberry increases progressively with the decrease of the acidity, because organic acids are a source of energy to sustain the ripening process of the fruit (Núñez *et al*., 2004). For other fruits, the relationship between pH and maturity is also evident. Millan and Ciro (2012) determined that organic acids decrease with the increase in the degree of maturity and the respiratory intensity of the banana.

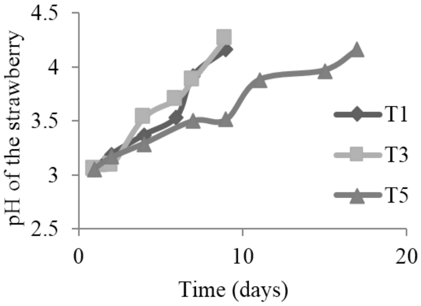

Fig. 1: Kinetic behavior and pH variation for PET polyethylene terephthalate packaging

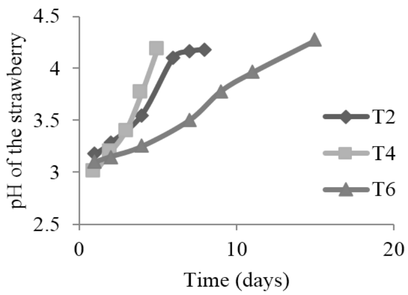

Fig. 2: Kinetic behavior and pH variation for packaging Expanded polystyrene-plastic film

Table 4: Kinetic parameters and goodness of fit of the exponential model

T (°C)	T (K)	1/T	K	ln(K)
30	303,15	0.0032	0.038	-3.270
18	291,15	0.0034	0.0348	-3.358
4	277,15	0.0036	0.0199	-3.917

The experimentation determined that the best packaging be polyethylene terephthalate, since, in this package, there was less deterioration of the fruit. On the other hand, only the cooling temperatures presented no statistically significant differences ($p<0.05$). Therefore the determination of useful life by Arrhenius was made for PET packaging from the kinetics of the three temperatures used.

Activation energy: Table 4 shows the data of three temperatures evaluated for the pH variable in PET packaging, in addition to the kinetics for which it is necessary to linearize the Eq. (6) (Arrhenius).
From Eq. (6) (Arrhenius) it is determined that:

$$ln(k) = ln\, k_0 + \frac{Ea}{RT}$$

$$y = -2141{,}4x + 3{,}8665$$

Therefore,

$$Ea = 32{,}14\ kJoules/mol$$

The activation energy was calculated from the slope of Fig. 3, (Arrhenius graph), determining a value of 32.14 kJ/mol. The value is within the range of fruits reported by various authors such as Ruiz *et al*. (2010), who said activation energy values for peach, apple and pear of 34.35, 29.97 and 37.29 kJ/mol, respectively; also, Alvarado (1993) reports that the activation energy for non-climacteric fruits such as grape, pineapple, lemon, lime, mandarin and orange is 20.6, 22.2, 18.1, 16.5, 21.3 and 19.7 kJ/mol, respectively. These values represent the energy required for molecules can participate in a reaction.

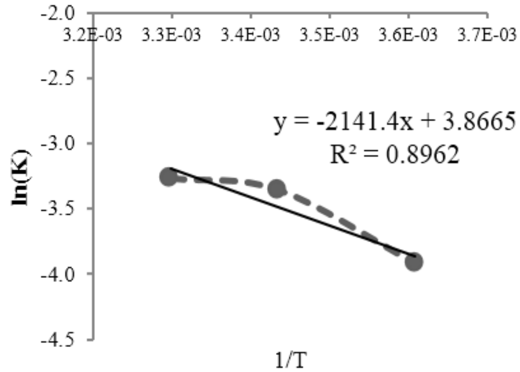

Fig. 3: Arrhenius graph

Table 5: Estimated and experimental useful life at each incubation temperature

Temperature °C	Estimated useful life	Experimental useful life
4	15.281	17
18	8.0068	9
30	7.7631	7

The determination of the pH was carried out, from the one-order equations determined in the deterioration kinetics for the PET packaging of polyethylene terephthalate at different temperatures:

$$\ln pH_{4°C} = 0{,}0200x + 1{,}1031$$

$$\ln pH_{18°C} = 0{,}0348x + 1{,}0992$$

$$\ln pH_{30°C} = 0{,}0380x + 1{,}085$$

Knowing that at pH greater than 4.01 the strawberry in the Albion variety is no longer acceptable as Martínez *et al*. (2008) found that ideal pH is 3.4 to 4.01; therefore the pH of 4 is taken to determine the maximum value of useful life:

$$\ln pH_{18°C} = 0{,}0348x + 1{,}0992$$

$$\ln 4 = 0{,}0348x + 1{,}0992$$

Theoretical useful life: In Table 5, the experimental and estimated useful life values are very close, confirming that the kinetics of strawberry deterioration as a function of pH follows a reaction of order 1. The strawberry in PET packaging at high temperatures

Table 6: Kinetic constants of deterioration and useful life at different temperatures

Temperature (°C)	Kinetics constants (K)	Estimated useful life (Days)
5	0.0216	12.784
10	0.0248	11.315
15	0.0283	9.924
20	0.0322	8.742
25	0.0363	7.665

shows more deterioration than at lower temperatures. At temperatures of 18°C and 30°C the pH increases rapidly.

From the Arrhenius equation, the deterioration kineticsis determined as indicated by García *et al*. (2011):

$$\text{Ln}\,(k) = K_0 + \frac{Ea}{RT}$$
$$\text{Ln}\,(k) = 3.8665 - \frac{2141.4}{T}$$
$$\text{Ln}\,(k)_{25°C} = 3.8665 - \frac{2141.4}{298.15}$$
$$\text{Ln}\,(k)_{25°C} = 3.8665 - 7.1823$$
$$(k)_{25°C} = e^{-3.3558}$$
$$(k)_{25°C} = 0.0363$$

The determination of the useful life equation requires knowledge of the kinetics of deterioration (k) for different temperatures, as shown in Table 6.

CONCLUSION

Strawberry showed an increasing tendency over time concerning pH. In both vessels at temperatures of (30 and 18) °C, there were statistically significant differences ($p<0.05$). There were no statistically significant differences at 4°C. Therefore; PET packaging preserves better the physicochemical characteristics of the fruit at low temperature.

Within the kinetic parameters analyzed for the Albion strawberry variety, the pH showed a good fit quality in the exponential model. The mathematical model resulted in order one, with a kinetic deterioration constant of $(0.0380 \pm 0.0036, 0.0348 \pm 0.0041, 0.0199 \pm 0.0012)$ 1/day for the temperatures (30, 18 and 4) °C, respectively. Activation energy resulted in 32.14 KJ/mol, which is within the established ranges for fruits.

With the equation and graphs of Arrhenius analyzed it was obtained the equation: Useful life = 10-0.0115T+1.1938 (T in °C), for estimate the useful life of the strawberry at different storage temperatures. Therefore, the estimated useful life for of fruit to 30, 18 and 4°C is 7, 8 and 15 days, respectively.

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