Kinetic Models for Colour Changes in Kiwifruit Slices During Hot Air Drying

¹Ali Mohammadi, ¹Shahin Rafiee, ²Zahra Emam-Djomeh and ¹Alireza Keyhani

¹Department of Agricultural Machinery Engineering, Faculty of Biosystems Engineering, University of Tehran, Karaj, Iran ²Department of Food Science and Engineering, Faculty of Biosystems Engineering, University of Tehran, Karaj, Iran

Abstract: The colour changes that occur in kiwifruit during the dry process were experimentally studied in order to determine the magnitudes of the parameters for a corresponding colour change model. The drying experiments were carried out under five air temperatures of 40, 50, 60, 70 and 80°C, air velocity of 1.0 m/s and kiwifruit slice thickness of 4 mm. The colour parameters for the colour change of the materials were quantified by the Hunter L (whiteness/darkness), a (redness/greenness) and b (yellowness/blueness) system. These values were also used for calculation of the total colour change (ΔE), chroma, hue angle and browning index. The values of L and b decreased, while values of a and total colour change (ΔE) increased during hot air drying. The mathematical modeling study of colour change kinetic showed that changes in L, b values, chroma and Browning index fitted well to the first-order kinetic model while ΔE , a value and hue angle followed the zero order kinetic.

Key words: Colour change • Drying • Kiwifruit • Model

INTRODUCTION

Kiwifruit (Actinidia deliciosa) is a highly nutritional fruit due to its high level of vitamin C and its strong antioxidant capacity due to a wide number of phytonutrients including carotenoids, lutein, phenolics, flavonoids and chlorophyll [1]. The cultivation of kiwifruit trees in orchards of northern Iran, with more than 3500 hectares and 87000 tone produce (2005), making this country one of the most important producers of kiwifruit in the world. Iran has exported more than 48000 tones to different countries in 2005 [2]. The colour observed by human beings is the perception of the wavelengths coming from the surface of the object on the retina of the eyes [3]. When light strikes an object, it is reflected, absorbed or transmitted, but it is the reflected light which determines the colour of a material. Therefore, the appearance can change depending on the amount of light, the light source, the observer's angle of view, size and background differences [4]. However, standardized instrumental colour measurements correspond to visual assessments of food colour and it is a critical objective parameter that can be used as a quality index (raw and processed foods), for the determination of conformity of food quality to specifications and for analysis of quality

changes as a result of food processing, storage and other factors. Several colour scales have been used to describe colour, those most used in the food industry are the Hunter colour L, a, b CIE system and the Munsell colour solid [4]. Maintaining the natural colour in processed and stored foods has been a major challenge in food processing [5, 6]. The colour of green vegetables is mainly determined by the chlorophyll pigments present in plant material to catch the energy from sun light. Kidmose and Hansen [7] reported a good relationship between instrumental colour, sensory yellowness and chlorophyll content in cooked and stored broccoli florets. These chlorophyll pigments degrade during heat treatments, with the consequence that the green colour changes. Most studies on changes in green colour due to time and temperature treatments only mention a decrease of green colour. For an important part, this is related to the time scale during which the colour development is studied. Process modeling is of great significance in the analysis of design and optimization of drying in order to produce high quality food products. There are numerous publications on the kinetics of colour change of food material. The majority of these works report zero order (Eq. (1)) or first order (Eq. (2)) degradation reaction kinetics [8].

$$C = C_0 \pm k_0 t \tag{1}$$

$$C = C_0 \exp(\pm k_1 t) \tag{2}$$

where C is the measured value of color variables at time t, C_0 the initial value of color variables at time zero, t the drying time (min), k_0 the zero-order kinetic constant (\min^{-1}) and k_i is the first-order kinetic constant (\min^{-1}) . Where (+) and (-) indicate formation and degradation of quality parameter respectively. Hunter colour parameter (L, a, b) has previously proved valuable in describing visual colour deterioration and providing useful information for quality control in fruits and fruit products [9]. Although many experimental works are conducted on the drying and kinetics of colour change in fruits and agro-food materials [10-22], there are a few studies on the kinetics of colour change of kiwifruits: Maskan [23, 24] studied to comparison of the microwave, hot air and hot air-microwave drying methods for the kinetics of colour change and processing of kiwifruits in respect to drying, shrinkage and rehydration characteristics obtained by the three drying techniques.

The purpose of this study was to investigate combination of colour change kinetics and improvement of the optical properties of kiwifruit slices during combined coating and hot air drying in order to predict colour changes with time by foregoing drying techniques.

MATERIALS AND METHODS

Fresh kiwifruit samples were purchased from a local market in Tehran. They were stored at $4 \pm 0.5^{\circ}$ C at refrigerator. To determine the initial moisture content, four 50-g samples were dried in an oven at 65°C for 24 h [25]. The initial moisture content of kiwifruit was calculated as 4.69 d.b. as an average of the results obtained. The reproducibility of the initial moisture content measurements was within the range of $\pm 5\%$.

Preparing Samples and the Dryer for Testing: Drying treatment was performed in a thin layer laboratory dryer which has recently been designed and built in the Department of Agricultural Machinery at University of Tehran. A portable, 0-15 m/s range digital anemometer (TESTO, 405-V1) was used to occasionally measure air flow velocity of air passing through the system. The airflow was adjusted by means of a variable speed blower. The heating system was consisted of four heating elements placed inside the duct. A simple control

algorithm was used to control and adjust the drying tunnel temperature. The opening side on the right was used to load or unload the tunnel and to measure drying air velocity. The travs were supported by lightweight steel rods placed under the digital balance [26]. Measured variables were air temperature, air velocity, relative humidity (RH) and sample mass loss during drying. After turning on the computer, fan, scale, elements and data acquisition system, the essential velocity for the fan was set. A manual TESTO 405-V1 model sensor was used to measure the velocity. The control software was implemented and the required temperature for the experiment was adjusted. Specifications regarding the measurement instruments including their rated accuracy are summarized in Table 1. Experiments were carried out 30 minutes after the system was turned on to reach to its steady state condition. Then, the tray holding the samples is carefully put in the dryer. Prior to drying, samples were taken out of storage, Kiwifruits were washed and sliced in thickness of 4 mm using a cutting machine. The uniform thickness of $t \pm 0.01$ mm was prepared by adjusting the opening of the slicer with a vernier caliper having a least count of 0.01 mm. About 150 g of kiwifruit slices were weighed and uniformly spread in a tray and kept inside the dryer. Three replications of each experiment were performed according to a preset air temperature and time schedule and the data given are an average of these results. The reproducibility of the experiments was within the range of $\pm 5\%$. The hot air drying was applied until the weight of the sample reduced to a level corresponding to moisture content of about 0.5 d.b. The drying experiment was conducted at five air temperatures of 40, 50, 60, 70 and 80°C and constant air velocity at 1.0 m/s.

Colour: Sample colour was measured before drying and at pre-specified time intervals during drying period by a Hunter- Lab ColorFlex, A60-1010-615 model colormeter (Hunter Lab, Reston, VA). This system uses three values (L, a and b) to describe the precise location of a colour inside a three-dimensional visible colour space. The colorimeter was calibrated against standard white and green plates before each actual colour measurement. For each sample at least five measurements were performed at different positions and the measured values (mean values). The measurements were displayed in L, a and b values which represents light-dark spectrum with a range from 0 (black) to 100 (white), the green-red spectrum with a range from -60 (green) to +60 (red) and the blue-yellow spectrum with a range from -60 (blue) to +60 (yellow) dimensions respectively.

Total colour difference was calculated using following equation, where subscript "0" refers to the colour reading of fresh kiwifruit. Fresh kiwifruit was used as the reference and a larger ΔE denotes greater colour change from the reference material.

$$\Delta E = \sqrt{\left(L_0 - L\right)^2 + \left(a_0 - a\right)^2 + \left(b_0 - b\right)^2}$$
(3)

Chroma =
$$(a^2 + b^2)^{0.5}$$
 (4)

Hue Angle =
$$tan^{-1}(b/a)$$
 (5)

where L is degree of lightness to darkness, L_o is initial value of L, a is degree of redness to greenness, a_o is initial value of a, b is degree of yellowness to blueness and b_o is initial value of b. Browning index (BI) represents the purity of brown colour and is considered as an important parameter associated with browning [9].

$$BI = \frac{\left[100(x - 0.31)\right]}{0.17} \tag{6}$$

Where

$$x = \frac{\left(a + 1.75L\right)}{\left(5.645L + a - 3.012b\right)}$$

Statistical Analysis: Experimental data for the different parameters were fitted to two kinetic models and processed by using SPSS version 13.0 software. Zero (Eq. (1)) and first-order (Eq. (2)) kinetic rate constants were calculated from non-linear regression. Correlation coefficient value was used as the basis to select the best fitting for estimation of the parameters of the models (Eqs. (1)-(6)).

RESULTS AND DISCUSSION

Effect of Hot Air Temperature on Colour Kinetics of Kiwifruit: To investigate the effect of hot air on colour change kinetics of kiwifruit, five air temperatures of 40, 50, 60, 70 and 80°C, were used for drying of constant amount of 150 g. The values of L, a, b and total colour change (ΔE) obtained from the experimental data during hot air drying and model data are presented in Fig. 1a-d, 2a-d. The L value is illustrated in Fig. 1a, 2a. As can be seen from this figures, the L value decreased with drying time. It has been stated that the change in the brightness of dried samples can be taken as a measurement of browning [10–13], which reduced from 42.2 to 36.24 and 35.76 during hot air drying of kiwifruit samples at various

Table 1: Specifications of measurement instruments including their rated accuracy

Total	M. 1.1	A	M-1 -
Instrument	Model	Accuracy	Make
Digital balance	GF3000	±0.02	A&D, Japan
T-sensor	LM35	±1°C	NSC, USA
RH-sensor	Capacitive	±3%	PHILIPS, UK
V-sensor	405-V1	±3%	TESTO, UK

air temperatures ranged from 40 to 80°C, respectively. Browning was due to the non-enzymatic browning reaction. For redness/greenness scale, initial colour of samples showed a negative a value (about-2.21), indicating greenness (Fig. 3b, 4b). The final a values were varied changed from 2.10 to 2.74 as the air temperature increased. Therefore, kiwifruit sample lose its greenness when dried by hot air. A decrease of the b value (Fig. 1c, 2c) was also observed during hot air drying. The initial and final b values were varied changed from 17.21 to 15.47 and 14.98 as the air temperature increased. This may be due to decomposition of chlorophyll and carotenoid pigments [13, 15, 16], non-enzymatic Maillard browning and formation of brown pigments [23, 27]. As a whole, the total colour change (ΔE) of kiwifruit increased during hot air drying with drying time and also ranged from 7.66 to 9.22 as air temperature increased from 40 to 80°C, respectively, (Fig. 1d, 2d) [22].

For the mathematical modeling of colour change of kiwifruit, zero-order and first-order kinetic models were used (Fig. 1, 2). It was observed that L and b values were fitted to the first-order kinetic model (Fig. 2a, 2c); on the other hand, the values of a and total colour change (ΔE) followed a zero-order kinetic model (Fig. 1b, 1d). The estimated kinetic parameters of these models and the statistical values of coefficients of determination R² are represented in Table 2. The kinetic rate constant of L increased from 0.0003 to 0.0012 min^{-1} , for a value from 0.0099 to 0.0337 min⁻¹, for b value from 0.0002 to 0.0009 min^{-1} and for total colour change (ΔE) increased from 0.0171 to 0.0580 min⁻¹ as the air temperature increased. This implies that with increase in air temperature, the degradation rate of colour becomes faster as a result of high energy transferred to the inside of food material. The results obtained were in agreement with the studies published in the literature and several authors have stated that the first-order kinetic model was better for L and b values of double-concentrated tomato paste [28], kiwifruits [23], pineapple [21] and peach puree [10] and zero-order kinetic

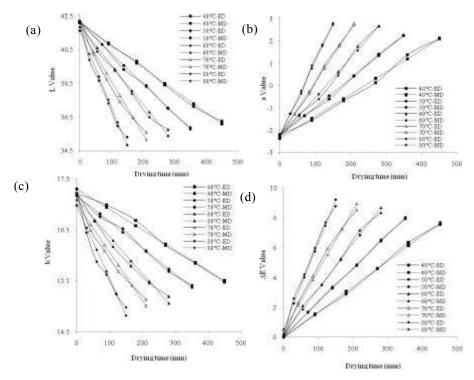


Fig. 1: Kinetics of change of L value (a), a value (b), b value (c) and total colour change (? E) (d) as a function of drying time at various air temperatures for Zero order model, ED (Experimental Data) and MD (Model Data)

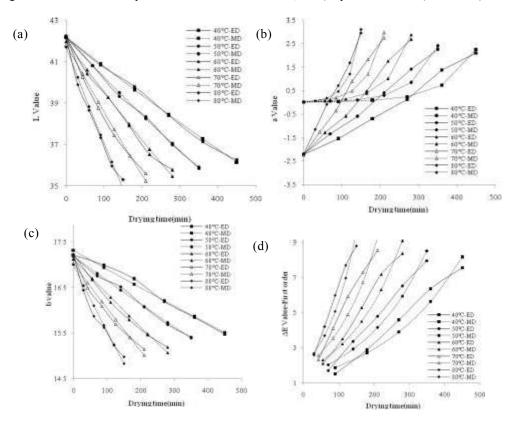


Fig. 2: Kinetics of change of L value (a), a value (b), b value (c) and total colour change (? E) (d) as a function of drying time at various air temperatures for First order model, ED (Experimental Data) and MD (Model Data)

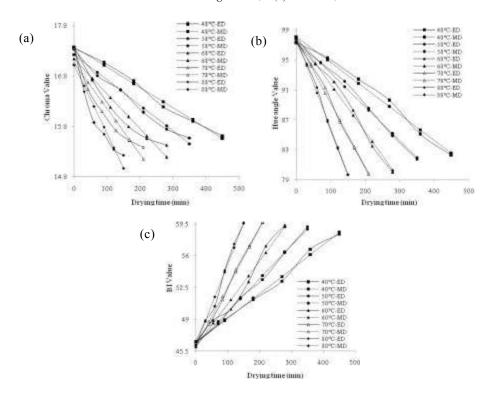


Fig. 3: Kinetics of change of chroma (a), hue angle (b), and Browning index (c) as a function of drying time at various air temperatures for Zero order model, ED (Experimental Data) and MD (Model Data)

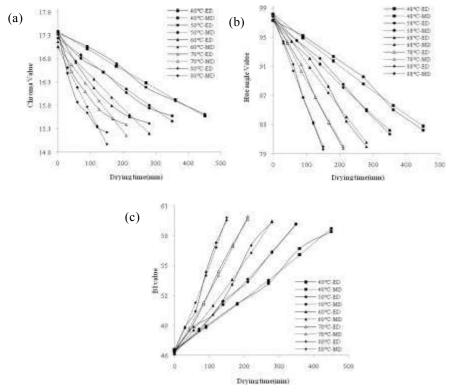


Fig. 4: Kinetics of change of chroma (a), hue angle (b), and Browning index (c) as a function of drying time at various air temperatures for First order model, ED (Experimental Data) and MD (Model Data)

Table 2: The estimated kinetic parameters and the statistical values of zero-order and first-order models for L, a, b and total colour change (ΔE) for various air temperatures

		Zero-order model			First-order model		
Temperature (°C)	Parameter	k(min ⁻¹)	C ₀	R^2	k (min ⁻¹)	C ₀	R ²
40	L	0.0134	42.1057	0.9969	0.0003	42.1696	0.9978
	a	0.0099	-2.3700	0.9923	0.0126	0.0079	0.3940
	b	0.0040	17.2995	0.9902	0.0002	17.3104	0.9878
	ΔE	0.0171	-0.0392	0.9978	0.0041	1.2871	0.9244
50	L	0.0180	42.0762	0.9969	0.0005	42.1476	0.9983
	а	0.0128	-2.2576	0.9976	0.0150	0.0124	0.4612
	b	0.0051	17.1648	0.9947	0.0003	17.1781	0.9950
	ΔE	0.0227	0.0814	0.9992	0.0051	1.4190	0.9231
60	L	0.0232	41.8799	0.9875	0.0006	41.9648	0.9916
	a	0.0179	-2.3370	0.9939	0.0174	0.0218	0.5363
	b	0.0073	17.0913	0.9783	0.0005	17.1137	0.9834
	ΔE	0.0301	0.2362	0.9940	0.0061	1.6535	0.9046
70	L	0.0312	41.7252	0.9771	0.0008	41.8220	0.9839
	а	0.0241	-2.2619	0.9981	0.0214	0.0330	0.5618
	b	0.0095	17.0043	0.9655	0.0006	17.0271	0.9715
	ΔE	0.0405	0.4439	0.9885	0.0077	1.8592	0.8870
80	L	0.0452	41.5990	0.9752	0.0012	41.7019	0.9819
	a	0.0337	-2.2619	0.9981	0.0316	0.0271	0.6131
	b	0.0144	16.9705	0.9532	0.0009	16.9982	0.9606
	ΔE	0.0580	0.5210	0.9866	0.0106	1.9519	0.8870

Table 3: The estimated kinetic parameters and the statistical values of zero-order and first-order models for chroma, hue angle and Browning index for various air temperatures

Temperature (°C)	Parameter	Zero-order model			First-order model		
		k(min ⁻¹)	C_0	R ²	k (min ⁻¹)	C ₀	R ²
40	Chroma	0.0040	17.3744	0.9925	0.0002	17.3879	0.9929
	Hue angle	0.0345	98.0629	0.9882	0.0004	98.1984	0.9834
	BI	0.0270	46.4175	0.9938	0.0005	46.6101	0.9936
50	Chroma	0.0051	17.2272	0.9817	0.0003	17.2430	0.9850
	Hue angle	0.0450	97.7301	0.9949	0.0005	97.8816	0.9912
	BI	0.0366	46.1394	0.9966	0.0007	46.3419	0.9983
60	Chroma	0.0070	17.1391	0.9331	0.0004	17.1637	0.9418
	Hue angle	0.0634	98.0560	0.9893	0.0007	98.2387	0.9840
	BI	0.0473	45.9792	0.9804	0.0009	46.1750	0.9856
70	Chroma	0.0090	17.0496	0.9125	0.0006	17.0742	0.9218
	Hue angle	0.0859	97.8174	0.9966	0.0010	98.0315	0.9939
	BI	0.0651	46.0440	0.9968	0.0012	46.2852	0.9969
80	Chroma	0.0137	17.0153	0.8996	0.0009	17.0450	0.9103
	Hue angle	0.1210	97.8473	0.9963	0.0014	98.0623	0.9934
	BI	0.0901	46.0785	0.9880	0.0017	46.3008	0.9902

model was better for a and total colour change (ΔE) values of kiwifruits [23], pineapple [21] and sunflower seed oil [18].

Chroma, Hue Angle and Browning Index: Chroma, hue angle and Browning index were calculated by using Eqs. (4)–(6) and the results are illustrated in Fig. 5a-d. The values of chroma and hue angle decreased as a function

of drying time (Fig. 3a, 3c). The hue angle value corresponds to whether the object is red, orange, yellow, green, blue, or violet. The initial hue angle of kiwifruit was about 97°, which represents a colour in the very slightly green-predominantly yellow region (hue angle between 90° and 180°) of the colour solid dimensions. Upon heating, the hue angle decreased [22], shifting towards the slightly more reddish yellow region (hue angle less

than 90°). The chroma closely followed the b values. On the other hand, Browning index was direct proportional to time drying (Fig. 3c). In modeling studies (Fig. 3, 4), chroma and Browning index data calculated were accurately fitted to a first-order kinetic model with high value for coefficients of determination R² (Table 3). On the other hand, the data of hue angle followed a zero-order kinetic model. The results obtained were in agreement with the study published in literature by Fernando Reyes and Cisneros-Zevallos [20] for purple- and red-flesh potatoes and it has been stated that the first-order kinetic model was better for chroma and zero-order kinetic model was better for hue angle. The kinetic rate constants of chroma, hue angle and Browning index increased as the sample amount decreased. The kinetic rate constant for chroma increased from 0.0002 to 0.0009 min⁻¹, for hue angle from 0.0345 to 0.1210 min⁻¹ and for Browning index from 0.0005 to 0.0017 min⁻¹ as the sample amount decreased (Table 3).

CONCLUSION

The colour change of kiwifruit slices using the L, aand b system totally explained the real behavior of kiwifruit samples undergoing hot air drying. The final values of L, a, b, total colour change (ΔE), chroma and hue angle were influenced by hot air drying. The values of Browning index showed that hot air drying caused more brown compound(s). This result was supported by the increase in a value. The zero-order and first-order kinetic models were used to explain the colour change kinetics and it was observed that L, b, chroma and Browning index were fitted to a first-order kinetic model. On the other hand, a, total colour change (ΔE) and hue angle followed a zero order kinetic model. The a, total colour change (ΔE) and Browning index increased; on the other hand, L, b, chroma and hue angle decreased when the air temperature was increased.

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