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Kinetic Models of β-Carotene Degradation During Air Drying of Carrots

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The objective of this study was to determine the kinetic parameters of models that describe the joint influence of temperature and moisture content on the thermal degradation of β-carotene in a drying process of carrots. Two models were used: a first-order decay model with an Arrhenius and a polynomial dependency on temperature and water content, respectively, and a decay model with a WLF dependency of the decimal reduction time on glass transition temperature and water content, respectively, and a decay model with an Arrhenius and a polynomial dependency on temperature. The models were evaluated by comparing their predictions and experimental data during drying nonlinear regression. In addition, the models were evaluated by drawing at 20-min intervals and analyzed for moisture and β-carotene content. The parameters of the two models were estimated by nonlinear regression. In addition, the models were evaluated by comparing their predictions and experimental data during drying at 80 °C of carrot slices with thickness of 3, 6, and 9 mm. Both models were found suitable for modeling the β-carotene degradation, though the lower sum of squares of residuals (SSQ) of the Tg approach model and the similar WLF parameters calculated at different drying air temperatures demonstrated the higher predictive ability of the Tg model over the more common empirical dependence model.

Keywords Carrot; Glass transition; Kinetics; Thermal degradation; WLF model

INTRODUCTION

Carrot (Daucus carota L.) is one of the important root vegetable crops and is highly nutritious because it contains appreciable amount of vitamins B1, B2, B6, and B12. It also contains many important minerals. Moreover, carrots have the highest β-carotene content among human foods. β-carotene is one of the common carotenoid hydrocarbons that contain specific end groups or two beta rings and it acts as provitamin A, which is converted by humans to vitamin A. However, in the food industry, carrots must generally be processed prior to their use and drying is one of the most frequently used processes. Dehydrated carrots are used as an ingredient in instant soups or meals and an excellent candidate for developing oil-free, healthy snack food if the nutritional value can be well preserved. Many studies were done to process carrot by air drying, sun drying, microwave drying, solar drying, a combination of freeze drying, microwave heating, and air or vacuum drying, and low-pressure superheated steam drying.

Over the past three decades, there has been an increased concern for food quality, with a significant amount of work accomplished in the area of kinetics of nutrient destruction or general quality degradation during drying processes. Generally, the problem of chemical conversions during drying is extremely complicated. The rate constants of the reactions depend on temperature, concentration of the reactants, and concentration of water (water activity). The question arises regarding which cases the temperature dependence may be described by the simple Arrhenius equation. During the drying process, concentrations change and it is not clear to what extent thereby the chemical changes are influenced. The influence of the water activity is important but insufficiently understood. Water acts as solvent for the chemicals of nutritional importance present in the product. As water is removed, the concentration of the chemicals increases. The loss of nutrients is concentration dependent and would increase as dehydration progresses. On the other hand, some of the water-soluble compounds may act as catalysts to the decomposition process. These catalytic effects are greatly reduced as the moisture is removed. Although various oxidation reactions show a minimum rate of reaction at a certain water activity, in general, chemical reactions are slower as the water activity decreases. Because during drying the product temperature increases and the water activity decreases, the reaction rate constant may first increase when the temperature effect is dominating, whereas it may decrease later on when the influence of the lower water activity becomes the dominating factor.
On the other hand, according to Nicoleti et al.,\textsuperscript{[23]} 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. There is an important increase in molecular mobility across $T_g$ that can affect reaction kinetics in situations where diffusion of reactants or products is the controlling factor. During drying, the removal of water increases the glass transition temperature of the matrix substantially. Thus, as drying progresses the matrix approaches the onset of glass transition and may even vitrify during drying.\textsuperscript{[24]}

Several studies have been published that analyze reaction kinetics in foods according to the food matrix state. Karmas et al.\textsuperscript{[25]} found that the reactions rates of non-enzymatic browning were influenced by glass transition temperature in diffusion-limited systems. Buera et al.\textsuperscript{[26]} reported that the stabilization at the glassy state was effective for the hydrolysis of sucrose in polyvinylpyrrolidone (PVP) systems, and according to Kerr et al.\textsuperscript{[27]} the DNPP-hydrolysis reaction in homologous series of frozen maltodextrin solutions was related to ($T - T_g$). The glass transition temperature approach was also found to adequately describe the thermal degradation of ascorbic acid during hot air drying of maltodextrin solutions\textsuperscript{[24]} and convective drying of whole persimmons.\textsuperscript{[23]} On the contrary, Bell and Hageman,\textsuperscript{[28]} who studied the degradation of aspartame in a solid-state system, concluded that water activity could be more influential than glass transition temperature on this reaction.

Generally, a disagreement exists involving the role of the glass transition temperature on the rates of chemical reactions. The question arises as to whether molecular mobility of reactants as dictated by the state of the system (glassy versus rubbery) or the chemical potential of water (i.e., water activity) controls reaction rates. It is the opinion of several authors that both aspects are compatible and perfectly complementary, and knowledge of both is necessary to understand the food–water relationships.\textsuperscript{[29]} According to Frias and Oliveira,\textsuperscript{[24]} it can be dangerous to neglect one approach in detriment of the other without perfectly understanding the implications, but in some specific situations it can be interesting to separate the $a_w$ approach or the $T_g$ one to foresee which dominates the decay in a specific matrix. Nicoleti et al.\textsuperscript{[23]} reported that using the glass transition temperature approach to describe chemical reaction rates during drying showed to be advantageous, from a mathematical point of view, in the high moisture content domain, whereas in the low moisture content domain, this advantage was lost. A different behavior was observed by other authors, who concluded that the physical state of the product would be important to degradation rates at the low moisture content range.\textsuperscript{[24,30,31]}

The stability of β-carotene during drying of carrots has been extensively studied.\textsuperscript{[1,8,13,32–34]} However, little work has been done on its degradation kinetics as a function of carrot moisture content\textsuperscript{[17,20,33]} and works analyzing reaction kinetics in relation to the carrot matrix state were not found in the literature. Thus, the objectives of this work were to apply the glass transition temperature approach to describe the kinetics of β-carotene degradation during drying of carrots and to compare this approach with a traditional semi-empirical modeling.

**MATERIALS AND METHODS**

**Raw Material**

Fresh, good quality carrots procured from the local market were used. Samples were stored in a refrigerator at 4°C prior to the drying experiments. At the start of each experiment, the carrots were trimmed, hand-peeled, and washed with cold water. The washed carrots were sliced into circular discs (3 mm thickness) using a hand-operated slicer. The sliced carrots were subjected to hot water blanching by holding them in a muslin cloth in boiling water (100°C) for 6 min to inactivate peroxidase.\textsuperscript{[1]} The blanched samples were immediately cooled to room temperature under running cold water and then spread on a sieve tray to drain.

**Moisture Content Determination**

Moisture content of carrot samples was determined by a gravimetric method. About 5.00 ± 0.05 g of samples in triplicate were dried on aluminum dishes at 70°C. The dishes were kept in a desiccator for 30 min before recording their final weights. All measurements were done in triplicate and the averages of these triplicate measurements were used. Additional parallels were analyzed if the single values from the triplicates deviated more than 0.60% from the triplicate mean.

**β-Carotene Measurement**

The β-carotene content was spectrophotometrically determined on extracts in petroleum ether at 452 nm\textsuperscript{[1,20,34,35]} using a Helios UV-Visible spectrophotometer (Helios Gamma, Thermo Spectronic, Madison, WI). All determinations were done in triplicate and the averages of these triplicate measurements were used. An amount of carrot sample to have 0.5–1.0 g total solids was accurately weighed. The sample was extracted with 20-mL portions of acetone until the residue became colorless. The extracts were transferred to a separating funnel, to which 50 mL distilled water and 10 mL petroleum ether were added. The water–acetone layer was drawn into another separating funnel and reextracted using the same procedure. The petroleum ether extract was collected from all the extractions and passed through anhydrous sodium sulphate; volume was brought up to 50 mL with petroleum ether. This
extract was loaded onto a 10-cm column of supercel (Sigma-Aldrich Chemie, St. Louis, MO, USA) and magnesium oxide (3:1) overlaid by 1 cm of anhydrous sodium sulphate. The column was washed using an eluent (3 mL acetone: 97 mL petroleum ether) until the β-carotene moved off the column and the filtrate became colorless. The contents were diluted to 100 mL with eluent. The intensity of color was measured at 452 nm. The concentration of β-carotene was determined from a standard curve.

Glass Transition Temperature Measurement

Carrot samples were dehydrated in a cabinet air dryer at 60°C to final moisture content of around 10% wb (0.11 g/g ds). Dehydrated carrot samples of about 1 g (+0.01 g) were conditioned at 25°C using sulphuric acid solutions to maintain the moisture content level between 0.11 and 9.11 g/g ds, according to sorption isotherm methodology. After equilibrium was reached, samples of about 10 mg were taken for differential scanning calorimetry (DSC) analysis and the remaining material was analyzed for moisture content. The glass transition temperature was determined by DSC, with a differential scanning calorimeter (Perkin-Elmer Pyris 1, PerkinElmer Life and Analytical Sciences Inc., Wellesley, MA) supplied with proper software. All measurements were done in triplicate. The samples were heated at 10°C/min in an inert atmosphere. Preliminary runs with 2 and 5°C/min heating rates gave virtually the same results, so the 10°C/min rate was chosen for convenience. The reference was an empty pan, and liquid nitrogen was used for sample cooling before the runs. The glass transition temperature can be reported as either the midpoint or the onset of $T_g$. The onset of $T_g$ is generally considered the most appropriate temperature to report. However, most investigators report midpoint $T_g$ values, because a plot of the first derivative of the glass transition curve shows a peak at the midpoint glass transition temperature, making this point easy to identify. Thus, in this work, the midpoint of the glass transition was considered as the characteristic temperature of the transition.

The glass transition temperature of a binary solid–water mixture is strongly dependent on the water concentration. Once the moisture content is known, the $T_g$ can be determined using the model proposed by Gordon and Taylor:

$$T_g = \frac{(1 - x_w) \cdot T_{gw} + K \cdot x_w \cdot T_{gsw}}{(1 - x_w) + K \cdot x_w}$$

where $T_g$, $T_{gw}$, and $T_{gsw}$ are the glass transition temperatures of the mixture, solids, and water, respectively; $x_w$ is the mass fraction of water; and $K$ is the Gordon-Taylor parameter.

Drying Procedure

Carrot samples of about 300 g were dehydrated in a cabinet air dryer at 50, 60, 70, and 80°C. Air of about 7% relative humidity was used at 2 m/s air velocity. The drying was carried out to final moisture content of around 9% from initial moisture content of about 90% (wb). During drying, the temperatures of the hot air and the drying sample were measured continuously using type-K thermocouples, which were connected to an expansion board. Thermocouple signals were multiplexed to a data acquisition card installed in a desktop computer. Carrot samples of about 10 g were drawn at 20-min intervals. β-carotene content of the drying carrots was determined by using half of the samples removed. The samples were stored at −18°C until β-carotene analyses were done. The remaining half of the samples was used for moisture content determination. All drying experiments were carried out in triplicate.

Empirical Dependence Approach

The kinetic model representative of β-carotene degradation during air drying was obtained using a dynamic test approach. According to Saguy et al.,[36] the dynamic method for determining decay kinetics requires the acquisition of moisture, temperature, and quality factor concentration during the actual drying process. The degradation achieved is the common and indistinguishable effect of both temperature and moisture integrated in time. This experimental design allows for the determination of the kinetic parameters using a more reduced sample size, on conditions similar to real drying, compared to the alternative of using isothermal or constant water content designs performed at several combinations of the variables.[24,37]

An empirical first-order kinetic model was used for degradation kinetics of β-carotene:[18,20,33]

$$-\frac{dC}{dt} = k \cdot C$$

where $C$ is the concentration of β-carotene at time $t$ and $k$ is the reaction rate constant, which is a function of temperature and moisture content:[20,38]

$$k = k_T \cdot k_X$$

$$k_T = k_o \cdot \exp \left( \frac{-E_a}{R \cdot T} \right)$$

$$k_X = A_1 + A_2 \cdot X + A_3 \cdot X^2$$

where $k_o$ is the so-called frequency factor, $E_a$ is the activation energy, $X$ is the carrot moisture content in g/g dry solids, and $A_1$, $A_2$, and $A_3$ are constants.

Glass Transition Temperature Approach

An alternative for describing the joint influence of water content and temperature on the degradation kinetics is the
application of the glass transition temperature theory. According to this theory, in amorphous systems the increase in viscosity with the increase of temperature above \( T_g \) follows Williams-Landel-Ferry (WLF) kinetics.\[39\] The WLF model is basically a derivation of the well-known Vogel, Taumman, and Fulscher (VTF) equation expressing viscosity as a function of the free volume of the matrix. According to Frias and Oliveira,\[24\] applying the WLF model to drying process conditions gives:

\[
\log \frac{C}{C_0} = \int_0^t \frac{10^{C_T(T_r-T_g)}}{D_r} \, dt
\]

where \( C \) is the concentration of \( \beta \)-carotene at time \( t \), \( C_0 \) is the initial \( \beta \)-carotene concentration, \( C_1 \) and \( C_2 \) are WLF constants, \( T \) is the temperature of the drying sample, \( T_r \) is the reference temperature, \( T_g \) is the glass transition temperature, and \( D_r \) is the decimal reduction time at \( T_r \).

**Statistical Analysis**

The parameters of the models were estimated by nonlinear regression. To evaluate the goodness of fit of each approach, two criteria were used: the coefficient of determination, \( R^2 \), which is the relative variance explained by the model with respect to the total variance, and the sum of squares of residuals, SSQ (Eq. (7)), which indicates the error of the predictions.

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

where \( C_{\text{exp}} \) is the experimental value and \( C_{\text{pred}} \) the predicted value of \( \beta \)-carotene content.

**RESULTS AND DISCUSSION**

**Glass Transition Temperature**

Values of \( T_g \) obtained for the different carrot samples as a function of moisture content are shown in Fig. 1. As can be seen, the plasticizing effect of water on the glass transition temperature is evident, with a great reduction of \( T_g \) caused by increasing moisture content. This plasticizing activity of water may be based on the weakening of hydrogen bonds and dipole–dipole intra- and intermacromolecular interactions due to the shielding of these mainly attractive forces by water molecules. One more contributory factor is the low \( T_g \) of amorphous water, because this difference in \( T_g \) between water and food macromolecules decreases the viscosity of biopolymer–water mixtures over a wide range of temperatures. \( T_g \) values presented in Fig. 1 are slightly different than those obtained by Karmas et al.\[25\] This difference in the measured values may be due to the fact that the glass transition occurs over a 10–20°C range, but usually only a single temperature is quoted as \( T_g \). In addition, sample preparation can lead to discrepancies in \( T_g \) data and foods have wide-spanning thermal peaks, leading to difficulties in pinpointing the \( T_g \).

The Gordon and Taylor model was fitted to experimental points using \( T_{g_w} = -135^\circ \text{C} \), with the following parameters calculated by nonlinear regression: \( T_{g_s} = 61.61^\circ \text{C} \) and \( K = 5.68 \), with \( R^2 = 0.992 \). Figure 1 shows the curve predicted by the Gordon and Taylor model. The calculated \( K \) value was similar to those reported for fruits and vegetables.\[41\] Karmas et al.\[25\] fitted glass transition temperature–moisture content data for carrot to the model proposed by Gordon and Taylor and found a \( T_{g_s} \) value of 55°C. This difference can be attributed to differences in composition (mean molecular weight of the solutes) of the carrot liquid phase.

**Drying Kinetics and \( \beta \)-Carotene Degradation**

Figure 2 shows drying kinetics of carrot for each drying experiment and the relevant temperature profiles of the product, and the carrot drying rate curves are given in Fig. 3. In all experiments drying was characterized by a short equilibration period, during which solid surface conditions came into equilibrium with the drying air. The constant rate period was not exhibited and drying moved quickly to the falling rate period with two critical moisture contents. This observation is similar to that reported by Doymaz\[42\] and Wang and Xi.\[13\] On the contrary, Pan et al.\[20\] reported that during drying of 20 × 20 × 5-mm
carrot slices with an inlet air temperature of 100°C, the drying rate remained constant for over 40 min. However, in that case the drying was carried out in a bed dryer. Thus, the absence of a constant rate period observed in this work may be due to the thin layer of the product that did not provide a constant supply of water for an appreciable period of time. The reason for existence of two falling rate periods may be the case hardening, which acts as a barrier to moisture migration during prolonged drying. According to Wang and Xi,\textsuperscript{[13]} when considering the influence of the internal structure changes on carrot drying, it must be considered that there are three possible ways for the water movement in and out of cells: transmembrane transport (through plasmalemma membrane boundaries), symplastic transport (via cytoplasmic strands or plasmodesmatas), and the cell wall pathway. During the first drying period, moisture content is greater and the movement of water is mostly by transmembrane transport and the cell wall pathway. The dehydration rate is higher but decreases rapidly with moisture content. In the second drying phase, the moisture content is lower, the water movement is mostly by symplastic transport, and the dehydration rate is lower.

The time taken to reduce moisture content of carrot slices from the initial 90% to a final 9% was 460, 420, 380, and 340 min at 50, 60, 70, and 80°C, respectively. These drying times are lower than those reported by other researchers.\textsuperscript{[2]} This difference can be attributed to the fact that the carrot slices used in this work were blanched prior to their drying. According to Gornicki and Kaleta,\textsuperscript{[2]} blanching can shorten the drying times of fruits and vegetables due to (1) changes in physical properties of the tissue, such as destruction of the cell membranes by heat; and (2) loss of soluble solids, which affects the drying rate. As can be observed, increasing the drying temperature caused an important increase in the drying rate, and thus the drying time decreased. This is due to the fact that drying at higher temperature implied a larger driving force for heat transfer, which was, in this case, the temperature difference between the drying medium and the temperature close to the wet-bulb temperature. A higher drying temperature also led to a higher value of moisture diffusivity. In addition, the higher drying temperature provided a larger water vapor pressure deficit or the difference between the saturated water vapor pressure and partial pressure of water vapor in air at a given temperature, which is one of the driving forces for drying.\textsuperscript{[11]}

The β-carotene retention in carrots during each drying experiment is shown in Fig. 4. Final β-carotene contents were found as 79, 76, 74, and 71% for 50, 60, 70, and 80°C, respectively. These results agree with previous reports showing that β-carotene in carrot is relatively heat stable during drying processes.\textsuperscript{[8]} This is probably due to the presence of α-tocopherol, which functions as a natural antioxidant. The amount of α-tocopherol in carrot, as reported in the literature, is about 0.11–0.50 mg/100 g.\textsuperscript{[8]} Cui et al.\textsuperscript{[32]} reported a β-carotene retention of about 70% during drying of carrots at 60–65°C in a cabinet laboratory dryer. However, in that case the carrot samples were not blanched before drying. Many researchers reported that blanching before drying enhances the stability of carotenoids.\textsuperscript{[18]} The stabilizing effect of blanching
on carotenoids can be attributed to the inactivation of peroxidase and lipoxidase activity. These enzymes can act during the dehydration process until substrate mobility becomes a limiting factor for catalytic activity.

As can be observed in Fig. 4, 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, raising the drying temperature increased the loss of β-carotene. A similar observation was reported by Silva et al., who studied the ascorbic acid degradation during drying of camu camu slices at different temperatures. However, Erenturk et al. reported that during hot air drying of roesehip fruits, the maximum retention of vitamin C occurred during drying at 70°C, due to the shorter drying time necessary to attain the specific moisture content, whereas at 50°C the longer time of exposure to hot air, even at lower temperature, led to less nutrient retention.

**Modeling the β-Carotene Degradation**

Figure 4 presents the adjustment of (1) the empirical dependence approach model; and (2) the Tg approach model to the experimental data of β-carotene retention during each drying experiment. Estimated parameters for the two models are presented in Table 1. As can be seen in Fig. 4 and Table 1, both models give comparable results, though the SSQ value of the Tg approach model is lower. The $R^2$ for both models is very good, but these values must be taken with caution, because $R^2$ assumes model linearity and in strongly nonlinear models it can be a poor estimate of the percentage of variance explained by the model.

The values of the Tg model parameters, obtained by nonlinear regression of the data set for each drying experiment, are in agreement with reported values. Frias et al. mentioned that $C_1$, which is the difference in order of magnitude between the molecular relaxation time in a glassy matrix (around $10^3$ s) and that of atomic vibration (around $10^{-13}$ s), should be around 16. For a large number of polymers the value of 17.44 has been suggested as universal constant, whereas Nicoleti et al. and Frias and Oliveira reported $C_1$ values of 0.28 and 6 for ascorbic acid degradation during drying of persimmons and maltodextrin solutions, respectively. Peleg reported that $C_2$ usually varies between $-249.15$ and $-193.15°C$. The estimated values of $T_r$ and $D_t$ are also in agreement with values reported for various degradation reactions in foods.

In addition, the values of the parameters $C_1$, $C_2$, $T_r$, and $D_t$ were found independent of the drying air temperature. This observation is similar to that obtained by Nicoleti et al. who mentioned that the values of the WLF parameters $C_2$, $T_r$, and $D_t$ should depend only on the physicochemical properties of a material, in such a way that a unique value for each adjustable constant would be expected independently of the drying conditions (drying air temperature and velocity). However, they found that air temperature had a significant effect ($p < 0.05$) on the parameter $C_1$, which increased with a decrease in drying temperature. Frias and Oliveira also used the WLF approach to model the ascorbic acid degradation during drying of maltodextrin model solutions and observed a high variability of $C_1$ and $C_2$ with drying conditions.
According to them, similar WLF parameters calculated at different processing conditions demonstrate the higher predictive ability of the $T_g$ approach model over the more common empirical dependence models used for representing reaction rates. Thus, in the case studied in this work, the matrix effect of the carrot is strong enough to influence the kinetics of $\beta$-carotene degradation and overlap the water content chemical effect per se on the kinetics.

The two models were also evaluated by comparing their predictions and experimental data during drying at $80^\circ$C of carrot slices with thickness of 3, 6, and 9 mm. The moisture content versus time curves for drying of carrot samples as influenced by thickness are shown in Fig. 5. As the thickness of the sample increased, the time required to achieve a certain moisture content increased. This is because the drying surface area of the carrots with a thickness of 3 mm is greater than that of the thicker samples. For example, the drying times for reaching a moisture content of about 0.18 g H$_2$O/g dry solids at $80^\circ$C were about 240, 280, and 320 min for sample thickness of 3, 6, and 9 mm, respectively.

The effect of carrot slice thickness on $\beta$-carotene content is shown in Fig. 6. As can be concluded, at relatively higher moisture the rate of $\beta$-carotene retention increased as sample thickness increased. This observation is similar to that reported by Erenturk et al.,$^{[38]}$ who reported that during drying of rosehip, total amount of vitamin C decreased when the rosehip thickness decreased. This effect may be due to the increase in the surface area exposed to oxygen when the sample dimensions decreased. However, as can be seen in Fig. 6, at lower moisture contents, $\beta$-carotene retention increased as slice thickness decreased. A similar finding was reported by Wang and Xi,$^{[13]}$ who studied the drying characteristics and drying quality of carrot using a two-stage microwave process and concluded that $\beta$-carotene contents decreased with increasing carrot slice thickness. This observation may be attributed to the fact that high volumetric heating, generating high pressure inside the carrot samples, resulted in boiling and bubbling.
of the samples. Nindo et al.[45] observed that, during drying of asparagus, freeze drying resulted in lower retention of ascorbic acid compared to other methods of drying. A probable explanation was that the freeze-dried samples were voluminous and fluffy in texture and had a large surface area and an open-pore structure. The significant effect of product form on the various degradation reactions occurring during drying was observed for several products.[46–48] In general, quantitative studies on the effects of light and oxygen on reactions involving nutrients in foods are very limited and do not lend themselves to the formulation of models for predicting nutrient retention as a function of history of exposure to oxygen and light.

Figure 6 shows the two models’ predictions compared with the experimental values of β-carotene retention for carrot slices with a thickness of 3, 6, and 9 mm dried at 80°C. R² and SSQ values were 0.999 and 0.0016 and 0.983 and 0.0265 for the Tg and the empirical dependence model, respectively. Figure 7 illustrates the two models’ experimental and predicted β-carotene retention data. To evaluate the goodness of fit of each model, linear regression and paired t-test were applied. The slope and the intercept of predicted values versus experimental values for both models are not significantly different (p = 0.05) from the theoretical values 1.00 and 0.00, respectively, whereas applying paired t-test for each model the calculated t values were found lower than the theoretical t values (p = 0.05). Therefore, the null hypothesis was retained: the two models are suitable for modeling the degradation of β-carotene during air drying of carrots.

As can be seen from Figs. 6 and 7, the Tg model predicts the β-carotene loss more accurately than the empirical dependence model. However, in the high moisture content domain, the empirical dependence model provides equally good fit. This observation can be attributed to the fact that in the high moisture content range, the role of water as a solvent and reactant in the reaction kinetics may have surpassed its effect as a food matrix plasticizer.

CONCLUSIONS

The thermal degradation of β-carotene during air drying of carrots at different air temperatures was described by two models: (i) an empirical dependence approach model, which is a first-order decay model with an Arrhenius and a polynomial dependency on temperature and water content, respectively; and (ii) a Tg approach model that is a model with a WLF dependency of the decimal reduction time on Tg, with the Gordon and Taylor equation describing the influence of moisture content on Tg. Both models provided good fits of the experimental data. However, the parameters of the Tg approach model were found independent of the drying temperature, demonstrating its higher predictive ability over the more common empirical dependence model. In addition, the Tg model predicted the β-carotene loss during drying at 80°C of carrot slices with thickness of 3, 6, and 9 mm more accurately than the empirical dependence model. Thus, the matrix effect of the carrot can be considered strong enough to influence the kinetics of β-carotene degradation and overlap the water content chemical effect per se on the kinetics.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>A₁, A₂, A₃</td>
<td>Constants of the empirical dependence approach model</td>
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<tr>
<td>C</td>
<td>Concentration of β-carotene (mg/g)</td>
</tr>
<tr>
<td>C₁, C₂</td>
<td>WLF constants (–, °C)</td>
</tr>
<tr>
<td>D</td>
<td>Decimal reduction time (min)</td>
</tr>
<tr>
<td>Eₐ</td>
<td>Activation energy (J/mol)</td>
</tr>
<tr>
<td>K</td>
<td>Gordon-Taylor parameter</td>
</tr>
<tr>
<td>k</td>
<td>Reaction rate constant (min⁻¹)</td>
</tr>
<tr>
<td>k₀</td>
<td>Frequency factor (min⁻¹)</td>
</tr>
<tr>
<td>L</td>
<td>Thickness of carrot slices (mm)</td>
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<tr>
<td>R</td>
<td>Universal gas constant (8.314 J/K mol)</td>
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<tr>
<td>R²</td>
<td>Correlation coefficient</td>
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<td>T</td>
<td>Temperature (°C)</td>
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<td>Drying air temperature (°C)</td>
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<td>Tg</td>
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<td>Tₛ</td>
<td>Carrot temperature (°C)</td>
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<tr>
<td>t</td>
<td>Drying time (min)</td>
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<td>X</td>
<td>Moisture content (g/g dry solids)</td>
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<td>X_w</td>
<td>Mass fraction of water</td>
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FIG. 7. Experimental and calculated values of β-carotene retention during drying at 80°C of carrot slices with thickness of 3, 6, and 9 mm by the two models.
REFERENCES