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Influence of Drying Conditions on Ascorbic Acid during Convective Drying of Whole Persimmons

Joel F. Nicoleti,1 Vivaldo Silveira Jr.,1 Javier Telis-Romero,2 and Vânia R. N. Telis2
1UNICAMP—Universidade Estadual de Campinas, Departamento de Engenharia de Alimentos, Campinas, SP, Brazil
2UNESP—Universidade Estadual Paulista, Departamento de Engenharia e Tecnologia de Alimentos, São José do Rio Preto, SP, Brazil

Degradation kinetics of food constituents may be related to the matrix molecular mobility by glass transition temperature. Our objective was to test this approach to describe ascorbic acid degradation during drying of persimmons in an automatically controlled tray dryer with temperatures (40 to 70°C) and air velocities (0.8 to 2.0 m/s) varying according a second order central composite design. The Williams-Landel-Ferry model was satisfactorily adjusted to degradation curves for both control strategies adopted—constant air temperature and temperature fixed inside the fruit. Degradation rates were higher at higher drying temperatures, independent of the necessary time to attain the desired moisture content.

Keywords Glass transition; Kinetics; Thermal degradation; Vitamin C; WLF model

INTRODUCTION

The persimmon (Diospyros kaki) is an edible fruit native to East Asia, most likely China, but Italy, Brazil, Israel, Spain, United States, Australia, and New Zealand have significant plantings of this crop. When fully mature the fruit has a tough, glossy, orange-red skin and a yellow-orange flesh, which is very sweet and juicy. Persimmon is rich in some nutrients such as vitamin C (70 mg/100 g of pulp), vitamin A (65 mg/100 g of pulp), calcium (9 mg/100 g of pulp), and iron (0.2 mg/100 g of pulp).[1] It is also rich in phenolics compounds and antioxidant effects are associated with these constituents.[2]

A number of persimmon varieties present a marked astringency due to their highly soluble tannin contents, but this undesirable attribute can be removed by several methods, such as exposing the fruit to anaerobic conditions or to products of anaerobic respiration, or even by immersion in water at moderate temperatures (40 to 60°C).[3] The relatively high temperatures commonly applied during convective drying also lead to tannin degradation, whereas sugars present in the fruit exude to the surface where they crystallize. The result is a sweet, tasteful, and non-astringent dried product, which is already traditionally consumed in oriental countries.[4,5]


In modern food technology, the trend is to maximize nutrients retention in both processing and storage and it is generally observed that, if ascorbic acid is well retained, the other nutrients are also well retained. Hence, ascorbic acid is usually considered as an index of nutrient quality during processing and storage of foods.[13] Ascorbic acid is known to be a labile vitamin that loses activity due to a number of factors, including pH, moisture content, oxygen, temperature, and metal ion catalysis.[14]

Several works concerning ascorbic acid degradation in foods have suggested decay kinetics of first-order and the Bigelow equation has been applied in modeling.[15,16] It is common to characterize first-order reactions in terms of DT and z values (thermal death time concept). Singh and Lund[17] developed a mathematical model to describe ascorbic acid degradation in stored apples as function of temperature and water activity. Akinyele et al.[18]
investigated nutrient losses during and after processing of pineapples and oranges and a number of authors studied vitamin C degradation in various foodstuffs.\textsuperscript{[14,19–22]}

The degradation kinetics of food constituents may be related to molecular mobility of food matrix, which is affected by the free volume and by the molecular relaxation time of the food structure, and the glass transition temperature (\(T_g\)) has been used as the main indicator of this mobility. The glass transition involves change from a solid “glassy” to a liquid-like “rubbery” state. This transition occurs within a temperature range characteristic for each material and the midpoint temperature of such change is taken as the glass transition temperature (\(T_g\)). There is an important increase in molecular mobility across \(T_g\) that can affect reactions kinetics in situations where molecular mobility (diffusion of reactants or products) is the controlling factor.

Application of the glass transition approach to describe kinetics of ascorbic acid degradation during drying of food models has already been reported.\textsuperscript{[23]} The kinetic model is based in the Williams-Landel-Ferry (WLF) dependency of the DT value on \(T_g\), which encompasses the influence of water content. At temperatures above \(T_g\), plasticization by water affects the viscoelastic, thermomechanical, electrical, guest/host diffusion, and gas permeability properties of completely amorphous and partially crystalline polymer systems. In the rubbery range above \(T_g\), the dependence of viscoelastic properties on temperature is successfully predicted by the WLF equation, an empirical equation whose form was originally derived from free volume theory, and can be written as:

\[
\log_{10}\left(\frac{\eta/(\rho T_g)}{\eta_g/(\rho_g T_g)}\right) = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}
\]

where \(\eta\) is the viscosity or other diffusion-limited relaxation process, \(\rho\) is the density, and \(C_1\) and \(C_2\) are coefficients that describe the temperature dependence of the relaxation process at temperatures above the reference temperature, \(T_g\), and may vary somewhat with the system. The WLF equation is based on the assumptions that the matrix free volume increases linearly with increasing temperature above \(T_g\) and that the segmental or mobile unit viscosity, in turn, decreases rapidly with increasing free volume.\textsuperscript{[24]}

During drying, the removal of water substantially increases the glass transition temperature of the matrix: totally dried food matrices have glass transition temperatures ranging mostly from 150 to 220°C. Thus, as drying progresses, the matrix approaches the onset of glass transition and may even vitrify.\textsuperscript{[23]} Several other studies have been published that analyze reaction kinetics in relation to the food matrix state by using the WLF model.\textsuperscript{[25–28]}

The purpose of this work was to apply the glass transition approach to describe the kinetics of ascorbic acid degradation during drying of whole persimmons assuming distinct control strategies in the dryer: constant air temperature and fixed temperature inside the fruit.

**MATERIALS AND METHODS**

**Raw Material**

Ripe, fresh persimmons (\textit{Diospyros kaki}) of the Rama Forte cultivar were obtained at the local market (São José do Rio Preto, SP, Brazil). The selected fruits presented a uniform orange color, regular size, and intermediate degree of firmness. The soluble solids content ranged from 14 to 18°Brix and moisture content from 0.79 to 0.84 kg water/kg wet material. The fruits were washed in fresh water and hand peeled.

**Air-Drying**

The drying equipment was a pilot-scale tray dryer that consists of three basic sections, an air flow rate control system, a drying air heating section, and a drying chamber, and is equipped with a process control system based on Fieldbus technology, supplied by SMAR Industrial Equipment Ltda. (Sertãozinho, SP, Brazil). The dryer was previously described elsewhere.\textsuperscript{[29]} A centrifugal fan (model VCI-350M, Ibram, São Paulo, SP, Brazil) was used to force air through the drying chamber (Fig. 1). The fan was driven by an electric motor with the air flow rate controlled by a frequency modulator (model MMV, Siemens, Erlangen, Germany). An orifice plate connected to a pressure transmitter (model LD302, SMAR, Sertãozinho, SP, Brazil) was installed after the fan to measure the air flow during process. Dry bulb and wet bulb temperatures of the air stream were measured online using temperature transmitters (model TT302, SMAR, Sertãozinho, SP, Brazil). The drying air was heated by passing through electric resistances controlled by a power converter (model TH 6021A/80, Therma, São Paulo, SP, Brazil). A “honeycomb” was installed before the drying chamber to allow better distribution of air in the product. The drying compartment consisted of two square metal trays, placed perpendicular to the air flow. Thermocouples connected with temperature transmitters (model TT302, SMAR, Sertãozinho, SP, Brazil) were placed before and after trays and inside one of the whole persimmons to analyze the evolution of temperature inside the product during experiments. In order to integrate the instruments with the Fieldbus system, a 4- to 20-mA current converter (model IF302, SMAR, Sertãozinho, SP, Brazil) was used. The equipment operation was monitored and controlled by means of a computer running the software AIMAX\textsuperscript{8}.-WIN.

Once desired operation conditions were achieved in the dryer, the specimens—30 whole persimmons to each drying run—were inserted into the dryer cabinet and kept hanging by a string tied from their stems to a fixed support. The sample mass and ascorbic acid content were determined at regular time intervals. The initial moisture contents of persimmons...
were determined gravimetrically using a vacuum oven (model MA-030, Marconi, Piracicaba, SP, Brazil) at 60°C for 48 h.

In order to evaluate the effect of air temperature and velocity on the ascorbic acid degradation kinetics, a second-order central composite rotatable design combined with response surface methodology[30] was applied, with temperature varying from 40 to 70°C and velocity from 0.8 to 2.0 m/s, according to Table 1.

### Ascorbic Acid Content
At regular time intervals, one whole persimmon was removed from the dryer and a sample of 25 g was homogenized with 50 g of the extraction solution (oxalic acid at 2%). An aliquot of 10 g was taken and diluted to 50 mL with the extraction solution in a volumetric flask and then vacuum filtered. Aliquots of 10 g of the filtrate were taken for titration with 2,6-dichlorophenolindophenol 0.01%.

The titration end point was visually detected and all analyses were conducted in duplicate.[31]

The average ascorbic acid experimental content determined in persimmons in natura was of 3.4 ± 1.63 mg ascorbic acid/g dry matter and this value was adopted as the initial concentration, C₀, in all experimental runs. Figure 2 shows the distribution of experimental values of C₀ in the 16 fruits analyzed, with the maximum and minimum concentrations being, respectively, 6.66 and 1.13 mg ascorbic acid/g dry matter. The high standard deviation of C₀ (around 48%) could be attributed to the heterogeneity inherent to products of biological origin.

### Mathematical Modeling
Considering that the process is controlled by molecular mobility, which will change as the matrix dries and its glass transition temperature rises, the thermal death time Dₜ is related to Tₐ by the WLF model according to Eq. (2):

$$D_T = \frac{10^{\frac{C_1(T - T_0)}{C_2 + (T - T_0)}}}{10^{\frac{C_1(T - T_0)}{C_2 + (T - T_0)}}}$$

where Dₜ is the Dₜ value at the glass transition temperature (Tₑ). Sobral et al.[9] determined the state diagram for persimmon and, in the range of average moisture contents attained by samples tested in the present work, the value of Tₑ could be assumed as constant and equal to the glass transition temperature of the maximally concentrated food matrix, Tₑ = 216.5 K Since Dₑ is much higher than Dₜ,
Eq. (2) is written for a reference temperature $T_r$:

$$\frac{D_r}{D_g} = \frac{10^{c_1 (T_r/T_g)}}{C_0 C_1 C_2 \left(\frac{T}{C_0 T_r}\right)^{1/3} + \left(\frac{T_r}{C_0 T_g}\right)^{1/3}}.$$  

(3)

Dividing Eq. (2) by Eq. (3) we obtain:

$$\frac{D_T}{D_r} = 10^{c_1 c_2 (T-T_r)}.$$  

(4)

Applying this model to the drying process conditions:

$$\log \frac{C}{C_0} = -\int_0^t \frac{c_1 c_2 (T-T_r)}{D_r} \, dt.$$  

(5)

where $C$ is the ascorbic acid content at time $t$ and $C_0$ is the initial ascorbic acid content.

For the two control strategies employed in drying experiments, Eq. (5) was solved by two different approaches:

1. Constant air temperature: referring to the temperature inside the fruit, these experiments resulted in nonisothermal conditions, since temperature inside the fruit increased as drying progressed, as shown by temperature histories presented in Figs. 3a and 4a, which exemplify typical data. In this case, a polynomial function for $T$ versus time was fitted to the recorded temperature histories and inserted in Eq. (5). The resulting equation was expanded in Taylor series and adjusted to the experimental data of ascorbic acid concentration versus time by nonlinear regression.

2. Temperature fixed inside the fruit: this class of assays was carried out under isothermal conditions inside the fruit, which was maintained by means of the dryer automatic control system. A constant temperature set point was assigned to a thermocouple inserted in the center of one of the fruits in the dryer, in such a way that air...
temperature was varied in order to keep a constant temperature inside the fruit. Typical temperature histories corresponding to this control strategy are shown in Figs. 5a and 6a. Except for a short time at the beginning of drying runs (not more than 60 min), temperature $T$ was constant inside the fruits and the solution of Eq. (5) was simplified, as $C_1$, $C_2$, $T_g$, $T_r$, and $D_r$ were constants too.

The quality of the model fitting to experimental data was evaluated by the sum of squares of residuals (SSQ), given by Eq. (6).

$$SSQ = \sum \left( \frac{(C_{exp} - C_{pred})}{C_{exp}} \right)^2$$

where $C_{exp}$ is the experimental value and $C_{pred}$ the predicted value of ascorbic acid content.

RESULTS AND DISCUSSION

Drying with Constant Air Temperature

According to the second-order central composite rotatable design, nine drying runs were carried out at different air temperatures and velocities with a replicate at the central point (Table 1). Figures 3 and 4 present the adjustment of the WLF model to experimental data obtained during drying of persimmons with air velocity of 1.4 m/s and temperatures of 40 and 70°C, respectively. Values of the adjustable constants in Eq. (5) were obtained by nonlinear regression of the data set obtained for each experimental condition. Based on the model estimates, along the decrease in moisture content to a final value of 1.5 g water/g dry matter, 38% of the initial ascorbic acid content was lost during drying at 40°C, whereas for the same moisture...
content reduction, a loss of 93% of initial ascorbic acid concentration was observed during drying at 70°C.

The reference moisture content of 1.5 g water/g dry matter, which corresponds to 60% moisture in wet basis, was adopted because ascorbic acid analyses in fruits with lower moisture content could not be done, since there was great difficulty in homogenizing the dried product with the oxalic acid solution due to crust formation. It must be also taken into account that whole persimmons may be considered as intermediate moisture products. It is very time and energy consuming to attain smaller moisture contents, as this would demand removing internal moisture through the thick external dried layer with reduced water permeability that is formed during the first drying stages.

On the effect of both time and temperature over ascorbic acid degradation rates, it is possible to conclude that the nutrient loss was mainly affected by temperature. Even considering that in order to attain the same final moisture content, samples dried at higher temperatures were exposed for a shorter period to hot air, the ascorbic acid loss showed a sharp increase with increasing drying temperatures. A similar trend was observed by Silva et al. for ascorbic acid degradation during drying of camu camu slices at different temperatures. On the other hand, Erenturk et al. reported that, for hot air drying of rosehip fruits, the maximum retention of vitamin C occurred during drying at 70°C due to the shorter drying time necessary to attain the adequate final moisture content, whereas at 50°C the longer time of exposure to hot air, even at smaller temperature, led to less nutrient retention.

According to the free-volume theory, from which the WLF model was derived, values of the parameters in Eq. (5) should depend only on the physicochemical properties of the material, in such a way that a unique value for each adjustable constant would be expected, independently of the drying conditions. Although this fact has been confirmed in the case of constants \( D_r, T_r, \) and \( C_2 \) (Table 2), which were essentially the same for the entire range of air temperatures and velocities investigated, the parameter \( C_1 \) showed a high variability with drying conditions, leading to construction of a response surface in order to study the influence of air temperature and velocity on the value of \( C_1 \) (Fig. 7a). Air temperature had a significant effect \((p < 0.05)\) on \( C_1 \), which presented higher values for decreasing drying temperature and was not affected by air velocity. Taking into account the adopted values for \( T_g, T_r, \) and \( C_2 \) in Eq. (5), higher values of \( C_1 \) implies in higher \( D_T \) values or, consequently, lower degradation rates.

### TABLE 2

Parameters of WLF model for different drying conditions

<table>
<thead>
<tr>
<th>Drying condition</th>
<th>( D_r ) (min)</th>
<th>( C_1 )</th>
<th>( C_2 ) (K)</th>
<th>( T_r ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying with constant air temperature</td>
<td>200.00 ± 0.00</td>
<td>0.28 ± 0.13</td>
<td>30.03 ± 0.19</td>
<td>180.02 ± 0.15</td>
</tr>
<tr>
<td>Drying with fixed temperature inside</td>
<td>200.00 ± 0.00</td>
<td>0.21 ± 0.07</td>
<td>29.91 ± 0.09</td>
<td>179.93 ± 0.07</td>
</tr>
</tbody>
</table>

![FIG. 7. Influence of drying conditions on parameter C1 of the WLF model during drying: (a) with constant air temperature; (b) with fixed temperature inside the fruit.](image-url)
of ascorbic acid. Frías and Oliveira[23] applied Eq. (5) to modeling ascorbic acid degradation during drying of maltodextrin model solutions and observed higher deviations in $C_1$ and $C_2$ parameters when compared with $T_r$ and $D_r$, even dealing with a model system and not with a natural foodstuff as in the present work.

**Fixed Temperature Inside the Fruit**

Adoption of this control strategy, which was originally proposed by Nicoleti et al.[29] was justified considering that at the start of drying, when the product moisture content is higher, the drying air temperature could be elevated, being gradually reduced as the fruit moisture decreased. This would present the potential advantage of preventing heat damage in heat-sensitive food products, since at the end of drying air temperature would tend toward a previously established maximum solid temperature. The opposite happens at constant air temperature runs, in which heat damage risks are greatly increased at the final drying periods, due to the tendency of the solid to approach the air dry-bulb temperature.

For this control strategy, additional nine drying runs were carried out at different temperatures and velocities with a replicate at the central point (Table 1). In this case, the drying process could be considered as isothermal inside the fruit, since it is shown in typical temperature histories (Figs. 5a and 6a) that the necessary time to stabilization of a constant temperature in the fruit center was not higher than 60 min. Actually, there is a temperature profile through the fruit diameter as the thermal conductivity of the material is not high enough to guarantee true isothermal conditions. On the other hand, measuring this temperature profile would be a difficult experimental task. Other alternatives, such as adopting an average value between temperatures of drying air and of the fruit center, would also lead to approximations.

Figures 5b and 6b present, respectively, the WLF model fitted to experimental data of ascorbic acid concentration during drying with temperature inside the fruit fixed at 40°C (air velocity of 1.4 m/s) and 52.8°C (air velocity of 1.0 m/s). Comparison of the drying run presented in Fig. 5 with that presented in Fig. 3 shows that, contrary to what was expected, drying with temperature fixed inside the fruit resulted in higher loss of ascorbic acid (loss of 55%) than when drying with constant air temperature (38% loss). This fact is explained by the higher air temperature attained in the initial stage of drying with fixed temperature inside the fruit. The temperature history (Fig. 5a) shows that only after 7 h of drying the air temperature dropped to less than 50°C, whereas stabilization around 45°C occurred only after 23 h of processing. Drying with temperature inside the fruit fixed at 52.8°C and air velocity of 1.0 m/s increased the ascorbic acid loss to 90% of the initial content when moisture content was 1.5 g water/g dry matter.

In this case, the initial air temperature attained a maximum of 110°C, falling to less than 70°C after 9 h of drying and being stabilized around 61°C after 31 h of processing.

The failure of the control strategy based on keeping constant the product temperature to prevent ascorbic acid degradation may be attributed to the fact that, when drying whole persimmons, the relatively large size of fruits (diameter around 5 cm) delays the heat and moisture transfer inside the fruit, in such a way that a high air temperature is applied for a long time at the beginning of drying. The high initial air temperature also provokes case hardening, decreasing moisture loss from the fruit. The combined action of high temperature and elevated moisture content may have contributed for increased vitamin C degradation rates at the first stages of drying. In fact, modeling chemical reactions during drying is a complex matter. During the drying process, reactants concentrations and temperature vary simultaneously and it is not easy to separate each effect. Several hypotheses on how water content and molecular mobility affect chemical reactions involved in quality decay have been proposed, including: (1) increasing mobility of reactants with increasing moisture content, (2) increasing activation energy with decreasing water activity, and (3) changing concentration of water soluble reactants.[34] Effects (1) and (3) could even neutralize each other if water is not a participant of the reaction. On the other hand, if water is an important reactant, effect (1) would complement the higher water availability at the first stages of drying.

Fitting the WLF model was carried out similarly to that described above and values of the adjustable constants in Eq. (5) were also included in Table 2. The standard deviations of parameters for this control strategy were lower than in case of constant air temperature. Only parameter $C_1$ remained with a high deviation. Values of $D_r$, $T_r$, and $C_2$ were essentially the same observed in drying with constant air temperature, which agrees with the model hypothesis that the parameters should depend only on the physicochemical nature of the product. Nevertheless, the constant $C_1$ varied systematically with drying conditions, as shown by the response surface in Fig. 7b. Again it was observed that only the product temperature had a significant effect ($p < 0.05$) on $C_1$, but there was a clear trend of decreasing $C_1$ with increasing air velocity at lower product temperatures. A possible explanation for this result would be the fact that, at lower temperatures fixed inside the fruit, higher air velocity would not contribute to reduce the necessary drying time and heat exposure because the heat transfer is probably controlled by internal resistances. On the other hand, higher air velocity would increase the rate of vitamin loss due to a higher amount of available oxygen in contact with the fruits.

Using the WLF model to describe chemical reaction rates during drying showed to be advantageous, from a mathematical point of view, in the high moisture content domain, where $T_g$ is constant and equal to the glass
transition temperature of the maximally concentrated food matrix, \( T_g' \). In this case, the glass transition temperature encompassed the effect of the variable moisture content in the reaction rate constant of a first-order rate equation.\(^{[34]}\) In the low moisture content domain, where \( T_g \) is highly dependent on the plasticizing effect of water, this advantage would be lost, since an expression for \( T_g \) as a function of moisture content, such as the Gordon-Taylor model\(^{[9]}\) would have to be introduced in Eq. (5). On the other hand, taking into account the phenomenological description of ascorbic acid degradation in the specific situation studied in the present work, it is not clear if using the free-volume approach would present some benefit. Since during drying the average moisture content of whole persimmons remained in a high \( a_w \) domain, the role of water as a solvent and reactant in the reaction kinetics may have surpassed its effect as a food matrix plasticizer. This conclusion is reinforced by the significant dependence of constant \( C_1 \) on drying conditions. A different behavior was observed by Frias and Oliveira,\(^{[23]}\) who concluded that the matrix effect would be more important to degradation rates at the low moisture content range and that the higher predictive power of WLF model over the more common polynomial equations used for representing reaction rates could be demonstrated by similar WLF parameters calculated at different processing conditions.

**CONCLUSIONS**

The WLF model could be successfully employed to describe ascorbic acid degradation kinetics during drying of persimmons. For both control strategies adopted—the constant air temperature and temperature fixed inside the fruit—model fitting was satisfactory, although an unexpected dependence of the model parameter \( C_1 \) on drying conditions was detected. A high dispersion of the experimental data was observed around the model estimate and was associated with the heterogeneity of the samples, which is an inherent characteristic of natural products such as fruits and vegetables. The ascorbic acid degradation rates were significantly affected by temperature in both control strategies, with higher losses being observed at higher temperatures, independent of the necessary time to attain the desired moisture content. Due to the higher air temperatures attained in the first stages of drying with fixed temperature inside the fruit, this control strategy led to higher losses in the nutrient when compared with drying at constant air temperature.

**NOMENCLATURE**

- \( C \) Concentration (mg/g dry matter)
- \( C_0 \) Initial concentration (mg/g dry matter)
- \( C_1 \) Constant in the WLF model
- \( C_2 \) Constant in the WLF model (K)
- \( C_{\exp} \) Experimental concentration (mg/g dry matter)
- \( C_{\text{pred}} \) Predicted concentration (mg/g dry matter)
- \( D_g \) Thermal decay time at the glass transition temperature (min)
- \( D_r \) Thermal decay time at the reference temperature (min)
- \( D_T \) Thermal decay time (min)
- \( T \) Temperature (°C or K)
- \( T_{\text{air}} \) Temperature of the drying air (°C)
- \( T_g \) Glass transition temperature (K)
- \( T_g' \) Glass transition temperature of the maximally concentrated matrix (K)
- \( T_r \) Reference temperature (K)
- \( t \) Time (min)
- \( V_{\text{air}} \) Air velocity (m/s)

**Greek Letters**

- \( \eta \) Viscosity (Pa.s)
- \( \eta_g \) Viscosity at the glass transition temperature (Pa.s)
- \( \rho \) Density (kg/m\(^3\))
- \( \rho_g \) Density at the glass transition temperature (kg/m\(^3\))

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