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Modelling the Shelf-life of Apple Products According to their Water Activity

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Shelf-life is the period of time corresponding, under certain conditions, to an acceptable reduction in food quality; it depends on various intrinsic and extrinsic factors. Food nature, its water activity, conservation process, the storage conditions and the packaging materials influence primarilythe stability. This work was performed in order to establish mathematical models to predict the shelf-life of foods, by using apple samples, with different water activity: dehydrated slices, compote and fresh cut pieces, for low, medium and high water activity, respectively. To the dehydrated slices which have more stability, and depend only on the absorption of a certain amount of moisture through the packaging, the adsorption isotherm was determined at 30 °C and 65% RH; the shelf-life was predicted according to the modified Hoerl model. For baby food, such as apple compote, it was taken into account the microbiologicalrequirements and the sensory acceptance. Accelerated shelf-life study at 37 °C and 90% RH was conducted and it was performed a multivariate prediction of the characteristics pH, Brix and aroma through Labuza kinetic models. Estimation of microbial growth was completed through Gompertz equation. Refrigerated storage assays at 4°C were performed for cut fresh whichquality is related with physical appearance, taste and odour. Colour and odour were monitoredby instrumental sensory analysis by using colourimeter and electronic nose. Different models obtained could predict the decay time of these foods by knowing the value of the initial qualitycharacteristic.

1. Introduction

Shelf-life is the period of time corresponding, under certain conditions, to an acceptable reduction in the quality of foods; it depends on several intrinsic and extrinsic factors. Food nature, its water activity, the type of conservation process, the storage conditions and the packaging materials have mainly an influence in the stability. Water activity (aw) is the factor that affects stability in the highest level, caused by being the available water for growth of microorganisms and the resource for various chemical reactions. Due to this important factor, shelf-life determination is different for every food and is mainly based in the changes which occur in the product. Food items with high and intermediate water activity are liable to lose their shelf-life when microbiologically the food exceeds the limits established in the standards (Petrus et al. 2009). In the case of apple compote these limits are found in the norm NTC 1474 (Icontec 2009a), however the end of the shelf-life can be stated when the food is perceived as unacceptable by a sensory panel (Palazón et al. 2009). Nevertheless the food with low water activity is less likely to microbial growth and kinetics changes in the physicochemical properties, the sensory properties, especially texture perception, turn to be critical factor in shelf-life determination, as in the dehydrated apples. Due the relation of texture properties of low water activity products with the protection given by packages against gaining moisture, gain the study of adsorption and desorption isotherms has been widely used to estimate the shelf-life of those products. Thus, the objective of this study was modelling shelf-life of apple products according to their water activity.

2. Methodology

This study was based on apple (*Malus domestica* Royal Gala from Chile) products elaborated in the Institute of Food Science and Technology (ICTA) of the National University of Colombia. Radial pieces of fresh apples

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were chemically treated during 3 min in a solution 1 % (w/v) of citric acid and 0.05% (w/v) of calcium chloride and were stored in a shelf-life chamber at 4ºC. It was evaluated different changes in colour and aromatic profile. Samples of apple compote elaborated with 78 % of apple pulp and lower quantities of water, sugar, corn starch and citric acid were pasteurized to 80 ºC during 10 min. Changes in soluble solids, pH, microbiological safety and aroma changes analyzed by electronic nose were evaluated in these samples. Finally, the absorption isotherm at 30 ºC was estimated for dehydrated apple samples with crunchy texture.

2.1 Physicochemical properties

The aromatic profile of the fresh apples pieces and compote samples was determined in a portable commercial electronic nose Airsense PEN3, with an array of 10 semiconductor sensors, where W1C (aromatic compounds) , W5S (nitrous oxide and ozone), W3C (aromatic compounds), W6S (H_2, O_2 and CO_2), W5C (Alkanes), W1S (Methane), W1W (Therpens andorganophulfur compounds), W2S (Alcohols), W2W (Organophulfur compounds) y W3S (Methane and aliphatic compounds), according to the methodology used by Torri et al. (2010). The results were analyzed in a *PCA (*Principal Component Analysis) using software MATLAB. The change in colour was determined in the Hunter LAB scale, CIELAB (L, a, b) where: L*, indicates brightness, a*, indicates chromaticity in the green (–) and red (+) axis, and b*, chromaticity in the blue (–) and yellow (+) axis, using a colourimeter MiniScan Spectro colourimeter model MS/B of diffused geometry. Finally, the soluble solid content was determined by using a digital refractometer, and the pH according to the methodology AOAC 2005**.**

2.2 Microbiological analysis

Aerobic mesophilic total microorganism count was made according to the standard NTC 4519 (Icontec, 2009b), molds and yeasts according to the standard NTC 5698-2 (Icontec, 2009c).

2.3 Determination of shelf-life for high and intermediate water activity food products

2.3.1. According to changes in the physicochemical properties: the physicochemical parameters data obtained were adjusted to equations which describe their evolution during storage. These equations could predict their evolution by means of the use of kinetic models (Labuza and Riboh, 1982). The most used studies for estimating shelf-life of food products are zero order reactions, which represent a linear evolution of gain or loss of each parameter evaluated. On the other hand, first order reactions represent an exponential evolution of the parameter values (Labuza and Riboh, 1982). The following equations describe models of zero Eq(1), first Eq(2) and second Eq(3) order; where Q is the parameter, Q_0 is Q in the time zero, k is the constant and T is the time.

$$Q = Q_0 - kt_{sl} \quad (1) \qquad Q = Q_0 e^{-kt_{sl}} \quad (2) \qquad \frac{1}{Q_0} = \frac{1}{Q} + kt_{sl} \quad (3)$$

2.3.2 According to microbiological safety

It was used the empiric kinetic model of Gompertz Eq(4) to describe completely the microbial growth curve (Gibson et al. 1987) of aerobic mesophilic microorganisms, molds and yeasts in the samples.

$$N(t) = N_0 + \mu_{max}.\exp^{(-\exp^{(-B(t-M))})} \quad (4)$$

Where: N(t) = microbial count (log10 CFU/g) in the time t; N_0 = initial bacterial count ($\log_{10}$ CFU/g); $\mu_{max.}$= maximum level of population (log10 CFU/g) and B = relative growth rate in the time M(h_{-1}); M = time of maximum growth rate; t = time (h).

2.4 Determination of shelf-life for low water activity food products

Shelf-life of low water activity food products could be calculated from the moisture adsorption isotherm by using the equation 6 according to the methodology of Escobedo-Avellaneda et al. 2012, in which X (g water / g product) is the moisture content of food products with subscripts i, c and e for: initial content, critical (initial level of moisture content where the product becomes unacceptable), and the equilibrium moisture content (level of moisture content when the product would be in equilibrium with the external relative humidity) respectively. From the equation 3, k/x ($g.m^{-2}.d^{-1}.mm\ Hg^{-1}$) is the vapour permeability of the package; A (m^2) is the package area, Ws (g of solids) is the amount of dry solids in the food, p^o_v (mm de Hg) is the water vapour pressure at the storage temperature; m is the slope of the linearized region of the isotherm in the range of interest (that is from Xi to Xc), and , t_{sl} (d) time of shelf-life (Labuza and Altunakar 2007). The critical moisture content and the moisture content when the food product is in equilibrium with a certain relative humidity could be found from the adsorption isotherm estimated.

$$\frac{k}{x}=\frac{WVTR}{\Delta p_v}\frac{WVTR}{0.9p_v^{\circ}} \quad (5) \qquad \ln\frac{X_e-X_i}{X_e-X_c}=\frac{k}{x}\frac{Ap_v^{\circ}}{W_s m}t_{sl} \quad (6)$$

2.4.1 Evaluation of the adsorption isotherms of dehydrated apple

The absorption isotherms were determined at 30ºC by means of the method of Bell and Labuza 1984,using saturated salt solutions of LiCl, $MgCl_2$, K_2CO_3, NaBr y K_2SO_4. To determine the best adjust of experimental values of the equilibrium moisture content the following mathematical models were tested: Oswin, GAB, BET, Langmuir, Wavy, Peleg, Weibull, Ratkowsky and Henderson. The parameters of the tested models were calculated by a nonlinear regression, with the software Curve Expert V Professional. The criteria used to determine the adjustment quality of the experimental values in the adsorption models were the correlation coefficient (r^2) and the mean percentage error (MPE, %).

3 Results and discussion

3.1 Fresh apple

During the storage at 4 ºC, the apple pieces did not suffer significant changes in the aromatic profile (Figure 1), however they experienced important changes in colour. The brightness decreased (Figure 2), and the parameters a* (Figure 3) and b* (Figure 4) had a significant rise. The change of colour in the surface of the apple pieces could occur due to the oxidative browning caused by the damage in the tissues and the enzymatic browning, reason that explains why the accelerated changes in colour have been considered as the characteristic that limits the shelf-life of fresh cut fruits (Odriozola-Serrano et al. 2008). The changes in brightness, the parameters a* and b* were adjusted to zero order models (Labuza, 1982), as showed in the equations 7 to 9. The critical point of shelf-life loss was established when a reduction of 30 % of the initial value of each characteristic was reached, assumption that makes possible to estimate the shelf-life of apple pieces stored at 4 ºC, knowing only the initial values of colour parameters.

$$L_{sl}=\frac{0.3L_0-L_0}{-0{,}0095} \quad (7) \qquad a*_{sl}=\frac{0.3a*_0-a*_0}{0{,}0036} \quad (8) \qquad b*_{sl}=\frac{0.3b*_0-b*_0}{0{,}0158} \quad (9)$$

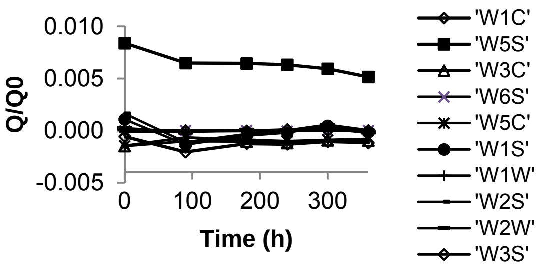

Figure 1: Answer of electronic nose sensors

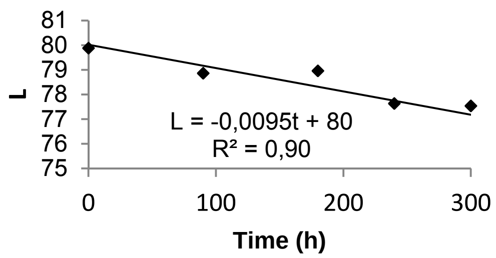

Figure 2: Changes of brightness

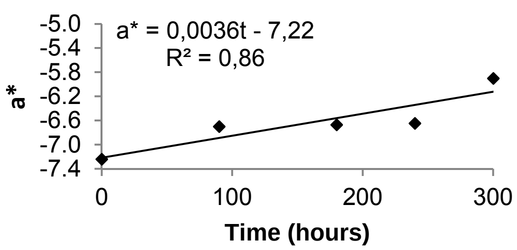

*Figure 3: Change of parameter a**

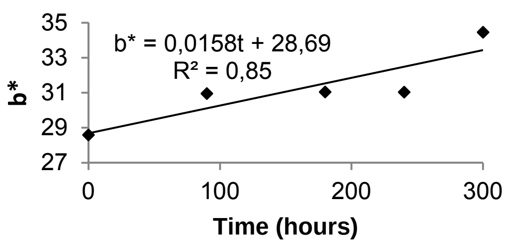

*Figure 4: Change of parameter b**

3.2 Apple compote

During the storage of compote samples at 30 ºC, total soluble solids (Figure 5) had a rise from 21.83 (day 0) to 23.20 ± 0.015 (day 49), and pH (Figure 6) increased slightly from 3.95 ± 0.015 to 3.99 ± 0.015, although it was not considered as a significant change. According to Balestra et al. (2011), the pH increase is probably due to the degradation of sugar to acid caused by Maillard reactions. However, several authors have reported no significant variations in terms of total soluble solids and pH in fruit purees during storage (Ledeker et al. 2014).

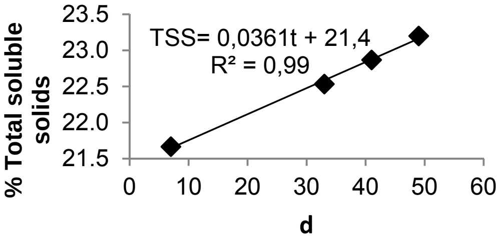

Figure 5: Variation of total soluble solids

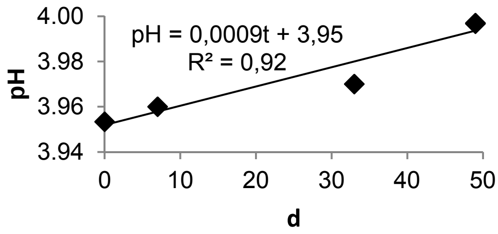

Figure 6: Change of pH

The aroma variation exhibited in the compote samples during their time of storage at 37 ºC and 90 % RH could be demonstrated by the following facts. The initial aroma of compotes was characterized for being mainly represented by the sensor sensitive to nitrous oxide and ozone. According to this, could be noticed that temperature and storage time caused an important change in the apple compote aroma, since at the end of the storage the aroma was differentiated mostly by the sensors reactive to therpens and organophulfur compounds(W1W and W2W),which indicated the samples were decomposed. After applying the Wilks´Lamda test to the matrix of electronic nose data was found that sensors sensitive to methane and aliphatic compounds (W3S) showed the best aroma differentiation of the apple compote samples during storage.

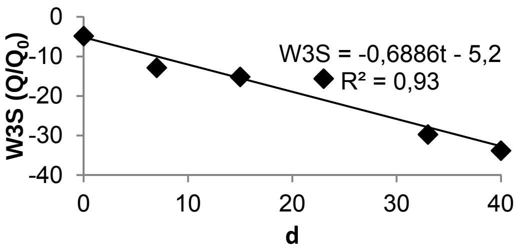

Figure 7: Variation of aroma according to sensor W3S

The estimation of growth of aerobic mesophilic microorganisms, molds and yeasts in compote samples stored at 37 ºC was obtained with the Gompertz model (Figure 8) and the Eq(4). The highest growth rate was showedafter 1176 h, having values of 0.00533 and 0.00364 log CFU/h for aerobic mesophilic microorganism, molds and yeasts. The growth limit for aerobic mesophilic microorganism, molds and yeasts was stated in 0 Log CFU/g according to the standard NTC 1474 (Icontec 2009) for baby complementary food, which implied the end of the shelf-life around 900 h (37.5 d) of storage at 37 ºC.

The variations of total soluble solids, pH and aroma represented by sensor W3S were adjusted to zero order models (Labuza, 1982).The models that allow establishing the shelf-life of compote samples monitoring their initial physicochemical properties Eqs.(10) to (12) were obtained according to the Figures 5 to 7.

$$\mathrm{TSS_{sl}} = \frac{22.75 - \mathrm{Tss_0}}{0.0361} \quad (10) \qquad \mathrm{pH_{sl}} = \frac{3.98 - \mathrm{pH_0}}{0.0009} \quad (11) \qquad \mathrm{W3S_{sl}} = \frac{-31.02 - \mathrm{W3S_0}}{-0.6886} \quad (12)$$

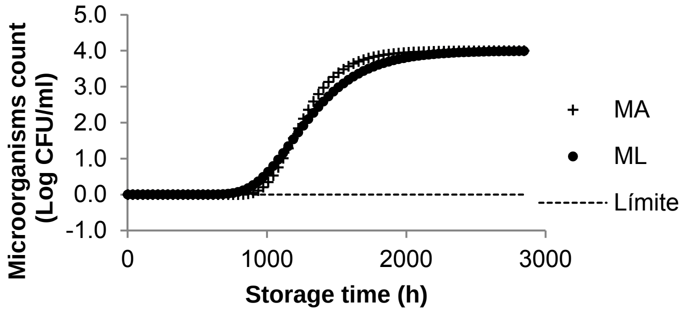

Figure 8: Prediction of microbial growth. MA: aerobic mesophilic microorganism. ML: molds and yeasts.

3.3 Determination of the shelf-life of low water activity food products

The initial moisture content of dehydrated apple pieces was 7.35 %, Figure 9 shows the absorption isotherm of dehydrated apple pieces at 30 ºC. The models that showed better adjustments according to MPE fewer than10 % and r^2 close to 1 were: Power modified and Langmuir models, being Power modified model the best adjustment for the absorption isotherm of dehydrated apples at 30 ºC and 65 % RH with values of MPE 4.49 % and r^2 0.9798.

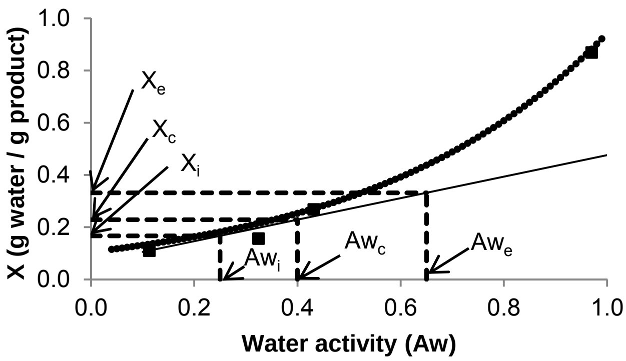

Figure 9: Moisture absorption isotherm that describes the parameters of the shelf-life model

The equilibrium moisture content was estimated for dehydrated apple slices using the Eq(2). The initial and final aw condition of the dehydrated apples were 0.25 and 0.40. These values and a linearized form of the moisture isotherm in the region of interest, with the intersection I and slope m, were used to calculate the initial moisture content Xi and the critical moisture content Xc. The packaging material used in this study was polyethylene 0.92 (PE) with 1.222 $g.m^{-2}.d^{-1}$. The water vapour transmission rate (WVTR) was estimated with a gradient of relative humidity from 90 to 0 % at 30 ºC. The shelf-life determination of dehydrated apples stored at 30 ºC and 65 % RH in PE bags (A = 0.111 m^2), without considering the aw variations of the saturated salt solutions, according to the Eq(3), was 121 d. In a similar study of Escobedo-Avellaneda et al. (2012), based on moisture absorption isotherms, was found a shelf-life for tomato slices of 243 d. For dehydrated apple slices, the shelf-life was defined as the time needed to reach an increase in aw from 0.25 to 0.4, due to the changes in texture properties, including agglomeration and clarity loss (Labuza and Altunakar, 2007).

4 Conclusions

Food products with high aw have a short shelf-life and a sensorial analysis is required to establish the shelf-life loss criteria, for intermediate aw food is necessary to make a microbiological safety check in order to estimate the shelf-life time, while food products with low aw show an extend shelf-life and the quality loss of these products is mainly related to texture changes. For high and intermediate aw is possible to predict the shelf-life of food through several mathematical models and different quality characteristics, only knowing their initial value. Finally, studies of adsorption isotherms are mainly used to estimate the shelf-life of low aw products.

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