

Shelf Life of Pretreated Dried Tomato

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Abstract Determining the shelf life has become a factor of major importance in the development of foods designed to meet consumer demands in terms of quality and safety. The goal of the present study was to investigate the shelf life of vacuum-packed dried tomatoes, stored at both room and refrigeration temperature (4°C) for a period of 180 days. The following determinations were performed during the storage period studied: microbiological analysis, instrumental color, lycopene, and ascorbic acid. Sorption isotherms were determined at both temperatures (room temperature and 4°C). The microbiological quality of vacuum-packed dried tomatoes remained unchanged during 180 days for the refrigerated samples and 90 days for the samples stored at room temperature. The rate constant (k) of lycopene degradation of the refrigerated samples and the samples stored at room temperature was 3.209×10^{-5} and $12.994 \times$

10^{-5} /day, respectively. The rate constant (k) of ascorbic acid degradation was 3.339×10^{-4} /day for cold storage and 76.655×10^{-4} /day for storage at room temperature. The tomatoes stored at room temperature were subjected to analysis over 90 days of storage, period after which both the appearance and sensory characteristics of the product fell below the levels of consumer acceptability. As for the tomatoes stored at refrigeration temperature, the original sensory characteristics were maintained throughout the entire storage period of 180 days.

Keywords Storage · Degradation · Lycopene · Ascorbic acid

Introduction

During processing and storage, tomato products undergo nutritional and sensory changes. The degradation reactions of individual compounds in tomato products, such as lycopene, sugars, or ascorbic acid, are very complex and very dependent on the following factors: initial content, oxygen access, presence of other compounds affecting or participating in oxidation and the Maillard reactions (non-enzymatic browning), in addition to processing conditions. These changes contribute, in some degree, to the typical sensory characteristics of tomato products (Rajchl et al. 2009).

The determination of a product's shelf life has become a factor of increasing importance in the food industry, targeting the consumers' demands and safety. Because food is usually a very complex system, it is hardly possible to identify and isolate a single chemical reaction, whose mechanism can completely explain the changes observed in a food product over time. In short, the reactions that usually occur during food processing are microbiological degradation, senescence, enzyme reactions, browning, lipid

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oxidation, vitamin degradation, as well as color, sensory, and physical changes.

Dried vacuum-packed tomatoes present the following major changes during their shelf life: (a) vitamin degradation, which occurs through a variety of mechanisms, such as hydrolysis under the action of light, heat or acid; direct oxidation by oxygen or by participation in other oxygen-reduction reactions: Vitamin degradation leads to a decrease in nutritional value, often having implications for minimum quantities stipulated on the labels. Vitamin C is one of the most sensitive to the processes of degradation, particularly at high humidity and temperature levels. Labuza (1982) presented results on the stability of vitamins dependent on the conditions and time of storage. (b) Changes in colors, which occur due to a large number of different reactions, especially oxidation of carotenoids; (c) sensory changes. All cited reactions lead to sensory changes, which often make it difficult to isolate a single type of reaction and its mechanism of action, making it necessary to make use of sensory evaluations using trained and non-trained panelists.

Temperature—both during processing and storage—is one of the most important parameters to determine the shelf life of a food sample. Most stages of preparation and storage of foods involve the application and removal of heat (refrigeration). Cooling consists of lowering a food's temperature to at least 0°C, seeking preservation for a relatively short period. There are several studies on this subject, and data on the influence that the decrease in temperature has on deterioration reactions are easily found in the literature (Fennema 1975).

The Brunauer–Emmett–Teller theory (Brunauer et al. 1938) of multilayer gas and vapor adsorption, known generally as the BET equation, has been widely used to estimate the amount of water bound to specific polar sites in dried food systems and is considered a valuable method to assess the stability of dried foods (Toupin et al. 1983). The equation gives an approximate value of a water monolayer adsorbed on a material. The BET monolayer value of a food corresponds to the moisture content at which many food systems exhibit maximum stability. Although the theory is based on assumptions that do not entirely hold for most materials, the BET model provides a useful tool for the analysis of water sorption isotherms in foods (Labuza 1968; Okos 1986). The BET isotherm generally gives a good fit over the range of water activity from 0.1 to 0.5. This range is sufficient to obtain the monolayer value.

The sorption equation analyzed according to the Guggenheim–Anderson–De Bôer model (GAB isotherm equation), which is considered an extension of the BET model, was proposed for food materials by Van Den Berg and Bruin (1981), and its use is recommended by the European Projects Group COST 90 on Physical Properties of Foods. The GAB has been reported

to be useful to adjust data within a wider water activity range (0.1 to 0.9) than the BET equation.

The goal of this study was to investigate the shelf life of pretreated vacuum-packed tomatoes, stored at room and refrigeration temperatures.

Materials and Methods

The production process (pretreatment and treatment) of dried tomatoes was established in a previous phase of this study, in which the levels of NaCl and citric acid were evaluated using a 2×5 experimental design with an additional central point further analyzed with the response surface method and the Statistica 6.0 software program. The experimental data and procedures for the recorded variables involved in the dehydration process, as well as the analyses of the effect of this process on the attributes of the selected product (tomatoes), are described in detail by Camargo (2005). This same author also lists the bibliographical references related to the surface response and sensory analysis methods used in this study.

In accordance with Camargo (2005), the following procedures were performed: (a) determination of the osmotic concentration by soaking the product in a solution of sugar, salt (5.85%), and citric acid (6.00%) with 65° Brix for 40 min at a temperature of 45° C; (b) application of antioxidants: Tomatoes were immersed in a solution of sodium metabisulfite and ascorbic acid in the proportion of 100:1,500 mg/l, for 1 min; (c) forced air drying for 12 h; (d) vacuum packing.

The dried tomatoes were evaluated during storage at two temperatures: room and at 4°C.

Room temperature was measured daily and the average calculated; the mean (25.2°C), maximum (38.67°C), and minimum (12.12°C) values were also recorded.

The product was vacuum-packed in a coextruded nylon-polyethylene packaging measuring 12×17×0.18 cm. The packaging was characterized by gravimetric analysis; the silica capsules were dried until constant weight, so as to allow the determination of the vapor transmission rate as calculated by linear regression.

In order to verify microbiological conditions, the dried tomatoes were analyzed for total coliforms, fecal coliforms (*Escherichia coli*), and *Salmonella*, in compliance with the current Brazilian norms (Brazil 2001). The water activity measured for the dried tomatoes was 0.86. In these conditions, the development of molds and yeasts can occur during storage. Due to this, therefore, the mold and yeast counts were included in the analysis. The water activity was measured using an Agua Lab TC-500 Brookfield equipment. The method applied for investigation of said microorganisms was according to that described in the Compendium of

Methods for the Microbiological Examination of Foods, edited by the American Public Health Association (APHA 2001). The microbiological analyses were done for 0, 30, 60, 90, and 180 days of storage, for both storage conditions (4°C and room temperature).

The lycopene content was determined as total carotenoids using a spectrophotometer by the following equation:

$$\text{LCP} = \frac{10^4 \text{ ABS}V}{EM} \times 1,000 \quad (1)$$

where LCP is the lycopene content (milligram per gram), ABS maximum absorbance (peak), V the sample volume, E (1% and 1 cm) the molar absorption coefficient of lycopene at 3,450 (Davies 1976), and M the sample weight (gram).

To determine the ascorbic acid content, a sample of 1 g crushed tomato was measured into 50 mL of a filtered 3% HPO₃ solution. These analyses were performed in accordance with the titration method using 2,6-dichlorophenol-indophenol, as described in Romero (1999) by the following equation:

$$A_a = \frac{(V_T) \left(\frac{0.5}{V_t} \right) (V)(100)}{(V_A)(m)} \quad (2)$$

where A_a =ascorbic acid (milligrams per 100 g), V_T =titration volume (milliliter), V_t =volume titrated to standardize the indicator solution (milliliter), V =volume measured (milliliter), V_A =volume of the aliquot (milliliter), m =tomato weight (gram).

The instrumental color of the final product was determined with a COLORQUEST II spectrophotometer (CIE $L^*a^*b^*$) using a D65 illuminant—which simulates average daylight—at a constant observation angle of 10°. This equipment quantifies the amount of incident light falling on the surface of the product, assigning precise values to the L^* , a^* , and b^* parameters. The L^* value gives the relative brightness of the color ranging from total black ($L^*=0$) to total white ($L^*=100$); the a^* value represents the color hue ranging from red (positive results) to green (negative results); the b^* value represents the color hue ranging from yellow (positive results) to blue (negative results).

Sensory analyses were carried out following the procedure described by Stone and Sidel (1985), which determines that preference tests using hedonic scales be performed with a

minimum of 30 panelists. The samples were presented to the panelists in a complete balanced block design within each session. Randomization was performed according to the procedure described by Macfie et al. (1989). The panelists were given an evaluation form containing the preference parameters: overall appearance, color, taste (flavor), and texture and were asked to assign a liking score for each parameter on a 9-point hedonic scale (“1—dislike extremely,” “2—dislike very much,” “3—dislike moderately,” “4—dislike slightly,” “5—neither like nor dislike,” “6—like slightly,” “7—like moderately,” “8—like very much,” “9—like extremely”). Using the same form, panelists were also asked to complete the consumer purchase intention test assigning a score on a 5-point scale (“1—certainly not purchase,” “2—possibly not purchase,” “3—perhaps purchase/perhaps not purchase,” “4—possibly purchase,” “5—certainly purchase”).

The limit of acceptability was set according to the meaning of each rating on the hedonic scale. In other words, on the 9-point scale, rating 6.0 (“like slightly”) represents the limit of acceptability of the panelist, indicating that he/she liked the product, whereas ratings lower than 6.0 indicated dislike. As for the purchase intention scale, ratings greater than 3.0 (“perhaps purchase/perhaps not purchase”) indicated that the panelist would be willing to consider purchasing the product. The results were analyzed using analysis of variance and the SAS software (SAS 2000).

The degradation kinetic constants were calculated from the experimental data, fitted to a model for a second-order reaction, in which the conversion rate depends on the reactant’s concentration, according to the equation below, which defines the reaction rate:

$$-\gamma A = \frac{-dC_A}{dt} = kC_A^n \quad (3)$$

Thus, for the reactions of the type A+B (apud Vitalli and Teixeira Neto 2002): A+B→products, where

$$-\gamma A = \frac{-dC_A}{dt} = \frac{dC_B}{dt} = kC_A C_B \quad (4)$$

Normally $A \approx B$, so $2A \rightarrow$ products, where

$$-\gamma A = \frac{-dC_A}{dt} = kC_A^2 \quad (5)$$

Table 1 Tri-parametric models used to predict sorption isotherms

Name of the equation	Models	Reference
GAB	$m = \frac{m_0 c k a_w}{[(1-k a_w)(1+(c-1)k a_w)]}$	Maroulis (1988)
BET	$m = \frac{m_0 c k a_w}{(1-a_w) \cdot \left(\frac{1-(n+1)a_w^n + n a_w^{n+1}}{1-(1-c)a_w - c a_w^{n+1}} \right)}$	Park and Nogueira (1992)

m =moisture equilibrium (gram per gram dry base); m_0 =monolayer moisture (gram per gram dry base); a_w =water activity (dimensionless); c , k =constants, n =number of layers

Table 2 Microbiological analysis of pretreated dried tomato, stored at two different temperatures: room and at 4° C

Storage time (days)	Temperature	Molds and yeasts (CFUg ⁻¹)	Total coliforms (MPNg ⁻¹)	Total fecal coliforms (MPNg ⁻¹)	Salmonella (in 25g)
0	After processing	<10	<3.6	<3.6	Default
30	4°C	<10	<3.6	<3.6	Default
30	Room	<10	<3.6	<3.6	Default
60	4°C	<10	<3.6	<3.6	Default
60	Room	<10	<3.6	<3.6	Default
90	4°C	<10	<3.6	<3.6	Default
90	Room	<10	<3.6	<3.6	Default
180	4°C	<10	<3.6	<3.6	Default
180	Room	Not realized			

CFU g⁻¹ colony forming units per gram, MPN g⁻¹ most probable number per gram

Integrating the last term:

$$\frac{1}{CA} - \frac{1}{CA_0} = k \cdot t \text{ or } \frac{1}{CA} = \frac{1}{CA_0} + k \cdot t \quad (6)$$

where k =reaction rate constant, CA_0 =initial concentration of component A, CA =concentration of component A, total lycopene in microgram per gram; ascorbic acid in milligram per gram; t =reaction time (days); γA =reaction rate (units of the component per day); n =order of the reaction (for food, normally $0 < n < 2$).

Thus, this results in a linear scale plot of the inverse of the reactant concentration as a function of the reaction time. The reaction studied is a second-order reaction. The slope of the line is the reaction rate constant (k).

The data of lycopene and ascorbic acid were adjusted with Microsoft Excel for to determine regression coefficient.

The vacuum-packed dried tomatoes were subjected to the following analyses over a 180-day period: microbiological analysis, instrumental color, total lycopene, vitamin C, and sensory analysis (preference and purchase intention tests).

The sorption isotherms were determined using the DVS system (The Sorption Solution), at the Transport Phenom-

ena Laboratory of the Faculty of Chemical Engineering/ UNICAMP.

The isotherm data were evaluated by nonlinear regression using the Statistica software program and BET and GAB models (Table 1) to calculate the parameters and best fit (R^2).

Results and Discussion

The calculated (water) vapor transmission rate was 3,092 g water/(m²day). The tomatoes stored at room temperature were analyzed over a period of up to 90 days; period after which the appearance and sensory characteristics of the product were considered unacceptable to consumers. The refrigerated product was found to meet all acceptability criteria in all tests conducted over up to 180 days. The absence of microbial development (Table 2) in the product stored under the two temperature conditions investigated showed that the barriers built into the product during processing resulted in a microbiologically safe food.

These barriers were (1) an increase in the solids concentration by immersing the product in the osmotic

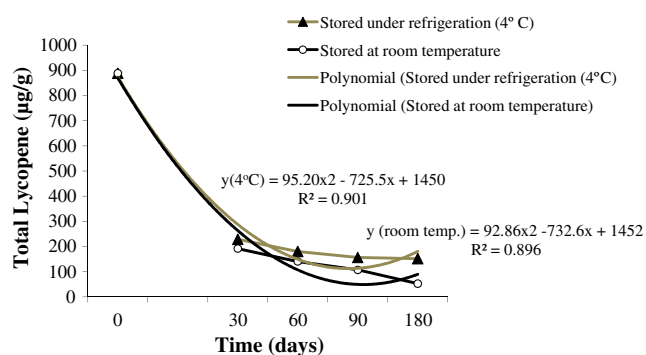


Fig. 1 Evolution of the lycopene content throughout 180 days in vacuum-packed dried tomatoes, stored at room temperature and at 4°C

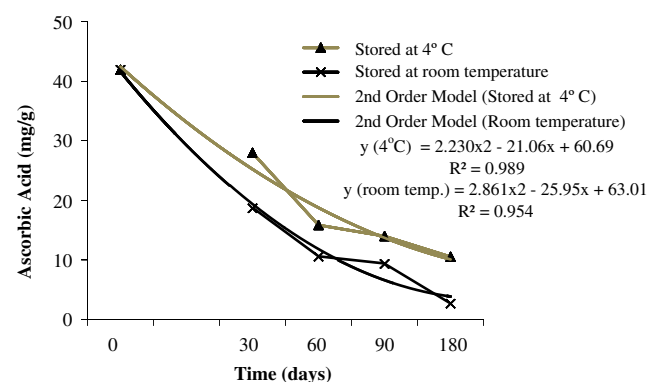
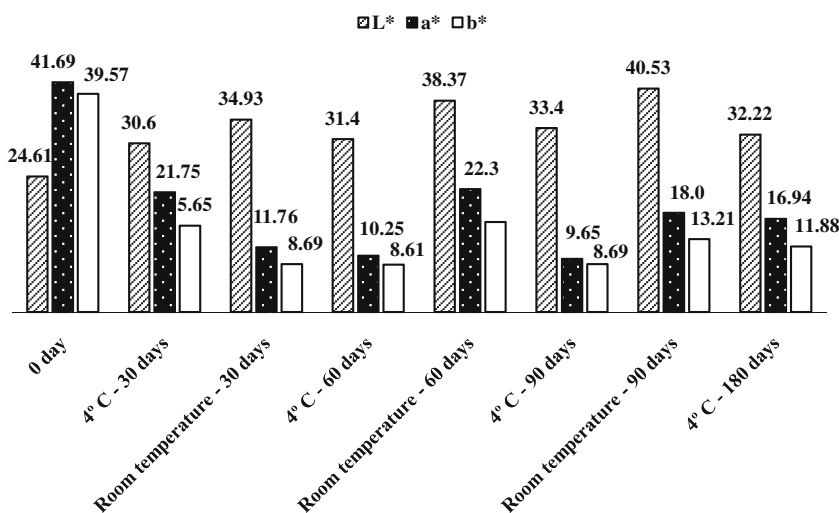


Fig. 2 Evolution of the ascorbic acid content throughout 180 days in vacuum-packed dried tomatoes, stored at room temperature and at 4°C

Fig. 3 Color analysis parameters over 180 days of storage at two storage conditions, 4°C and room temperature



sugar/salt solution; (2) acidification due to the presence of citric acid used in the syrup; and (3) the addition of antioxidant agents (ascorbic acid and sodium metabisulfite), all three of which combined produced the so-called Hurdle Effect (Leistner 1994). In tomato-based products, color is one of the main quality parameters. The darkening of the product to a reddish-brown is due to the oxidation of carotenoid pigments and the formation of dark compounds, in addition to the browning effect of the Maillard reaction. These changes are dependent on storage temperature, oxygen availability, packaging type, pH, and product activity.

Shelf Life Kinetic Study

Figure 1 shows the total lycopene concentration over 180 days of dried tomatoes stored at refrigeration (4°C) and room temperature. The degradation curve of the

lycopene content was found to be a third-order reaction, in which the reaction rate depends on the concentration of the reactant and time. The regression coefficient was 98.8% and 98.9% for the refrigerated tomatoes and room temperature, respectively. The degradation rate constant (*k*) calculated in the methodology for the second-order model was 3.209×10^{-5} /day for tomato stored at refrigeration. For the tomatoes stored at room temperature, the degradation rate constant was 12.9948×10^{-5} /day. The degradation rate of lycopene is four times higher in the product stored at room temperature than in the product stored under refrigeration (4°C). The adjustment coefficients allowed determining the type of third-order reaction that causes the degradation of lycopene during the shelf life of the tomatoes. In this case, higher concentrations of lycopene implied in greater losses, followed by a drop in the reaction rate proportional to the component’s concentration. It is possible to observe that loss of large amounts of lycopene

Fig. 4 Preference test results of tomatoes stored at room temperature

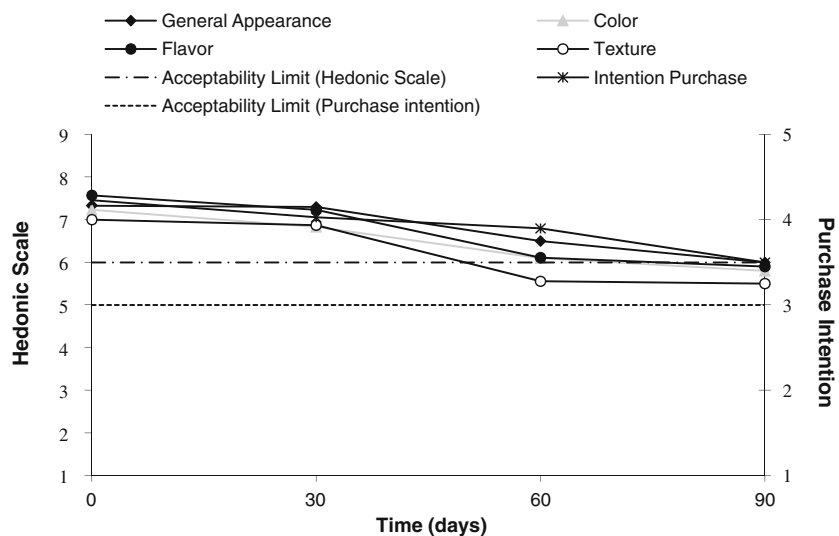
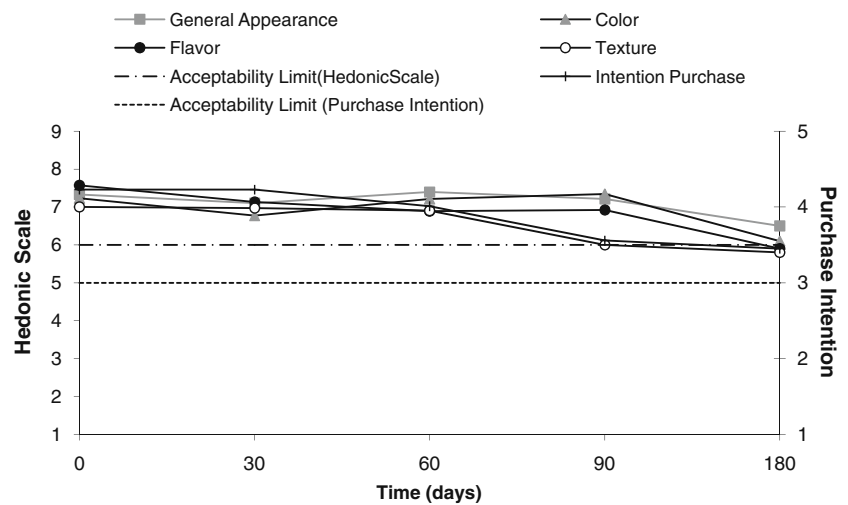


Fig. 5 Preference test results of tomatoes stored at refrigeration temperature (4°C)



occurred over the first 30 days, but after this period, the reaction slowed down and—according to Vitalli and Teixeira Neto (2002)—does not totally degrade the remaining lycopene. Lavelli and Giovanelli (2003) subjected tomato products (pulp in cans, puree in glass bottles, and paste in aluminum tubes) to accelerated aging (30, 40, and 50°C for 3 months). They found that lycopene remained stable in all samples. Anguelova and Warthesen (2000) subjected tomato powder to three treatments: exposure to light at room temperature and storage at 6 and 45°C in the dark. Differences among the storage treatments are not obvious from the data, but the amount of *cis* isomers as a percentage of the total lycopene increased to the 14–18% range, regardless of the storage conditions.

Degradation of ascorbic acid conforms to a second-order reaction model, which is common for vitamin degradation in foods, as can be seen in Fig. 2. The order of the reactions that occur in food usually lies between 0 and 2 (Vitalli and Teixeira Neto 2002). Calculation of the degradation rate constant (*k*) yielded 3.339×10^{-4} /day for storage at 4°C, with a regression coefficient of 98.94%. For storage at room temperature, *k* was found to be 76.655×10^{-4} /day, and the regression coefficient was 95.43%. As expected, at room temperature, the product presented a higher degradation rate: 23 times higher than the tomatoes stored under refrigeration and in the dark. Dermesonlouoglou et al. 2007 studied tomato slices pretreated with an osmotic high-DE maltodextrin syrup and subsequently frozen. Their objective was to evaluate the stabilization of quality of the osmodehydrofrozen samples during frozen storage over a wide temperature range ranging from -5 to -20°C. They concluded that after 12 months of storage at -20°C, the dehydrofrozen tomatoes, compared with the conventional frozen samples, unblanched and blanched, contained 20–28% more vitamin C.

Vitamin C is an important quality index, but the fact that commercial and consumer acceptability is mainly based on

sensory quality criteria, such as color, texture, taste, and flavor, should not be overlooked.

Color Measurement

Color changes occur simultaneously with odor and taste changes, which result in product deterioration. Figure 3 shows the parameters *L**, *a**, and *b** of the instrumental color of dried tomatoes during their shelf life (90 days for room temperature and 180 days for those stored at 4°C). As expected, darkening of the product occurred, as evidenced by the increase of the *L** color parameter, where 0 indicates absolute white and 100 absolute black. The data show that *L** parameter increased from 24.6 to 40.53 over 90 days of storage at room temperature. The refrigerated product (4°C) showed less intense darkening, with a final *L** value of 32.22 after 180 days storage. Parameters *a** and *b** decreased during storage, indicating the loss of color in tomatoes, particularly the color red (as indicated by parameter *a*). All parameters (*L**, *a**, and *b**) exhibited a significant statistical difference at the 5% level for all samples compared to the sample at the beginning of the product’s shelf life.

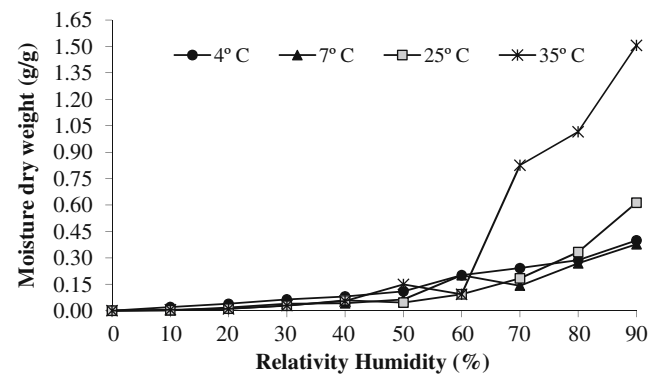


Fig. 6 Sorption isotherms at different temperatures

Table 3 Parameters for adjusting sorption isotherms of dried tomato stored at 4 and 7°C

Isotherms	4°C					7°C				
	m_0	c	k	n	R^2	m_0	c	k	n	R^2
Desorption (GAB)	8.305	0.041	0.460	–	0.995	6.610	0.011	0.718	–	0.993
Desorption (BET)	42.122	0.002	–	2.597	0.994	0.088	0.531	–	13.178	0.995

m_0 =monolayer moisture content (gram per gram dry weight), c , k =constants, n =number of layers

Preference Tests During Shelf Life

Figures 4 and 5 show the mean liking scores obtained in the preference and acceptability tests carried out throughout 90 and 180 days of storage at room temperature and 4°C, respectively. The product stored at room temperature presented a mean score approximately (5.5 for texture, 5.9 for flavor, 5.9 for color, 6.0 for general appearance) the threshold value of 6.0 (“like slightly”) in the preference tests and a score greater than the lower limit of 3.0 (“perhaps purchase/perhaps not purchase”) in the consumer acceptability tests carried out over 90 days of storage. This leads to the conclusion that dried vacuum-packed tomatoes stored at room temperature presented characteristics desirable to consumers for 90 days. Therefore, 90 days was set as the shelf life limit for this product. The refrigerated product presented a shelf life twice as long: 180 days, with mean scores above the aforementioned lower limits (general appearance, color, and intention purchase) and just about 6.0 (5.8 for texture and 5.9 for flavor).

It is important to note that during the initial 60 days of storage, the product’s purchase intention score remained close to 4.0 (“possibly purchase”), indicating a positive purchase attitude for the product. The product’s purchase intention score remained above the established limit (3.0) during its shelf life limit, 90 and 180 days for the product stored at room temperature and at 4°C, respectively.

Sorption Isotherms

In food storage and dehydration, the determination of ideal air conditions (temperature and humidity) is an essential

part of the process. Obtaining the sorption isotherms is essential to determine the final percentage of water that is necessary to stabilize a food product.

For the dried vacuum-packed tomatoes, the sorption isotherms were determined for four storage conditions: two different room temperatures (25 and 35°C) and two different cold storage temperature commonly used by commercial cold storage systems (4 and 7°C).

Figure 6 depicts the sorption isotherms for the four temperatures studied. All of these conform to a similar model: sigmoid form, type II, according to the classification by Brunauer et al. (1938).

The moisture adsorption and desorption data of the products stored at 4, 7, 25, and 35°C were submitted to nonlinear regression analysis using the mathematical models shown in Tables 3 and 4. The values for moisture content equivalent to the monolayer (m_0) for adsorption and desorption, calculated by the GAB and BET equation, are shown in Tables 3 and 4, along with the values of the constants and the determination coefficient (R^2).

It is important to observe that the equations (GAB and BET), when analyzed considering only their regression coefficient (R^2), adequately represent the sorption isotherms of dried tomato, with the exception of the desorption isotherm at 25°C.

For the cold storage temperatures (4 and 7°C), the BET equation was found to provide the best fit. It was also observed that under this storage condition, no adsorption occurred, only desorption of water from the product.

However, at the refrigeration temperatures (4 and 7°C), only desorption occurred. In other words, the product does not absorb water at lower temperatures, thereby preventing

Table 4 Parameters for adjusting sorption isotherms of dried tomato stored at 25 and 35°C

Isotherms	25°C					35°C				
	m_0	c	k	n	R^2	m_0	c	k	n	R^2
Adsorption (GAB)	3.079	0.018	0.830	–	0.998	36.394	0.015	0.619	–	0.970
Adsorption (BET)	0.669	0.042	–	9.916	0.999	1.072	0.185	–	5.984	0.976
Desorption (GAB)	19.235	0.021	0.210	–	0.920	0.028	0.873	1.690	–	0.999
Desorption (BET)	0.097	0.766	–	2.480	0.926	253.383	0.0002	–	1,245.759	0.973

m_0 =monolayer moisture content (gram per gram dry weight), c , k =constants, n =number of layers

an increase in the product's water activity during shelf life. Excessive drying can occur, but only in the case of extended storage periods (longer than 180 days, the limit studied in this project). Storage at room temperatures 25 and 35 °C produced adsorption and desorption curves. The dried tomatoes stored under relative humidity conditions greater than 50% presented adsorption, which translates into absorbing water. The coextruded nylon-polyethylene packaging was used to minimize this type of problem.

As for storage at room or ambient temperatures (25 and 35 °C), the BET equation was found to give the best fit for the adsorption isotherm. However, for the desorption isotherm at 25 °C, none of the two models give a good fit to the data. For storage at 35 °C, the GAB equation was the model that gave the best regression coefficients. It was found that the m_0 parameter of GAB and BET equations, in which this value represents the monolayer moisture content of the adsorbing material, did not exhibit any defined trend of variation with storage temperature.

It should be emphasized that the sorption isotherms were not included in the initial objectives of this study. For that reason, a more detailed evaluation of the different model fits and their effect on the final product will be conducted in the nearby future.

Conclusions

The microbiological quality of vacuum-packed dried tomatoes was maintained over a period of 180 days for tomatoes stored under refrigeration and 90 days for tomatoes stored at room temperature. The degradation rate constant (k) of lycopene was 3.209×10^{-5} /day for cold storage and 12.995×10^{-5} /day for storage at room temperature. The degradation rate constant (k) of ascorbic acid was 3.339×10^{-4} /day for refrigerated storage and 76.655×10^{-4} /day for storage at room temperature. The dried tomato absorbed water (according to the adsorption and desorption isotherms) above the relative humidity of 50%. The sorption isotherms of dried tomato conform to a type II, sigmoid form model, with the BET and GAB giving a good fit to the experimental data for the different temperatures investigated, with the exception of the desorption isotherm at 25 °C.

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