Modeling of drying and ameliorative effects of relative humidity (RH) against β -carotene degradation and color of carrot (*Daucus carota* var.) slices

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Abstract Drying and β -carotenes retention kinetics were predicted using models in relative humidity (RH) drying condition. This was achieved by drying carrot slices using RH-convective hot-air dryer at 60, 70 and 80 °C under RH (10% 20% and 30%) conditions at 2.0 m/s air velocity. Three mathematical models describing thin layer were compared to their goodness of fit in terms of coefficient of correlation (R^2), root mean square error (RMSE) and reduced Chi square (χ^2). The Wang and Singh model could satisfactorily describe RH-convective drying of carrot slices with R^2 , RMSE and χ^2 in the ranges of 0.996–0.999, 5.4×10^{-4} – 9.4×10^{-4} and 0.0150–0.03353 respectively. The results reveal that a range of 3.61–8.2% retention of β -carotene was observed for every 10% increase in RH in various drying air temperature. In summary, higher temperatures were mainly responsible for β -carotenes degradation however this can be mitigated when drying is conducted under higher RH.

Keywords β -Carotene · Carrot · Drying · Relative humidity · Modelling

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List of symbols

R^2	Coefficient of correlation
χ^2	Chi square
RMSE	Root mean square error
E_a	Activation energy
ΔG	Gibbs free energy change
ΔH	Enthalpy change
ΔS	Entropy change
ΔE^*	Total color difference
D_{eff}	Effective moisture diffusivity
RH	Relative humidity
k, k_1, a, n and b	Kinetic constants
C	Arrhenius constant
d.m.	Dry matter
A_w	Water activity
r	Person's coefficient of correlation

Introduction

Carrot, root vegetables is cultivated globally with annual world production of 42.71 million tons in 2016. China remains the leading grower of carrot in the world with approximately 20.57 million tons in 2016 (FAO, 2016). The vegetable is highly rich in antioxidants, carotenoids, especially β -carotene and according to Demiray and Tulek (2017) may account for the biological and medicinal properties of carrots. These nutrients have the tendency to degrade during storage and processing and this has necessitated the employment of preservation techniques. As part of preservation method in extending the shelf life of agricultural products, drying has been an ancient approach in food processing. Over the years one major problem with this preservation technique has been the degradation of bioactive substances such as carotenoids,

tocopherols, polyphenol and vitamin C (Zhou et al., 2016). For thorough understanding of the process from engineering point of view, it is important to model the controlling parameters to predict, design and improve the outcome of the process. Currently, mathematical models are often used for designing new and improving existing drying systems or even for the control of the drying process (Doymaz, 2017). For drying kinetics model, several mathematical models have been developed in drying thin-layer samples and can be grouped into theoretical, semi theoretical and empirical models (Ju et al., 2016). Again investigating the kinetics of β -carotenes is very crucial in understanding the degradation reaction in fruits during drying processing. Through kinetic degradation study, excessive losses of this compound could be prevented. Many authors have suggested various ameliorative mechanism for mitigating β -carotenes degradation (Abdelaali et al., 2018; Demiray and Tulek, 2017; Koca et al., 2007) during hot air drying, however, there mains a gap in literature on the use of RH. This study was therefore conducted to (1) model drying kinetic and investigate the ameliorative effect of RH on β -carotene degradation (2) evaluate the correlation between β -carotene degradation and color degradation of carrot using RH-convective hot air dryer.

Materials and methods

Raw material

Fresh carrot (*Daucus carota* var.) was purchased from Zhenjiang local market China, in June 2017 and kept in a refrigerator at 4 °C prior to use. Carrots were taken from refrigeration and left to equilibrate at the room temperature before samples were peeled and washed with tap water. Samples were sliced into disks shape (25 ± 0.1 mm diameter and 2.5 mm thick) using a cutting machine (SS-250, SEP Machinery Company Ltd, Guangzhou, China) prior to drying. The initial moisture content of the carrot was determined by vacuum drying at 60 °C for 24 h according to the method described by AOAC (1990) and was noted to be $83.05 \pm 3.4\%$ wet base (w.b.).

Drying with humidity control convective hot-air dryer

An advanced lab-scale hot-air dryer equipped with humidity controlling device (range 0–99%) as fully described in our previous work (Sarpong et al., 2018b) was used to carry out drying of the carrot slices. A sieve load tray was tarred to zero before carrot samples (65 g) were loaded. Three temperatures (60, 70 and 80 °C) at 2.0 m/s air velocity combined with three RH (10%, 20% and 30%) were the drying conditions. The drying system was allowed to run for 30 min to obtain steady drying conditions before samples were loaded. Drying continued until constant moisture content was obtained.

Modeling of drying kinetics

Drying theory initially described by Lewis (1921) based on Newton's law of cooling in heat transfer and is often used to explain the mass transfer in thin layer drying as follows:

$$MR = \frac{M - M_e}{M_o - M_e} = \exp(-kt) \quad (1)$$

where MR is the moisture ratio; M is the moisture content at time t and M_o and M_e are the initial and equilibrium moisture contents respectively, on a dry basis; and k is the drying constant. Equilibrium moisture content, M_e was assumed to be zero for analysis of MR (Mierzwa and Pawlowski, 2017; Sarpong et al., 2018b). The experimental set of (MR, t) drying kinetics of slices carrot were fitted to 3 thin-layer drying models, widely used in scientific literature shown in Eqs. (2–4) as described by the following authors (Akoy, 2014; O'Callaghan et al., 1971; Omolola et al., 2014).

$$MR = \exp(-kt) \quad (2)$$

$$MR = \exp(-kt^n) \quad (3)$$

$$MR = 1 + at + bt^2 \quad (4)$$

The regression analysis was performed using Origin-Pro 9.2 (Origin Lab Corporation, Northampton, MA, USA). Three primary parameters were used to evaluate the adjustment/goodness of fit to the models which included the coefficient of determination (R^2), the root mean square error (RMSE) and the reduced Chi square (χ^2). These parameters are calculated using the equations below.

$$R^2 = \frac{N \sum_{i=1}^N MR_{pred,i} MR_{expt,i} - \sum_{i=1}^N MR_{pred,i} \sum_{i=1}^N MR_{expt,i}}{\sqrt{\left(N \sum_{i=1}^N MR_{pred,i}^2 - \left(\sum_{i=1}^N MR_{pred,i} \right)^2 \right) \left(N \sum_{i=1}^N MR_{expt,i}^2 - \left(\sum_{i=1}^N MR_{expt,i} \right)^2 \right)}} \quad (5)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (MR_{\text{expt},i} - MR_{\text{pred},i})^2} \quad (6)$$

$$\chi^2 = \frac{\sum_{i=1}^N (MR_{\text{expt},i} - MR_{\text{pred},i})^2}{N - z} \quad (7)$$

where $MR_{\text{expt},i}$ and $MR_{\text{pred},i}$ are the experimental and predicted dimensionless MR respectively, N is the number of observations, and z is the number of constants. The best model to describe the drying kinetics of carrot slices under varied temperatures and RH conditions was chosen as the one with highest R^2 and least $RMSE$ and χ^2 (Doymaz, 2017; Ning and Han, 2012).

Calculation of moisture effective diffusion (D_{eff})

Fick's second law of diffusion is widely used to describe drying process (controlled by internal diffusion) during the falling rate period for most agricultural materials and shown in Eq. (8)

$$\frac{\partial M}{\partial t} = D_{\text{eff}} \nabla^2 M \quad (8)$$

Diffusivity, D_{eff} (m^2/s) equation was calculated for slab geometry on the assumption of constant diffusivity, uni-dimensional moisture movement, volume change, constant temperature and negligible external resistance (Crank, 1979). The equation is of the form:

$$MR = \frac{M - M_e}{M_o - M_e} = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp \left[-\frac{(2n-1)^2 \pi^2 D_{\text{eff}} t}{4L^2} \right] \quad (9)$$

where M , M_e and M_o are the average, initial and equilibrium moisture contents (g/g d.b.) of the sample respectively at time t , D_{eff} is the constant effective diffusivity (m^2/s). L and t represent half the thickness of the carrot slice and the drying time (s) respectively. Only the first terms of the Eq. (9) can be used for long drying times (López et al., 2010)

$$MR = \frac{M - M_e}{M_o - M_e} = \frac{8}{\pi^2} \exp \left(-\frac{\pi^2 D_{\text{eff}} t}{4L^2} \right) \quad (10)$$

The slope (k_0) is calculated by plotting $\ln(MR)$ against time

$$k_0 = \frac{\pi^2 D_{\text{eff}}}{4L^2} \quad (11)$$

Activation energy (E_a)

The rate constant is often temperature dependent. Hence, temperature dependency of drying kinetics, were determined by Arrhenius Eq. (12).

$$\ln(k) = \ln(C) - \frac{E_a}{RT} \quad (12)$$

where E_a is the activation energy (kJ/mol), T is the temperature (K), R is the universal gas constant (8.314 J/(mol K)) and C is the Arrhenius constant.

Determination of β -carotene

β -carotene extraction procedure were performed following the protocol described by Abdelaali et al. (2018) with minor modification. In sum, 5 g of dried samples was mixed with 3.0 mL extraction mixture (methanol-acetone-dichloromethane, 25:25:50, v/v/v) which was followed by vortex and sonication for 1 and 5 min respectively at room temperature. The samples were then centrifuged (model Z326K, Hermle Labortechnik, Wehingen, Germany) for 10 min at $3500 \times g$ and 4°C and the lower phase was recovered. The upper phase was re-extracted with 1.5 mL of dichloromethane, sonicated and centrifuged as before until being colorless.

Measurement of β -carotene was done using the procedure reported by Jatoti et al. (2017). In sum, 10 mL acetone-hexane (4:6 v/v) mixture was added to the extract (10 mL), vortexed for 1 min, and filtered through Whatman No. 4 filter paper. The final volume was set to 10 mL and the optical absorbance was measured at 453 nm, 505 nm, and 663 nm using ultraviolet-visible spectrophotometer (TU-1810; Purkinje General Instrument Co., Ltd., Beijing, China). The results are expressed as mg/100 g dm β -carotene based in Eq. (13) calculation:

$$\beta - \text{carotene (mg/100mL)} = 0.216 \times A_{663} - 0.304 \times A_{505} + 0.452 \times A_{453} \quad (13)$$

Kinetics models for β -carotene degradation

The evaluation of β -carotene change during RH-convective drying was based on the assumption follows first-order kinetics, as given in Eq. (14)

$$\frac{A_t}{A_0} = \exp(-k_1 t) \quad (14)$$

where A_0 the initial value is at time zero, A_t is the value at time t , k_1 is the kinetic parameter. The decimal reduction (D -value), defined as the time required for 90% β -carotene degradation during drying process and half-life ($t_{1/2}$) were calculated by Eqs. (15) and (16) respectively.

$$D = \ln(10) \times k_1^{-1} \quad (15)$$

$$t_{1/2} = \frac{0.693}{k_1} \quad (16)$$

Thermodynamic analysis of β -carotene degradation

Activation energy (E_a , kJ/mol) was determined by Arrhenius Eq. (9). The activation energy and rate constant of β -carotene degradation was used to determine the following thermodynamic parameters; the Gibbs free energy change (ΔG), the enthalpy change (ΔH) and entropy change (ΔS) by the Eqs. (17–19)

$$\Delta G = R * T * \ln \left(\frac{k * h_p}{T * K_B} \right) \quad (17)$$

$$\Delta H = E_a - RT \quad (18)$$

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T} \right) \quad (19)$$

where K_B the Boltzmann is constant (1.3806×10^{-23} J/K) and h_p is the Planck constant (6.6262×10^{-34} J s).

Color measurements

The lightness (L^*), redness (a^*), and yellowness (b^*) parameters were determined according to Sarpong et al. (2018b). The total color difference (ΔE^*) was computed using Eq. (20).

$$\Delta E^* = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (20)$$

Statistical analysis

Data was processed with OriginPro 9.2 (Origin Lab Corporation, Northampton, MA, USA) and presented as the means $\pm$ standard deviations. One-way Analysis of variance (ANOVA), Pearson's coefficient of correlation and Fisher's multiple comparison tests were used for further comparison.

Results and discussions

Influence of RH on drying kinetics of carrot slices

The drying curves (MR against time) of carrot slices dried using RH-hot air convective dryer at varied RH (10%, 20% and 30%) and temperatures (60, 70 and 80 °C) are presented in Fig. 1A–C. A faster decrease of moisture content was observed at the early stages of drying (within 20–60 min) and the rate of dehydration decreased over time in all drying conditions. The first stage (constant period) of drying kinetic theory was absent and most drying occurred in the falling rate period. This effect was related to the high amount of free moisture availability and this was removed in the initial stage of drying (Mghazli

et al., 2017). The falling period was governed by water diffusion in carrot sample and similar observation were made by other authors (Mghazli et al., 2017; Sarker et al., 2013). However, no clear drying rate was maintained in all drying condition as a result of varied water supply of the thin layer of carrot slices sample. Thus, drying rate was dominated by moisture diffusion from the inside to the surface as was found in many agricultural products (Ponkham et al., 2012; Shi et al., 2008).

According to the results in Fig. 1, RH and drying air temperature is very important parameter that affects the drying time of carrot slices. The samples dried under lower RH and higher drying air temperature conditions were found to have a shorter drying time compared to other drying conditions. Under the same temperature of 80 °C, time to reach the final moisture constant weight for 10%, 20% and 30% RH were 100, 110 and 130 min respectively. Thus, lower RH of 10% and 20% achieved 23.1% and 15.3% drying time reduction respectively when compared with 30% RH. Similarly, drying reduction time of 23.5% and 11.7% were also observed for 70 °C whilst 60 °C recorded 16.6% and 5.56% for 10 and 20% RH respectively. Lower RH significantly ($p < 0.05$) accelerated the drying rate under all temperatures. These results show that lower RH contributed to increase the permeability of the cell membranes of carrot slices, leading to an increase in water diffusivity to reduce the drying time. This phenomenon is due to rapidly rise of product internal temperature for lower RH. In order to appreciate the drying characteristics of carrot slices in RH-hot air convective dryer at different temperatures and RH, three thermocouples were inserted in three slices and placed at different locations in the drying chamber to measure the sample internal temperature at 15 min interval. A rapid rise of the internal temperature was observed [Fig. 1D–F] in all drying conditions due to the heat transfer from the hot air. It was observed that lower RH accelerated the rate of rise of internal temperature of sample for all drying temperatures and therefore caused a faster drying rate. The results show that the require drying time to obtain complete drying of sample (constant weight of sample) were decrease by 45–60 min for every 10 °C increase in air temperature and 10–30 min by every 10% decrease in RH. This was in agreement with the studies by Xiao et al. (2010) and Doymaz (2017) who reported a range of 30–60 min for every 10 °C increase in air temperature in the dehydration of carrot cubes and slices respectively. Drying time of carrot slices were significantly ($p < 0.05$) decreased for every 10 °C increase in air temperature and 10% decrease in RH.

Fig. 1 Variation of Moisture ratio and internal sample temperature versus drying time for varied temperatures and RH drying conditions for carrot

Evaluation of drying mathematical models

For the various drying conditions of each run, the experimental data fitted to 3 models and R^2 , χ^2 and RMSE were used to evaluate performance of each model. The obtained model constant parameters for the models are summarized in Table 1. The best mathematical model fitting experimental data was chosen based on maximized R^2 and minimized χ^2 and RMSE. All the models gave consistently R^2 values in the range of 0.992–0.999; indicating that all the models could be used to describe the drying behavior of carrot slices under 10–30% RH and 60–80 °C conditions. However, modified second order polynomials (Wang and Singh) displayed the highest average value of R^2 , lowest χ^2 and RMSE (Table 1) and were found to be the best descriptive model. The changes in the R^2 , χ^2 and RMSE range between 0.996–0.999, 5.4×10^{-4} – 9.4×10^{-4} and 0.0150–0.03353 respectively.

A good conformity is observed between the experimental and predicted moisture ratio shown in Fig. 2 under 10–30% RH and 60–80 °C temperature conditions for Wang and Singh model. Similar finding was reported by Zhu and Shen (2014) for drying peach slices. Among the three thin-layer drying models, the Wang and Singh model gave the best results based on the R^2 , χ^2 and RMSE values obtained. The different model parameters computed for MR in relation to drying time were determined and reported.

Effective moisture diffusivity (D_{eff})

The obtained D_{eff} values were in the range of 8.9×10^{-9} – 1.7×10^{-8} m²/s depending on the drying RH and temperature and are shown in Table 1. This indicates that moisture movement in the carrot slices was in the liquid form (Doymaz and Kocayigit, 2012; Saravacos and Kostaropoulos, 2002). The effective moisture diffusivity was increased from 8.9×10^{-9} m²/s in 30% RH to 1.2×10^{-8} m²/s in 10% RH for 60 °C drying condition. This increase was equivalent to 34.8% whilst 20% RH recorded 12.4% increase under same temperature. In the same order, an increase was also observed in 70 and 80 °C such that highest increase of 63.6% was observed for 10% RH when compared with 30% RH in 80 °C drying temperature. Eventually, increasing temperature and decreasing RH increased the moisture diffusivity values thereby causing a faster dehydration rate in the carrot slices. This is attributed to the increased of heat transfer rates in increasing temperature and decreasing RH drying conditions and this was also confirmed in our previous study (Sarpong et al., 2018a; 2018c). Also, this is corroborated by the higher sample internal temperatures observed in lower RH than higher RH as shown in Fig. 1D–F. The D_{eff} values in this study are close to the values of 2.65×10^{-10} – 1.052×10^{-8} m²/s reported by Zhu and Shen (2014), Doymaz (2017) and Liu et al. (2014) for carrot slices. According to Doymaz (2017) the differences between the

Table 1 Curve fitting criteria for 3 mathematical models and parameters at various temperature and RH

RH (%)	Temp (°C)	Model name	Model constants		R ²	χ ²	RMSE	D _{eff} (m ² /s)	E _a (kJ/mol)	R ²
10	60	Newton	k = 0.01855		0.998	0.00563	0.07504	1.2 × 10 ⁻⁸	11.39	0.99
		Page	k = 0.01836 n = 0.02136		0.994	0.00658	0.08113			
		Wang and Singh	a = - 0.0142 b = 5.4 × 10 ⁻⁵		0.998	5.5 × 10 ⁻⁴	0.02345			
	70	Newton	k = 0.02126		0.998	0.00744	0.08625	1.4 × 10 ⁻⁸		
		Page	k = 0.02178 n = - 0.05214		0.994	0.0081	0.09002			
		Wang and Singh	a = - 0.0154 b = 6.4 × 10 ⁻⁵		0.998	5.3 × 10 ⁻⁴	0.02304			
	80	Newton	k = 0.02738		0.999	0.00278	0.05273	1.7 × 10 ⁻⁸		
		Page	k = 0.02789 n = 0.03569		0.998	0.00326	0.0571			
		Wang and Singh	a = - 0.0206 b = 1.2 × 10 ⁻⁵		0.999	5.1 × 10 ⁻⁴	0.00711			
20	60	Newton	k = 0.01595		0.991	0.02836	0.16841	1.0 × 10 ⁻⁸	13.78	0.99
		Page	k = 0.015 n = 0.11983		0.970	0.02804	0.16744			
		Wang and Singh	a = - 0.0132 b = 4.7 × 10 ⁻⁵		0.996	8.8 × 10 ⁻⁴	0.02972			
	70	Newton	k = 0.01851		0.997	0.00832	0.0912	1.2 × 10 ⁻⁸		
		Page	k = 0.01835 n = 0.01883		0.992	0.00984	0.09921			
		Wang and Singh	a = - 0.0142 b = 5.4 × 10 ⁻⁵		0.998	5.7 × 10 ⁻⁴	0.0238			
	80	Newton	k = 0.0215		0.998	0.00399	0.06316	1.3 × 10 ⁻⁸		
		Page	k = 0.02174 n = 0.02013		0.996	0.0051	0.07144			
		Wang and Singh	a = - 0.0168 b = 7.9 × 10 ⁻⁵		0.999	5.4 × 10 ⁻⁴	0.02314			
30	60	Newton	k = 0.01411		0.988	0.03769	0.19414	8.9 × 10 ⁻⁹	22.09	0.99
		Page	k = 0.01277 n = 0.01277		0.957	0.03231	0.17976			
		Wang and Singh	a = - 0.0125 b = 4.2 × 10 ⁻⁵		0.995	0.00112	0.03353			
	70	Newton	k = 0.01637		0.998	0.00681	0.08252	1.0 × 10 ⁻⁸		
		Page	k = 0.01606 n = 0.03914		0.993	0.00741	0.08606			
		Wang and Singh	a = - 0.0127 b = 4.4 × 10 ⁻⁵		0.997	8.8 × 10 ⁻⁴	0.02967			
	80	Newton	k = 0.01743		0.999	9.4 × 10 ⁻⁴	0.03064	1.1 × 10 ⁻⁸		
		Page	k = 0.01746 n = 0.00301		0.998	0.00117	0.03419			
		Wang and Singh	a = - 0.0141 b = 5.7 × 10 ⁻⁵		0.999	2.3 × 10 ⁻⁴	0.01507

Fig. 2 Experimental and simulated curves using Wang and Singh model for drying carrots slices at various temperatures and RH

D_{eff} values are as a result of composition structure, shape and moisture content of material, as well as the drying temperature, pretreatments, and drying equipment.

Activation energy

From the Arrhenius plots [shown in Supplement sheet (S1)]; it is clear that the natural logarithm of the rate constant versus temperature ($1/(T + 273.15)$) suggesting the slope of the plots represented the activation energy (E_a). The E_a is generally used to describe the energy required to reach the active state of a reaction. Thus, the values of activation energy found to be 11.39 ($R^2 = 0.99$), 13.79 ($R^2 = 0.99$) and 22.09 kJ/mol ($R^2 = 0.99$) for 10%, 20% and 30% RH samples, respectively. The values obtained in this study are in the range of 10.7–110 kJ/mol for various foods reported by Zogzas et al. (1996). Interestingly, higher RH significantly ($p < 0.05$) increased the E_a . The relation between temperature and RH from the results revealed an inverse proportion, thus increasing RH was known to decrease temperature. For RH effect on E_a , decreasing RH (increasing temperature) increased the thermal agitation process of sample which in turn increased the self-diffusion of moisture. This is revealed in Fig. 1, where increase in sample internal temperatures by lower RH conditions caused a higher diffusion rate than higher RH drying conditions. Taheri-Garavand et al. (2011) in the drying of tomatoes under varied RH also confirmed that, E_a was also dependent on RH (direct relation) beside temperature. Similarly, other E_a values obtained for carrot slices drying were in the range of 20.17–59.06 kJ/mol by

the following authors (Doymaz, 2017; Wu et al., 2014; Xiao et al., 2010).

Degradation kinetics of β -carotene

From Fig. 3, β -carotene declined with increasing drying time in all RH and drying temperature conditions but rate of decrease intensified when RH and temperature decreased and increased respectively. This was reflected by the increase in the k -values (Table 2) in higher temperatures and lower RH conditions. This compound is heat labile and that prolong drying could cause irreversible chemical changes in them (Demiray and Tulek, 2017). The exponential reduction of the compound as a result of chemical degradation and was particularly observed in the early stages of drying especially in higher temperatures. Despite the decrease in the various temperatures, higher RH was observed to enhance the retention of β -carotene. For instance, at drying time of 30 min for 60 °C, β -carotene recorded a value of 59.09 ± 1.21 mg/100 g d.m., 60.84 ± 1.54 mg/100 g d.m. and 61.97 ± 1.94 mg/100 g d.m. for 10, 20 and 30% RH. At the same drying time and 10% RH drying condition, 48.31 ± 2.3 mg/100 g d.m. and 55.48 ± 1.57 mg/100 g d.m. were recorded for 70 and 80 °C respectively. Higher RH increased the water activity (A_w) in the drying chamber which eventually lowered the internal temperature of sample and led to high retention of the compound. This is possible as a result of established relation between temperature and RH (inverse proportion), thus increasing RH was known to decrease temperature and was also confirmed by the sample internal temperature [Fig. 1(D–F)]. From these results, a deduction

Fig. 3 Evolution of β -carotene degradation of carrot slices with drying times under varied RH and temperatures

Table 2 The constant for first-order model, half-life, D-value and thermodynamic parameters of β -carotene degradation for varied temperature and RH of dried carrot

RH (%)	Temp (°C)	$k(1/\text{Min}) \times 10^{-3}$	R^2	$t_{1/2}$ (Min)	D-value (Min)	E_a (kJ/mol)	R^2	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol)
10	60	5.67	0.998	122.2	406.1	15.69	0.98	12.92	187.94	– 525.35
	70	6.47	0.987	107.1	355.9			12.83	193.29	– 525.88
	80	7.82	0.996	88.6	294.4			12.75	198.45	– 525.83
20	60	3.55	0.988	195.2	648.6	16.27	0.99	13.50	189.24	– 527.50
	70	4.28	0.989	161.9	538.0			13.42	194.47	– 527.62
	80	4.95	0.985	140.0	465.2			13.33	199.79	– 527.99
30	60	2.15	0.970	322.3	1071.0	17.61	0.99	14.84	190.63	– 527.66
	70	2.67	0.985	259.6	862.4			14.75	195.81	– 527.64
	80	3.08	0.987	225.0	747.6			14.67	201.19	– 528.15

can be made that higher RH led to slower β -carotene decomposition or alterations in their molecular structure; thus a decrease in their chemical reactivity or/and an increase in their extractability in their analysis due to deceased polymerization. Also, this could be attributed to the ability of higher RH to increase the water activity (A_w) in the drying chamber; thus reducing the force to evaporate moisture continuously and increase oxidative stability of β -carotene in the drying sample (Kim et al., 2015).

At the end of various drying time, between 41.91 and 50.11% retention was achieved for 80 °C, 50.00–54.17% retention for 70 °C and a range of 62.05–65.66% gained for 60 °C. The results reveal that a range of 3.61–8.20% retention of β -carotene was gained at every 10% increase in RH for various drying air temperature. However, the effect of RH on the degradation of β -carotene cannot be compared with that of drying air temperature as 19.30–52.90% retention was observed for every 10 °C decrease in air temperature. From Table 2, kinetics of β -carotene degradation in dried carrots followed a first-order reaction for various RH and temperature ($R^2 = 0.970$ – 0.998). This first-order kinetic model was in good agreement with Demiray and Tulek (2017) and Koca et al. (2007) in degradation kinetic of β -carotene and color for carrot respectively. The k values for β -carotene degradation in carrot slices during RH-convective drying were in the range of 2.15 – 7.82×10^{-3} 1/min and significantly affected by temperature and RH. Observably, higher temperature and lower RH led to rapid degradation of the compounds with respect to drying time judging from the k values.

The half-time values ($t_{1/2}$), which ranged from 88.6 to 322.3 min, were determined from the k -values using Eq. (16). Observably, the higher the k -values, the shorter the $t_{1/2}$ value of the sample. Besides effect of higher temperatures on the reduction of $t_{1/2}$ value, lower RH also

played a significant ($p < 0.05$) role in reducing the $t_{1/2}$ value under same drying temperatures. Thus the effect of temperature of the degradation of β -carotene could greatly be improved when drying is conducted under higher RH. Again, D-value (90% reduction) evaluation were consistent with $t_{1/2}$ value. Similarly, higher D-values were recorded for lower temperatures and higher RH drying conditions such that 1071.0 min was recorded as highest D-values for 30% RH and 60 °C. The degradation of β -carotene declined with increasing drying time in all drying conditions but rate of decrease intensified when RH and temperature decrease and increase respectively. The results reveal that a range of 3.61–8.2% retention of β -carotene was retained at every 10% increase in RH for various temperatures. The results revealed that first-order model could satisfactorily be used to adequately predict the kinetic degradation of β -carotene and rate constant from the model regressions computed in relation to drying time were determined and reported. The results also show that the higher the k -values, the shorter the $t_{1/2}$ and D-values of the dried sample.

Thermodynamic analysis of β -carotene degradation

Through thermodynamic parameters, the physical, chemical, and biochemical phenomena of β -carotene degradation were evaluated. From the Arrhenius plots [shown in Supplement sheet (S2)]; it is clear that the natural logarithm of the rate constant versus $1/K$ of β -carotene degradation suggesting the slope of the plots represented the activation energy (E_a).

The E_a values range from 15.69 to 17.61 kJ/mol ($R^2 = 0.98$ – 0.99) depending on the varied RH condition. Observably, higher RH increased the E_a as explained in the drying kinetics. The enthalpy change (ΔH) is defined as the energy difference between the reactant and the activated

complex during the drying process. From Table 2, ΔH values calculated for different temperatures were similar and ranged from 12.75 to 14.84 kJ/mol. From Eq. (18), temperature variation had little effect on ΔH due to the small amount of the ideal gas constant (R). The variation in ΔH values was solely attributed to variation in RH such that a direct relation was exhibited between ΔH and RH. Thus, energy barrier that must be exceeded to achieve the transition state for β -carotene degradation was greater in higher RH when compared with lower RH. Lastly, positive ΔH values suggest that β -carotene degradation was an endothermic reaction.

The spontaneity of reaction of β -carotene degradation was also evaluated using Gibbs free energy (ΔG) as the fundamental criterion. The ΔG values ranged from 187.94 to 201.19 kJ/mol, an indicative of non-spontaneous reaction. The closeness of these values suggested that the total energy increase in the system at the approach of the reagents and the activated complex formation were similar for various RH. The disorder change of molecules in a system was measured by determining entropy change (ΔS) for β -carotene degradation of carrot slices. As a result of lower structural freedom of the transition state compared with reactant, negative values were obtained in this study. Thermodynamic analyses established a direct relation between RH and E_a as higher RH slightly increased the E_a . Also, RH caused a variation in ΔH values for same drying temperatures for β -carotene degradation. Positive and negative values of ΔG and ΔS also suggested a non-spontaneous reaction and lower structural freedom of the transition state compared with reactant in the β -carotene degradation reaction.

Effect of RH on color parameters

The evolution of color parameters (L^* , a^* , b^* and total color difference) with the drying time under the various RH

and temperatures [shown in Supplement sheet (S3 and 4)]. Oscillatory feature was exhibited by all color parameter; increasing during the early stages until sudden decrease in values. The measured L^* , a^* , b^* parameters for 30% RH (60 °C) carrots were 42.15 ± 0.95 , 23.14 ± 0.87 and 36.94 ± 1.14 from the initial values of 42.75 ± 1.28 , 8.55 ± 0.54 and 15.87 ± 1.08 respectively. Similarly, 10% recorded 34.12 ± 1.02 , 18.06 ± 1.07 and 34.12 ± 1.02 whilst 20% RH also measured 43.17 ± 1.22 , 20.08 ± 0.82 and 35.47 ± 1.07 for L^* , a^* , b^* parameters. The results demonstrate that RH significantly ($p \leq 0.05$) influenced the L^* , a^* , b^* parameters in color. Change in color parameters can be related to oxidative reactions that occur during air dehydration which is potentiated by higher temperature and lower RH drying conditions. According to Zielinska and Markowski (2012) increase in L^* parameter of carrot is attributed to carotenoids isomerization (from *trans*- to *cis*-) and creating lighter and less biologically active derivatives. Also, Aguiló-Aguayo et al. (2017) attribute carrot color change to vascular tissue composition of carrot tissues resulting from different treatments and drying conditions during thermal processing. Gupta et al. (2011) further stated that changes in color parameters from the initial values was attributed to decomposition of pigments and formation of browning pigments or ascorbic acid browning and non-enzymatic Maillard browning.

Considering the total color change (ΔE^*), 30% RH drying conditions had lower ΔE^* value compared to other RH conditions under all temperatures. The ΔE^* had a tendency to decrease with an increasing drying temperatures and drying time. Higher RH diluted released reactant species as a result of higher moisture content in the drying chamber, delaying chemical activities that usually occur in broken cells helps in maintaining color of the sample of carrot. Despite the significant ($p < 0.05$) increase in ΔE^* (depreciation of color) in all RH drying conditions (S 4),

Table 3 Pearson's coefficient of correlation and p value analysis of β -carotene and color parameters

RH (%)	TEMP (°C)	L^*		a^*		b^*		ΔE^*	
		r	p value	r	p value	r	p value	r	p value
10	60	- 0.22183	0.16022	- 0.63612	0.10422	- 0.85144	0.05745	- 0.68463	0.06901
	70	- 0.36544	0.10422	- 0.70261	0.09447	- 0.92035	0.05246	- 0.73309	0.06475
	80	- 0.85769	0.06305	- 0.86709	0.05699	- 0.96986	0.00000	- 0.88444	0.05525
20	60	- 0.39823	0.09125	- 0.47428	0.12874	- 0.65436	0.08917	- 0.60904	0.07345
	70	- 0.07184	0.06741	- 0.50678	0.11470	- 0.69105	0.08263	- 0.70528	0.06841
	80	- 0.58817	0.08422	- 0.85278	0.05743	- 0.83666	0.05841	- 0.76120	0.06246
30	60	- 0.65317	0.07841	- 0.50897	0.11084	- 0.56423	0.09754	- 0.56142	0.08064
	70	- 0.12720	0.15770	- 0.54556	0.10944	- 0.63009	0.09164	- 0.76992	0.06289
	80	- 0.31615	0.10424	- 0.65057	0.10142	- 0.72589	0.07212	- 0.68275	0.07012

$p < 0.05$

conclusively higher RH seems to enhance the color parameters better lower RH.

Correlation between β -carotene and color parameters

The color of drying carrot was evaluated by L^* , a^* , b^* and ΔE^* (Supplement sheet (S 3 and 4)) which also has various degree of correlation with the β -carotene concentration. Interestingly, all the correlation coefficient (r) obtained were inversely proportional to β -carotene concentration (Table 3). Although a significant correlation ($p < 0.05$) was found between β -carotene concentration in dried carrot slices and b^* parameter especially in higher temperatures and lower RH conditions, however L^* , a^* and ΔE^* correlation coefficient were not significant. For instances, the L^* , a^* and ΔE^* values showed correlations with β -carotene concentration, exhibiting a strong correlation coefficient of -0.82 , -0.87 and -0.88 . These correlation coefficient were not significant as compared with b^* parameter ($r = -0.97$) for 10% RH at 80 °C drying condition. Although, changes in L^* , a^* and ΔE affected the β -carotene concentration strongly (but not significant), b^* parameter only could alter the β -carotene concentration significantly ($p < 0.05$). The data also suggested that L^* color parameter had the least effect on the β -carotene concentration. According to Aguiló-Aguayo et al. (2017), lightness (L^*) correspond to peripheral cortex layer whilst a^* and b^* (red and yellow respectively) correspond to the inner cortex of carrot (containing parenchyma cells and may store sugars and carotenes). Therefore changes in a^* and b^* strongly could affect β -carotene concentrations which correspond to the color of carrot.

Also, b^* correlation coefficient were increased in 60 °C (10% RH) from -0.85 to -0.92 and -0.96 in 70 and 80 °C air drying temperatures respectively. Meanwhile, 20% and 30% RH recorded -0.66 and -0.56 correlation coefficient in 60 °C respectively. Thus β -carotene degradation was rapid in higher temperatures and lower RH and recorded higher correlation coefficient between color parameters and β -carotene concentrations compared with lower temperatures and higher RH. The results demonstrate that beside temperature, RH significantly ($p \leq 0.05$) influenced the L^* , a^* , b^* color parameters. Finally, a significant correlation ($p < 0.05$) was found between β -carotene concentration in dried carrot slices and b^* parameter especially higher temperatures and lower RH.

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