Kinetics Study on Hot-Air Drying Carrot Cubes

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Abstract:

Carrot is widely consumed as it contains bioactive compounds such as carotene. However these are very sensitive to heat. Therefore, degradation behaviors during thermal process should be considered. This study aimed to study kinetics of moisture content, shrinkage and β-carotene degradation of carrot cubes subjected to hot-air drying. Several empirical models were fitted to experimental data obtained under different hot-air temperatures ranging from 60°C to 80°C. Based on the highest coefficient of determination (R^2), lowest root mean square error (RMSE) and chi square (χ^2), the suitable equations were selected and employed to describe the change behavior of moisture, shrinkage and β-carotene. The results indicated that the Page and Modified Page models, the so-called Ratti model and the 2nd-order reaction kinetics equation suitably described the kinetics behaviors of moisture, shrinkage and degradation of β-carotene, respectively. Consequently, all suitable kinetics model obtained in this work can be further used as a basis for design and optimization purposes.

Keywords: Mathematical modeling, Drying characteristics, *β*-Carotene degradation, Shrinkage, Carrots

Introduction

Carrot (*Daucus carota* L.) is the one of vegetables widely consumed in the world due to its high nutritional values. Beta-carotene (β-carotene), bioactive compound mostly found in carrot, assesses high antioxidant properties as it turns into vitamin A after intake into human body [1, 2]. In the food industry, carrots are mostly dried with purposes of reducing weight, extending shelf-life and broadening product availability [3]. With the use of heat in drying process, qualities including physical and chemical properties change, resulting in consumer unacceptability. Therefore, in this work kinetics of moisture, shrinkage and *β*-carotene degradation were investigated in order to be served as a basis for process design and optimization.

Materials and methods

Experimental setup

All experiments were conducted using a laboratory tray dryer with a size of 43×69×39 cm. Air was supplied by centrifugal blowers connected to an inverter for adjusting air velocity which was kept constant as 0.5 m/s. The air was heated by 15-kW finned heater and its temperature was measured using K-type thermocouple. With a variation of air temperatures used in this work (60-80°C), the air temperature was controlled by PID controller.

Drying procedure and Drying characteristics modeling

Fresh carrots (*Daucus carota* L.) purchased from the local market in Nakhon Ratchasima province, Thailand were cleaned, peeled and subsequently cut into cubes with a size of 1 cm. Prior to experiments, initial moisture content of carrot cubes was randomly determined based on a standard method of AOAC [4]. Carrot cubes were placed into the drying chamber with the orientation in which hot air could pass through uniformly, as shown in Figure 1. The samples were subsequently subjected to hot-air drying with temperatures of 60, 70 and 80°C. During a drying run, the sample weights were measured every 30 min until reaching equilibrium. With the weight recorded, the moisture content could be determined for each time interval. All experiments were triplicated and averaged data were presented.

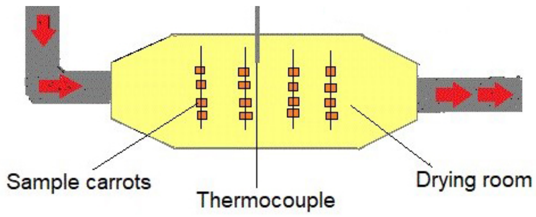

Figure 1 Sample orientation

In order to describe the drying behavior of carrots subjected hot-air drying under temperatures of 60-80°C, the experimental data of moisture ratio (MR) expressed in equation (1) were fitted to the proposed empirical drying model, as listed in Table 1. Statistical parameters including a coefficient of determination (R^2), root mean sqaure (RMSE) and chi square (χ^2) were used as criteria for model selection.

$$MR = \frac{M_t - M_e}{M_0 - M_e} \qquad (1)$$

In equation (1), M_t, M_0 and M_e denotes the moisture content at time t, at initial time and at equilibrium, respectively. All values were expressed in wet basis.

Table 1 The model used with the drying kinetics of hot air drying of carrot cubes [5].

Model	Model equation	
Lewis	$MR = exp(-kt)$	(2)
Page	$MR = exp(-kt^n)$	(3)
Modified Page	$MR = exp(-kt)^n$	(4)
Henderson and Pabis	$MR = a\ exp(-kt)$	(5)
Logarithmic	$MR = a\ exp(-kt)+c$	(6)
Two term	$MR = a\ exp(-k_0t)+b\ exp(-k_1t)$	(7)
Midilli	$MR = a\ exp(-kt^n)+bt$	(8)

a, b, c, n is constants in drying models and *k* is drying rate coefficient (1/minutes).

Kinetics modeling of Shrinkage

Change in shrinkage during process was analyzed by means of fluid replacement (Archimedes' principle) associated with n-heptane. Percentage of shrinkage was calculated using the volume before (V_0) and after drying (V_t) at each time interval, as expressed in Eq.(9).

$$\%shrinkage = \frac{V_0 - V_t}{V_t} \times 100 \qquad (9)$$

The shrinkage data were fitted to several empirical models summarized by [6] with little modification. The change in sample shrinkage was correlated with moisture content at specific drying time, as shown in Table 2. Again, the most suitable equation for describing the shrinkage kinetics was obtained using R^2, RMSE and χ^2.

Table 2 Empirical equations describing the shrinkage.

Name of the equation	Equation	Eq.
Lozano [7]	$S = b_1 \cdot MR + b_2$	(10)
Lozano [8]	$S = b_3 + b_4 \cdot MR + b_5 \cdot \exp\left(\frac{b_6}{b_7 + MR}\right)$	(11)
Ratti [9]	$S = b_8 + b_9 \cdot MR + b_{10} \cdot MR^2 + b_{11} \cdot MR^3$	(12)
Vazquez [10]	$S = b_{12} + b_{12} \cdot MR + b_{14} \cdot MR^{3/2} + b_{15} \exp(b_{16} \cdot MR)$	(13)
Mayor and Sereno [11]	$S = b_{17} + b_{18} \cdot MR + b_{19} \cdot MR^2$	(14)

From Table 2, *S* is shrinkage coefficient, b_i is numerical constants of empirical equations for shrinkage, MR is moisture content, g /g dry matter.

Determination of β-carotene concentration and its kinetics modeling of degradation

Concentration of β-carotene was determined according to [12]. Three grams of dried carrot cubes was placed into a test tube containing 10 mL of acetone solution, and mixed using a vortex-mixed equipment for 30 second. The mixture was then subjected to a centrifuge at a speed of 2100g for 5 minutes. The supernatant was filtered through a paper Whatman No. 1, and subsequently evaporated under temperature of 50°C. The evaporated supernatant was again extracted with 2-mL nitrile acetone, and finally filtered with a syringe filter with a pore size of 0.45 µm. β-carotene content was measured by means of high performance liquid chromatography (HPLC) method, following the protocol modified by [13]. Briefly, the mobile phase consisted of methanol and water (9:1 v/v) with a flow rate of 0.8 ml/min. UV detector was used at 472 nm under column temperature of 25°C.

As widely used to describe a change of reaction in biological materials, the kinetics equations with several orders (0^{th}-2^{nd}) were evaluated (see in equations (15-17)). The concentrations of β-carotene determined at each drying time intervals were fitted to the 0^{th}-, 0.5^{th}-, 1^{st}-, 1.5^{th}-, and 2^{nd}-order kinetics models. The best choice was chosen based on the highest R^2, and lowest RMSE and χ^2. The equation of concentration ratio (CR) as a function of drying time for each temperature is expressed as following [14]:

$$\frac{d(CR)}{dt} = -k(CR)^{1-n} \qquad (15)$$

Equation 10 was converted to logarithm form for different reaction order [15]:

$$\ln(CR) = -kt + b \; ; \qquad (n = 1) \qquad (16)$$

$$(CR)^{1-n} = -kt + b \; ; \qquad (n \neq 1) \qquad (17)$$

where *CR* is (C/C_0, C, C_0 denotes concentration of β-carotene at a specific and initial time, respectively), *t* is drying time (min), *k* is the reaction rate constant, and *b* is an equation constant. All constants in equations (16) and (17) were determined by means of linear regression method.

Statistical analyses

Besides the coefficient of determination, R^2, root mean square (RMSE) and chi square (χ^2) were evaluated using equations (18) and (19), respectively, at different temperatures.

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(V_{\exp,i} - V_{pre,i}\right)^2} \qquad (18)$$

$$\chi^2 = \frac{\sum_{i=1}^{n}\left(V_{\exp,i} - V_{pre,i}\right)^2}{n - z} \qquad (19)$$

In equations (18) and (19), V_{exp} and V_{pre} is experimental value and predicted value. *n* is a number of experimental data recorded and *z* is a number of constants in kinetics equations.

Results and discussion

Drying characteristics modeling

Commonly found in biological materials [16], moisture content (MC) of carrot cubes exponentially reduced with drying time for all temperatures, as shown in Figure 2. In addition, higher hot-air temperature resulted in increasing drying rate, as MC reduced to the desired level (~10%wb) faster due to higher driving force.

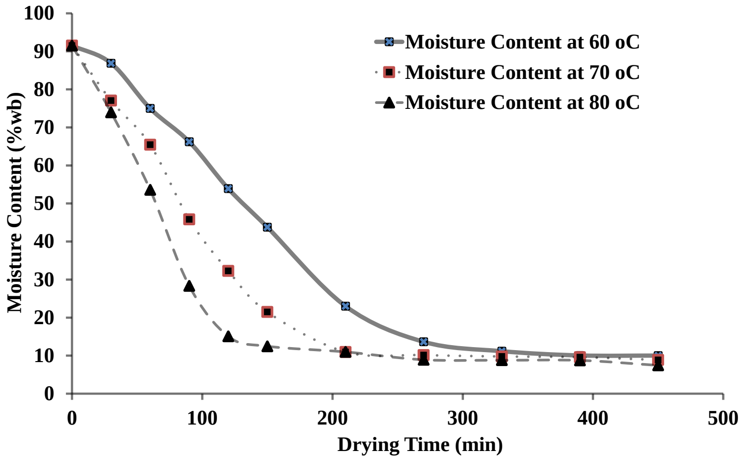

Figure 2 Comparison of moisture contents as a function of drying time at various temperatures.

Among several mathematical models in Table 1, the drying characteristics of carrot cubes tested in this work could be suitably described using the Page and modified Page model as the result that these models gave the highest R^2, and lowest RMSE and χ^2, as presented in Table 3.

Table 3 Statistical parameters of drying models at different temperatures.

Models	Statistical parameters	60 °C	70 °C	80 °C
Lewis	R^2	0.99543	0.99257	0.99543
	χ^2	0.00046	0.00065	0.00014
	RMSE	0.02052	0.02440	0.01147
Page	R^2	0.99612	0.99900	0.99612
	χ^2	0.00044	9.82×10^{-5}	3.76×10^{-5}
	RMSE	0.01892	0.00896	0.00555
Modified Page	R^2	0.99612	0.99900	0.99612
	χ^2	0.00044	9.82×10^{-5}	3.77×10^{-5}
	RMSE	0.01892	0.00896	0.00555
Henderson and Pabis	R^2	0.99558	0.99269	0.99558
	χ^2	0.00050	0.00072	0.00016
	RMSE	0.02019	0.02421	0.01145
Logarithmic	R^2	0.99558	0.99503	0.99558
	χ^2	0.00056	0.00055	5.15×10^{-5}
	RMSE	0.02015	0.01995	0.00612
Two term model	R^2	0.99558	0.99269	0.99558
	χ^2	0.00064	0.00092	0.00021
	RMSE	0.02019	0.02421	0.01145
Midilli	R^2	0.99658	0.70797	0.99658
	χ^2	0.00049	0.03677	0.04701
	RMSE	0.01775	0.15296	0.17297

With the use of non-linear regression method, all constants in each suitable equations were estimated, and therefore, the mathematical models that could best describe the drying characteristics of carrot cubes at different temperatures are summarized in Table 4. These findings were consistent with the results obtained by [17] of which the Page model suitably described the drying behavior of carrot shreds (4×4×20 mm) subjected to hot-air convective drying at temperatures ranging from 50-70°C.

Table 4 Suitable drying models and their constants.

Models	Conditions	Equations
Page	60 °C	$MR = exp(-0.53566t^{0.53566})$
	70 °C	$MR = exp(-1.14821t^{0.70908})$
	80 °C	$MR = exp(-1.34413t^{0.79351})$
Modified Page	60 °C	$MR = exp(-0.55986t)^{1.07616}$
	70 °C	$MR = exp(-1.21520t)^{0.70908}$
	80 °C	$MR = exp(-1.45166t)^{0.79351}$

Kinetics modeling of shrinkage

Figure 3 shows volume ratio (V/V_0) or shrinkage of carrot cubes as a function of drying time at different temperatures. It was found from Figure 3 that the sample volume decreased with drying time. This shrinkage was attributed to water evaporation inside the samples, resulting in a gap which caused the sample surface to collapse [18]. In addition, the samples shrank quicker when hot-air temperature increased, especially at the initial drying period (0-60 min), corresponding to higher drying rate, as seen in Figure 2. This results was also found in the work of [3].

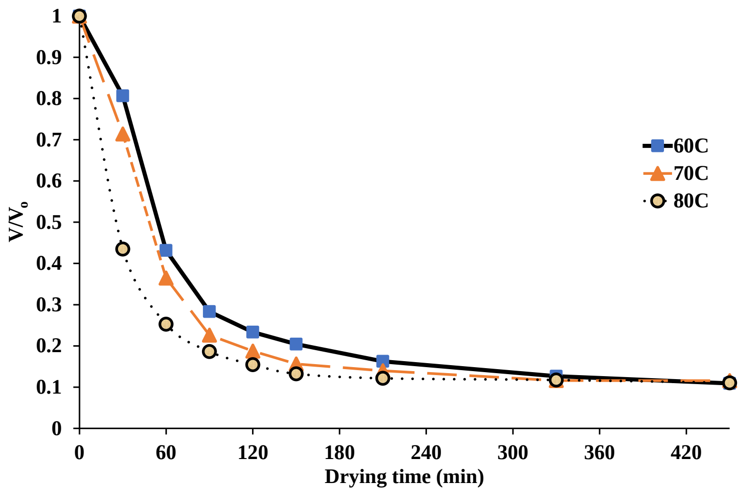

Figure 3 Comparison of shrinkage as a function of drying time at various temperatures.

Table 6 Statistical results for cubes mathematical models of shrinkage carrots.

Models	Statistical parameters	60 °C	70 °C	80 °C
Lozano [7]	R^2	0.97770	0.88920	0.98770
	χ^2	0.00260	0.01246	0.00118
	RMSE	0.04498	0.09843	0.03024
Lozano [8]	R^2	0.97778	0.98686	0.99790
	χ^2	0.00453	0.02195	0.00035
	RMSE	0.04486	0.03390	0.01252

Ratti [9]	R^2	0.99760	0.99670	0.99840
	χ^2	0.00111	0.10103	0.00073
	RMSE	0.02485	0.23691	0.02009
Vazquez [10]	R^2	0.97778	0.88840	0.98674
	χ^2	0.00453	0.02195	0.00222
	RMSE	0.04486	0.09876	0.03141
Mayor and Sereno [11]	R^2	0.99370	0.98530	0.99820
	χ^2	0.00086	0.00193	0.03418
	RMSE	0.02392	0.03587	0.15094

Due to time independcy, experimental data of sample shrinkage were fitted to well-known empirical models (see Table 2). Table 6 summarizes the statistical parameters of various equations. Based on the statistical criteria, the model proposed by Ratti [9] gave the highest suitability for describing the change in volume of carrot cubes and their influence of temperature. Furthermore, its model parameters were estimated by means of non-linear regression. The appropriate shrinkage kinetic models for various temperature are therefore expressed as follows:

60°C: $S = 0.1192 + 0.0852 \cdot X + 0.0078 \cdot X^2 - 0.0008 \cdot X^3$ (20a)

70 °C: $S = 0.1283 + 0.0637 \cdot X + 0.0463 \cdot X^2 - 0.0041 \cdot X^3$ (20b)

80 °C: $S = 0.1111 + 0.1472 \cdot X - 0.0140 \cdot X^2 + 0.0007 \cdot X^3$ (20c)

Degradation kinetics of beta-carotene

Figure 4 shows β-carotene content reduced from 58.03 mg/100g dry matter (fresh carrot) to approximately 2-4 mg/100g dry matter (at the end of drying process). With variation of hot-air temperature, β-carotene degraded with different rate, the higher temperature, the higher degradation rate. Therefore, at the same drying time, higher retention of beta-carotene was found when using lower drying temperature.

Again, kinetics was investigated for describing degradation of beta-carotene during drying process. Table 6 shows the statistical parameters of kinetic equations of reaction of carrot cubes dried under different temperatures. From this, the best parameters were found for the 2nd-order kinetic equation, R^2 in a range of 0.981-0.995. The suitable models for predicting concentration of β-carotene in carrot cubes during drying at different temperatures are summarized here,

60°C: $\left(\frac{1}{CR}\right) = -0.0398t + 0.1825$ (21a)

70 °C: $\left(\frac{1}{CR}\right) = -0.0573t + 0.2053$ (21b)

80 °C: $\left(\frac{1}{CR}\right) = -0.0806t - 0.7163$ (21c)

where *CR* denotes concentration ratio of β-carotene and *t* stands for drying time (minutes). It could be seen from equations 21a-c that the inverse of concentration ratio of β-carotene linearly correlated with process time. Therefore, the amount of β-carotene could be predicted and controlled under a certain drying time.

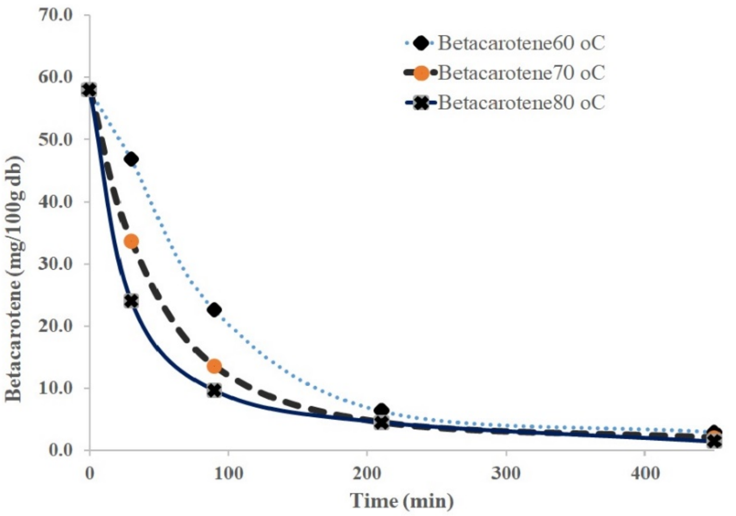

Figure 4 Comparison of β-carotene content as a function of drying time at different temperatures.

Conclusions

Carrot cubes were subjected to drying process with variation of temperature in order to investigate kinetic modeling for moisture content, shrinkage and β-carotene. The suitable equations used for describing the change in these qualities were the Page and modified Page model, the Ratti model and the 2nd-order reaction model, respectively. Moreover, hot-air temperatures significantly affected all qualities, the higher temperature, the higher rate of decreasing. Consequently, these kinetic equations could be very useful for further applications and research in numerical study of drying sytems such as computational fluidynamics investigation which could be served as a basis for process design and optimization.

Table 7 Statistical parameters of kinetic models of β-carotene degradation.

Temperature	Statistical parameters	0th	0.5th	1st	1.5th	2nd
60 °C	R^2	0.70370	0.8076	0.90490	0.97090	0.99010
	χ^2	0.00144	0.11060	0.01343	0.19635	0.17653
	RMSE	0.20102	0.25760	0.08977	0.34324	0.32545
70 °C	R^2	0.57890	0.72300	0.87350	0.97120	0.99580
	χ^2	0.09198	0.13082	0.06006	0.22954	0.04177
	RMSE	0.23492	0.28017	0.18983	0.37111	0.15831
80 °C	R^2	0.48380	0.66750	0.88080	0.99240	0.98190
	χ^2	0.10992	0.15278	0.08337	0.25417	0.07401
	RMSE	0.25681	0.30277	0.22366	0.39052	0.21073

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