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Mass and color kinetics of foamed and non foamed grape concentrate during convective drying process: A comparative study

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Experiments were conducted on drying of grape concentrate to form leather by using convective and foam mat drying process. Mass and color degradation kinetics of both non foamed and foamed grape concentrate were studied at selected temperatures (55, 65 and 75°C) at constant drying bed thickness of 5 mm. The results indicated that the drying took place in falling rate period where as higher drying rate was observed for foamed grape concentrate when compared with non foamed grape concentrate. The E_a values for foamed and non foamed grape concentrate for 5 mm was 36.35 and 29.10 kJ/mole, respectively. Two term exponential model was found to be the best fitted for drying data of foamed and non foamed grape concentrate. In order to explain the color degradation kinetics for various color parameters, the zero order was adjudged as the best fitted models for 'a', ΔE, 'hue angle' and first order model for 'L', 'b' 'Chroma'. Hue and b values, based on activation energy, were the most sensitive measures of color change for the temperature range of 55 to 75°C.

Key words: Grapes, thermal degradation kinetics, color degradation kinetics.

INTRODUCTION

Grape, *Vitis vinifera,* belongs to *Vitaceae* family, is one of the most important fruits consumed by human beings since ancient times. Grape is cultivated differently all over the world such as Europe, Asia, America and Africa; mainly the most considerable countries are America, Greece, Turkey, Australia and Iran. The major varieties of grapes grown in India are Thomson Seedless, Sonaka, Anab-e-Shahi, Perlette, Bangalore blue, Pusa seedless, Beauty seedless etc (Anonymous, 2013). Grapes are rich in antioxidants and can be eaten raw or used for making jam, juice, jelly, vinegar, drugs, wine, grape seed extracts, raisins, and grapes seed oil (Shikhamany, 2007). Approximately 71% of world grape production is used for wine, 27% as fresh fruit and 2% as dried fruit. In India, more than 70% of the total production is harvested in March to April, but as cold storage facilities are currently inadequate, there are frequent market gluts.

In order to minimize the post harvest losses of grapes, an exhaustive study on utilization of grapes in form of grape leather was undertaken. High quality value added

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product grape leather was developed with effective methods like simple convective drying and foam mat drying process was undertaken. Foam-mat drying is a process by which a liquid or semi-liquid is whipped to form a stable foam, and subsequently dehydrated by thermal means. The foaming agent egg albumen is used which increases the foam structure and also increases the nutritive value as it contains higher protein content. Foam mat drying which leads to increase of drying rate and significant reduction in drying time; improved the sensory, nutritional and functional properties of the product. The foam mat dried products are highly stabile against deteriorative microbial, chemical and biochemical reactions.

Prediction of drying curves, generally, the moisture content of the material at any time after it has been subjected to a constant relative humidity and temperature conditions are measured and correlated to the drying parameters (Karathanos and Belessiotis, 1999; Midilli et al., 2002; Togrul and Pehlivan, 2002). Among the wide range of mathematical models, thin layer drying models have been found wide application in drying process (Madamba et al., 1996). However, during processing, the food material exposed to temperatures that have an adverse effect on quality and making these products susceptible to color deterioration also (Barreiro et al., 1997; Lozano and Ibarz, 1997; Avila and Silva, 1999).

In view of scarce information on drying of grape concentrate, the present work aims at comparing the drying of foamed and non foamed grape concentrate in terms of process feasibility and drying kinetics to evaluate the following: (1) to study the drying kinetics of grape concentrate for different drying air temperature (55, 65 and 75°C) using tray dryer; (2) to select a suitable thin layer drying model and calculate the effective moisture diffusivities of non foamed and foamed grape concentrate; (3) to study the kinetics of color degradation of grape concentrate for different drying air temperature (55, 65 and 75°C) for both foamed and non foamed grape concentrate during convective drying and selection of suitable color degradation kinetic model.

MATERIALS AND METHODS

Sample preparation

The grapes of variety

'Thomson seedless' was procured from the market and sorted based on the uniform size, color and physical damage. The grapes were crushed and filtered through muslin cloth to get the clear juice. The clarified grape juice was boiled with starch 4 g/100 g and glucose 6 g/100 g to 40°Brix of the juice with constant stirring. The density of grape concentrate 1.2 g/cm^3 was determined. For foam mat drying, the prepared grape concentrate was given the foaming treatment with 6% egg albumen concentration, 0.3% methyl cellulose whipped for 8 min at constant speed of 421 rpm for foam generation by incorporating air in it to increase surface area of grape concentrate.

Drying characteristics

Drying experiments were carried out in a commercial hot air tray dryer. Each sample of the foamed and non foamed grape concentrate was spread uniformly 5 mm thick in rectangular stainless steel tray. They were subjected to drying at different air temperature (55, 65 and 75°C) to final moisture content (12 ± 1% wb) for development of grape leather. Moisture content was recorded at an interval of 30 min using a digital balance. Experiments were conducted in triplicate. Thin layer drying equation was used to calculate the drying rate constants (Liu and Bakker, 1999).

Mathematical modeling of drying models

The semi-theoretical and empirical models used to describe the drying kinetics of sample are shown in Table 1. Drying curves were fitted to the experimental data using these moisture ratio equations. MR is the moisture ratio defined as M/ M_0: M is the moisture content at time t and M_0 is the initial moisture content, dry basis. However, moisture ratio (MR) was simplified to M/M_0 instead of (M-Me/ M_0-Me) as used by many authors (Diamante and Munro, 1993; Yaldiz et al., 2001; Pokharkar and Parsad, 2002).

Regression analysis was conducted to fit the mathematical models by the statistical package for social sciences (SPSS version 7.5). The goodness of fit of the selected mathematical models to the experimental data was evaluated with the correlation coefficient (R^2), the reduced chi-square (χ^2), mean bias error (MBE), root mean square error (RMSE) and mean deviation modulus (P%) and are defined by the Equations 1 from 5 (Gomez and Gomez, 1983):

$$R^2 = \frac{\sum_{i=1}^{n}\left(MR_i - MR_{pre,i}\right).\sum_{i=1}^{n}\left(MR_i - MR_{\exp,i}\right)}{\sqrt{\left[\sum_{i=1}^{n}\left(MR_i - MR_{pre,i}\right)^2\right].\left[\sum_{i=1}^{n}\left(MR_i - MR_{\exp,i}\right)^2\right]}} \quad (1)$$

$$\chi^2 = \frac{\sum_{i=1}^{n}\left(MR_{\exp,i} - MR_{pre,i}\right)^2}{N-n} \quad (2)$$

$$MBE = \frac{1}{N}\sum_{i=1}^{N}\left(MR_{pre,i} - MR_{\exp,i}\right) \quad (3)$$

$$RMBE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(MR_{pre,i} - MR_{\exp,i}\right)^2\right]^{\frac{1}{2}} \quad (4)$$

$$P(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{Experimental\ value - predicted\ value}{Experimental\ value}\right| \quad (5)$$

Where, $MR_{exp,\ i}$ and $MR_{pre,\ i}$ are experimental and predicted dimensionless moisture ratios, respectively, N is number of observations and z is number of constants.

The best model describing the drying characteristics of samples was chosen as the one with the highest coefficient of determination, the least mean relative percent error, reduced chi-square and RMSE (Sarsavadia et al., 1999; Madamba, 2002; Sacilik et al., 2006). However, although these statistical indictors generally provide a reasonable procedure to compare models, they do not

Table 1. List of drying models.

Model no	Model equation	Model name	References
1	$MR = exp(-kt)$	Newton	Lewis (1921)
2	$MR = exp(-kt^n)$	Page	Page (1949)
3	$MR = a\ exp(-kt) + b$	Logarithmic	Yagcioglu (1999)
4	$MR = a\ exp(-k_0t) + b\ exp(k_1t)$	Two term	Henderson (1974)
5	$MR = a\ exp(-kt) + (1 – a)exp(-kat)$	Two-term exponential	Sharaf-Eldeen et al. (1980)
6	$MR = a\ exp(-kt^n) + bt$	Midilli et al.	Midilli et al. (2002)

objectively indicate whether a model's estimates are statistically significant, that is, not significantly different from their measured counterparts.

Effective moisture diffusivity during drying

Fick's diffusion equation for particles with slab geometry was used for calculation of effective moisture diffusivity. The foamed tomato juice spread on tray was considered for slab geometry (Doymaz, 2009). The equation is expressed as Equation 6 (Crank, 1975):

$$MR = \frac{M_t}{M_0} = \frac{8}{\pi^2}\exp\left[-\frac{D_{eff}\pi^2.\mathrm{t}}{4\,\mathrm{L}^2}\right] \tag{6}$$

The slope (*ko*) was calculated by plotting Ln (MR) versus time (t) according to Equation (6) to determine the effective diffusivity for different temperatures.

$$In\left(MR\right) = In\left(\frac{8}{\pi^2}\right) - \left(\frac{D_{eff}.\pi^2}{4L^2}.t\right) \tag{7}$$

Activation energy

The effective diffusivity can be related with the drying air temperature by Arrheious model like:

$$D_{eff} = D_0 \exp\left(\frac{-E_a}{R_g T_{abs}}\right) \tag{8}$$

Where, D_0 is the constant in Arrhenius equation in m^2s^{-1}, E_a is the activation energy in kJ. mol^{-1}, T is the temperature in °C and R is the universal gas constant in kJ. $mol^{-1}K^{-1}$. Equation 8 can be rearranged in the form of:

$$In\left(D_{eff}\right) = In\left(D_0\right)\frac{-E_a}{R_g T_{abs}} \tag{9}$$

The activation energy can be calculated by plotting a curve between ln (D_{eff}) v/s $1/T_{abs}$.

Color kinetics

Visual color was evaluated using a Miniscan XE plus Hunter lab colorimeter (Hunter Associates Laboratory, Reston, VA, USA) in terms of Hunter L (lightness), a (redness and greenness) and b (yellowness and blueness). The instrument was calibrated with standard white and black tiles. The instrument was placed over the sample and Hunter L, a and b values were recorded. The color of the samples was recorded manually at regular intervals of 60 min throughout the drying process till the desired moisture content was achieved. In terms of three coordinates L, a and b, the data can be converted to total color difference (ΔE), Chroma and hue angle as mentioned below:

$$\text{Total color difference}\left(\Delta E\right) = \left[\left(L-L_0\right)^2 + \left(a-a_0\right)^2 + \left(b-b_0\right)^2\right]^{\frac{1}{2}} \tag{10}$$

$$Chroma = \sqrt{\mathrm{a}^2 + \mathrm{b}^2} \tag{11}$$

$$Hue\ \text{angle} = \tan^{-1}(b/a) \tag{12}$$

Where, L_0, a_0 and b_0 represents the respective readings of samples. Process modeling is of great significance in the analysis of design and optimization of drying in order to produce high quality (color) food products. Kinetic modeling of color (L, a, b, ΔE, Chroma and hue angle) values were fitted to the zero order (Equation 13) and first order (Equation 14) model. The best fitted model was selected on the basis of highest coefficient of determination R^2 (Mujumdar, 2000):

$$C = C_0 \pm k_0 t \tag{13}$$

$$C = C_1\, exp\ (\pm k_1 t) \tag{14}$$

Where, C_0 = measured value of color variables at time zero, C_1 = measured value of color variables at time t, t = drying time (minutes) k_0 = the rate constant for zero order equation and k_1 = the rate constant for first order equation.
Corresponding color reaction rate constant values of fitted model was used for finding activation energy by using Arrhenious model. The Arrhenious model was applied to describe the temperature dependence of color reaction rate constant:

$$\mathrm{k} = \mathrm{k_o}\exp\ (-\mathrm{E_a} / \mathrm{RT}) \tag{15}$$

Where, k_o = frequency factor (1/min), E_a= activation energy (kJ/mol), R = Universal Gas Constant (8.314J/kmol), T = Absolute

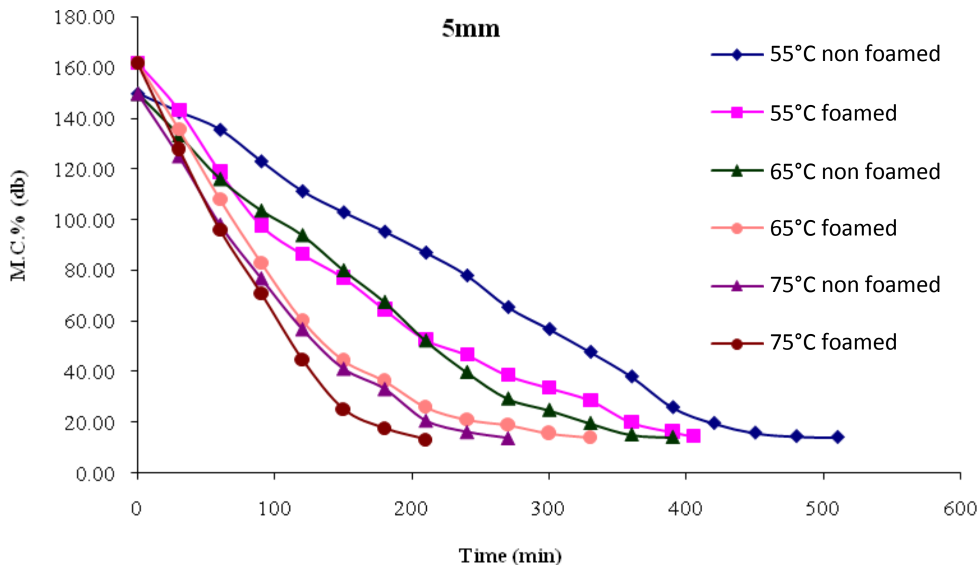

Figure 1. Comparison of drying curves for foamed and non foamed grape concentrate at different drying air temperature at constant drying bed thickness of 5 mm.

temperature (K).

RESULTS AND DISCUSSION

Drying characteristics

The prepared grape juice concentrate was dried by simple convective and foam mat drying with three replications. The effect of drying air temperature on non foamed and foamed grape concentrate is illustrated in Figure 1. Moisture content was decreased with increase in drying air temperature. The drying time was also reduced with incorporation of foaming agent and stabilizer. Simple convective drying took 510, 390 and 270 min at 55, 65 and 75°C temperature, respectively to reach at desired moisture content where as foam mat dried sample having 6% egg albumen, 0.3% methyl cellulose witnessed 405, 330 and 210 min of drying time at 55, 65 and 75°C temperature, respectively Thuwapanichayanan et al. (2008) dried the foamed banana at 60°C the time required for reducing their moisture content to about 0.03 kg/kg db was 120 and 300 min for the initial foam densities of 0.3 and 0.5 g/cm^3, respectively. It might be due to dense physical structure, high viscosity and bulk density with less exposed surface area of non foamed grape concentrate leading to slow moisture reduction (Rajkumar et al., 2007). Similar results were observed by Prakash et al. (2004) for carrots. Non-existence of a constant rate period was observed, the thin samples might be explained by the fact that at high temperatures the surface of products dries out very quickly (especially of the thin samples) and a partial barrier is generated to resist moisture movement freely (Maskan et al., 2002). It might also be due to addition of starch to grape juice for leather preparation resulting addition of additional hydrophilic interaction to the system (Maskan et al., 2002). Similar results were also reported for apple puree (Moyls, 1981), apple slabs (Roman et al., 1979) and banana slabs (Mowlah et al., 1983).

Table 2 showed that with increase in temperature, the drying rate was increased and also observed that the drying rate was higher at the beginning of drying than at the end of drying. This reduction in the drying rate at the end of drying might be due to reduction in moisture content as drying advances and also the rate of migration of moisture from inner surface to outer surface decreases at the final stage of drying and hence recorded lower drying rates (Rajkumar et al., 2007). It was also clear from Table 2 that the drying rate of the non-foamed pulps was lower than the drying rate of the foamed grape concentrate resulting reduced drying time. It might be due to less surface area exposed during drying. Similar results were reported for high moisture foods like tomato (Jayaraman et al., 1975) and papaya (Levi et al., 1983).

Effective moisture diffusivity for drying process

The effective diffusivity of the food material characterizes its intrinsic mass transport property of moisture which includes molecular diffusion, liquid diffusion, vapor diffusion, hydrodynamic flow and other possible mass transfer mechanics (Karathanos et al., 1990). The drying air temperature has a pronounced influence on the drying rate and as a consequence, markedly affects the value of the diffusion coefficient. The increase in temperature, the effective diffusivity increased due to the increase in the

Table 2. Drying characteristics of non-foamed and foamed grape concentrate.

Treatment	Temperature (°C)	Drying time (min)	Initial moisture content (% db)	Final moisture content (% db)	Initial drying rate	Final drying rate
	55	510 (10.00)		14.50	0.39	0.04
Non foamed grape concentrate	65	390 (5.00)	150	14.24	0.58	0.03
	75	270 (8.66)		14.18	0.82	0.08
	55	405 (4.00)		14.70	0.62	0.11
Foamed grape concentrate	65	330 (3.61)	162.01	14.16	0.87	0.05
	75	210 (6.56)		14.61	1.12	0.14

#Mean of N = 3 replications; values in parenthesis are the standard deviation based on N = 3 replications.

Table 3. Effective moisture diffusivity (m^2/sec) for non foamed and foamed grape concentrate.

Temperature (°C)	Non foamed grape concentrate		Foamed grape concentrate	
	$D_{eff} \times 10^{-10}$	R^2	$D_{eff} \times 10^{-10}$	R^2
55	3.10	0.95	9.8	0.99
65	3.96	0.98	13.3	0.99
75	5.66	0.99	21.1	0.99

vapor pressure inside the sample (Table 3). The foamed grape concentrate samples recorded higher value of D_{eff} in comparison to non foamed grape concentrate. This might be due to increase in air bubble formation resulting in increase moisture removal in foamed samples. These values are within the general range 10^{-9}–10^{-11} m^2/s for drying of food materials and comparable with the reported values of 1–3 ×10^{-11} m^2/s for air drying of apricots (Abdelhaq and Labuza, 1987), sun drying of differently treated grapes 10.4–9.9 × 10^{-11} m^2/s (Mahmutoglu et al., 1996), hot air drying of mulberry 2.32 × 10^{-10}–2.76 × 10^{-9} m^2/s (Maskan and Gogus, 1998) and hot air drying at 60°C of banana slices 8.33 × 10^{-10} m^2/s (Mowlah et al., 1983).

Activation energy for drying

The dependence of effective moisture diffusivity on drying air temperature was obtained by Arrhenius equation. The activation energy was calculated by plotting ln(D_{eff}) vs the reciprocal of the absolute temperature (1/T) as presented in Figure 2 and a straight line with a negative slope is obtained which implies that the diffusivity of the samples decrease linearly with increase in (1/T) during convective dehydration. The activation energy along with the D_o and R^2 are presented in Table 4. The value of Ea shows the sensitivity of the diffusivity against temperature. In contrast to non foamed grape concentrate, the foamed grape concentrate has more E_a which comprises that the more moisture diffusivity. These values are in the range or close to the Ea values reported (15–40 kJ/mol) by Rizvi (1986) for various foods.

Fitting of drying curves

In order to evaluate the performance of convective models, the values of statistical parameters for all the experiment runs were compared and model coefficients for each model was calculated by using non-linear regression techniques of SPSS version 7.5. The best model chosen was one having the highest R^2 and the least (χ^2), mean bias error (MBE), root mean square error (RMSE) and P%. From the drying models, the drying rates

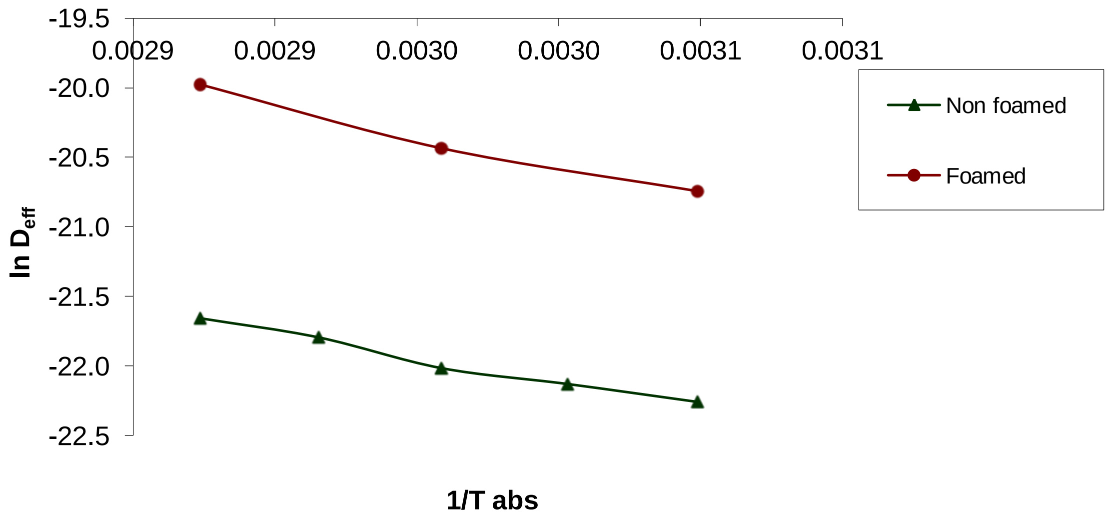

Figure 2. Effect of drying air temperature on average effective diffusivity.

Table 4. Activation energy and coefficients of Arrhenious model for grape concentrate of different temperature range (55 to 75°C).

Parameter	Ea (kJ/mole)	D_0 (m^2/s)	R2
Non Foamed grape concentrate	29.10	9.07488x10-6	0.99
Foamed grape concentrate	36.35	0.0005875	0.98

were determined. The result showed that the 'k' value increased with increase in drying air temperature. Also, the 'k' value for foamed pulp was higher than the non foamed pulp because the drying rate is higher in foamed pulps due to larger surface area exposed when compared to non-foamed grape concentrate (Table 5a and b).

From Table 5a and b) showed that all the models showed the higher R^2 value >0.90 except for the midilli model at higher drying temperature for both non foamed and foamed grape concentrate. It was also observed that the error term χ^2 value for the page model and the two term exponential have same value of χ^2 0.00001 followed by logarithmic model with χ^2 0.00004 for non foamed grape concentrate. For the foamed grape concentrate, the χ^2 value was 0.00002 found to be for two term exponential model followed by page model having the value is 0.00003 where as the minimum MBE and RMSE value was found for two term exponential model followed by page model. The same results were observed for foamed grape concentrate also. The minimum p% value was observed for two term exponential model for both concentrates. It is clear that the two terms exponential showed higher adequacy of fit between experimental and predicted data for both foamed and non foamed grape concentrate. The plot for predicted and experimental MR v/s time for the best fitted model, that is, two terms exponential is presented in Figure 3. The results were supported by the distribution of residuals (%) v/s MR showing random pattern for all the models (Figure 4). From Figure 4, it can be checked that for non foamed grape concentrate, the two term exponential model and page model have good distribution of residuals whereas, for foamed grape concentrate, the two term exponential model and logarithmic model have better distribution of residuals. Thus, two term exponential model was best fitted for describing the drying kinetics of both foamed and no foamed grape concentrate.

The values of the selected model coefficients (k, a) are reported in Table 2. The regression analysis was used to set up the relations between these parameters and the temperatures. Thus, the regression equations of these parameters against drying temperature, T (°C) for accepted model Fusing third order polynomial equation is as follow:

For non foamed grape concentrate,

$k = 1*10^{-5}T^2 - 0.001T + 0.0297 \quad R^2 = 1 \qquad a = 0.0004T^2 - 0.0581T + 4.147 \; R^2 = 1$

For foamed grape concentrate,

$k = 2*10^{-6}T^2 + 0.0001T - 0.0081 \; R^2 = 1 \qquad a = 9E\text{-}06T^2 + 0.0169T + 0.513 \; R2 = 1$

All the coefficients were dependent on drying air temperature. The coefficient 'k', and 'a' varied in nearly

Table 5a. Statistical results obtained from different thin layer drying models for non foamed grape concentrate.

Model No.	Temperature	Constants				R^2	CHI^2	MBE	RMSE	P%
Newton	55°C	K = 0.0042				0.9058	0.0114	0.0691	0.1037	22.1087
	65°C	K = 0.0058				0.9655	0.0047	0.0400	0.0658	12.1869
	75°C	K = 0.00881				0.9883	0.0016	0.0224	0.0382	7.3766
PAGE	55°C	K = 0.0003	n = 1.4259			0.9883	0.0011	0.0052	0.0318	10.7795
	65°C	K = 0.0016	n = 1.2219			0.9890	0.0008	0.0040	0.0269	7.2227
	75°C	K = 0.0031	n = 1.1987			0.9985	0.0001	-0.0006	0.0085	3.9218
LOG	55°C	K = 0.0010	a = 2.4643	b = -1.4333		0.9924	0.0006	-0.0035	0.0221	7.5072
	65°C	K = 0.0029	a = 1.3983	b = -0.3849		0.9945	0.0007	0.0000	0.0239	9.0360
	75°C	K = 0.0067	a = 1.1421	B = -0.1198		0.9970	0.0004	-0.0008	0.0170	6.2437
Two term	55°C	K_0 = 0.0037	K_1 = 0.0037	a = 0.5534	b = 0.5534	0.9539	0.0054	-0.0084	0.0649	25.9008
	65°C	K_0 = 0.0069	K_1 = 0.0069	a = 0.5328	b = 0.5328	0.9922	0.0114	0.0647	0.0904	19.1266
	75°C	K_0 = 0.0099	K_1 = 0.0099	a = 0.51	b = 0.51	0.9965	0.0006	-0.0031	0.0182	7.3050
Midilli	55°C	K = 0.0001	a = 0.9856	b = -0.0002	n = 1.4837	0.9954	0.0005	0.0001	0.0203	7.9323
	65°C	K = 0.0009	a = 0.9812	b = -0.0001	n = 1.2958	0.9963	0.0006	0.0000	0.0199	6.1743
	75°C	K = 0.5	a = 1.0	b = 0.0012	n = 1.2	0.3321	0.2178	0.1549	0.3615	87.8659
TWO TERM EXP	55°C	K = 0.0055	a = 2.0112			0.9864	0.0014	-0.0063	0.0351	13.6956
	65°C	K = 0.0074	a = 1.8510			0.9939	0.0007	-0.0041	0.0241	7.0253
	75°C	K = 0.0113	a = 1.7610			0.9995	0.0001	-0.0002	0.0084	3.7074

Table 5b. Statistical results obtained from different thin layer drying models for foamed grape concentrate.

Model No	Temperature (°C)	Constants		R^2	CHI^2	MBE	RMSE	P%
Newton	55	K = 0.0055		0.9879	0.0005	0.0130	0.0218	7.0082
	65°C	K = 0.0080		0.9874	0.0007	0.0039	0.0257	7.5839
	75°C	K = 0.0116		0.9778	0.0036	0.0328	0.0563	10.6578
PAGE	55°C	K = 0.0032	n = 1.0939	0.9949	0.0003	0.0002	0.0154	4.8749
	65°C	K = 0.0042	n = 1.1199	0.9909	0.0005	-0.0045	0.0202	9.4415
	75°C	K = 0.0031	n = 1.2580	0.9958	0.0003	0.0010	0.0151	5.4031

Table 5b. Contd.

LOG	55°C	K = 0.0047	a = 1.0608	b = -0.0581		0.9971	0.0002	-0.0001	0.0128	3.7606
	65°C	K = 0.0081	a = 1.0387	b = -0.0049		0.9942	0.0007	-0.0002	0.0222	8.2421
	75°C	K = 0.0073	a = 1.2297	b = -0.2147		0.9957	0.0008	0.0009	0.0226	10.6978
Two term	55°C	K = 0.0054	K = 0.0054	a = 0.5081	b = 0.5081	0.9960	0.0003	-0.0017	0.0158	6.3170
	65°C	K = 0.0082	K = 0.0082	a = 0.5195	b = 0.5157	0.9941	0.0007	-0.0005	0.0223	7.8256
	75°C	K = 0.0107	K = 0.0107	a = 0.5208	b = 0.5208	0.9855	0.0030	-0.0057	0.0388	16.2580
Midilli	55°C	K = 0.0062	a = 1.0100	b = -0.0002	n = 0.9516	0.9973	0.0002	0.0000	0.0124	2.9301
	65°C	K = 0.0022	a = 0.9991	b = 0.0002	n = 1.2831	0.9990	0.0001	-0.0002	0.0061	2.5570
	75°C	K = 0.5000	a = 1.0000	b = 0.0015	n = 1.2000	0.5576	0.2494	0.1464	0.3531	94.7746
Two term exp	55°C	K = 0.0062	a = 1.4672			0.9965	0.0002	-0.0004	0.0142	5.3448
	65°C	K = 0.0103	a = 1.6466			0.9957	0.0004	0.0046	0.0186	9.5142
	75°C	K = 0.0148	a = 1.8278			0.9977	0.0003	-0.0010	0.0154	5.2170

liner shape. The R^2 values for above equations were 1.00, thus the coefficients of selected model could be calculated using these equations to estimate moisture ratio of grape concentrate.

Color kinetics

The color parameters (*L, a* and *b*) for non foamed and foamed grape concentrate were recorded at regular intervals of time throughout the drying process and these values were also used for calculation of the total color change (Δ *E*), Chroma and hue angle. The color values kinetic data were fitted to zero and first-order kinetic model. The detailed description of the study is discussed below:

Effect of drying air temperature on color values L, a and b of grape concentrate

The effect of hot air temperature on color values (L, a and b) of non foamed and foamed grape concentrate was investigated for color degradation/formation during drying process. It was observed that the lightness of non foamed grape concentrate declined linearly thus clearly darkened with temperature and time. The initial 'L' value of grape concentrate 43.03 was reduced to 37.18, 37.42 and 36.02 with increase in temperature of 55, 65 and 75, respectively during drying process. For foamed grape concentrate, the lightness value was higher than non foaming grape concentrate due to the egg albumen was added for the foaming which already in white color. An increase the trend was also observed for 'L' values in foam mat drying process. The initial 'L' value of foamed grape concentrate was 57.08 which were higher than non foamed grape concentrate. All regressions explained <95% of the variation in lightness for zero and first order mathematical model for both grape concentrate. This lightness followed the first-order kinetic reaction (Figure 5). The rate constant for non foamed grape concentrate was increased with negative sign where as the rate constant for foamed grape concentrate was increased with temperature (Table 6) and it was consistent with previous works for double concentrated tomato paste (Barreiro et al., 1997), apple pulp, peach pulp and plum pulp (Lozano and Ibarz, 1997), peach puree (Garza et al., 1999) and pear puree (Ibarz et al., 1999).

For redness/greenness scale, initial 'a' values was 9.5 and 5.78 for non foamed and foamed grape concentrate, respectively. An increase in relative a values during heat treatment under various conditions was observed for both concentrates which might be due to non-enzymatic reaction resulting the browning of the product. The degradation of Hunter a values of grape concentrate was described by the Zero order kinetic model adequately over the entire temperature range. The estimated kinetic parameters of these models and the statistical values of coefficients of determination R^2 are

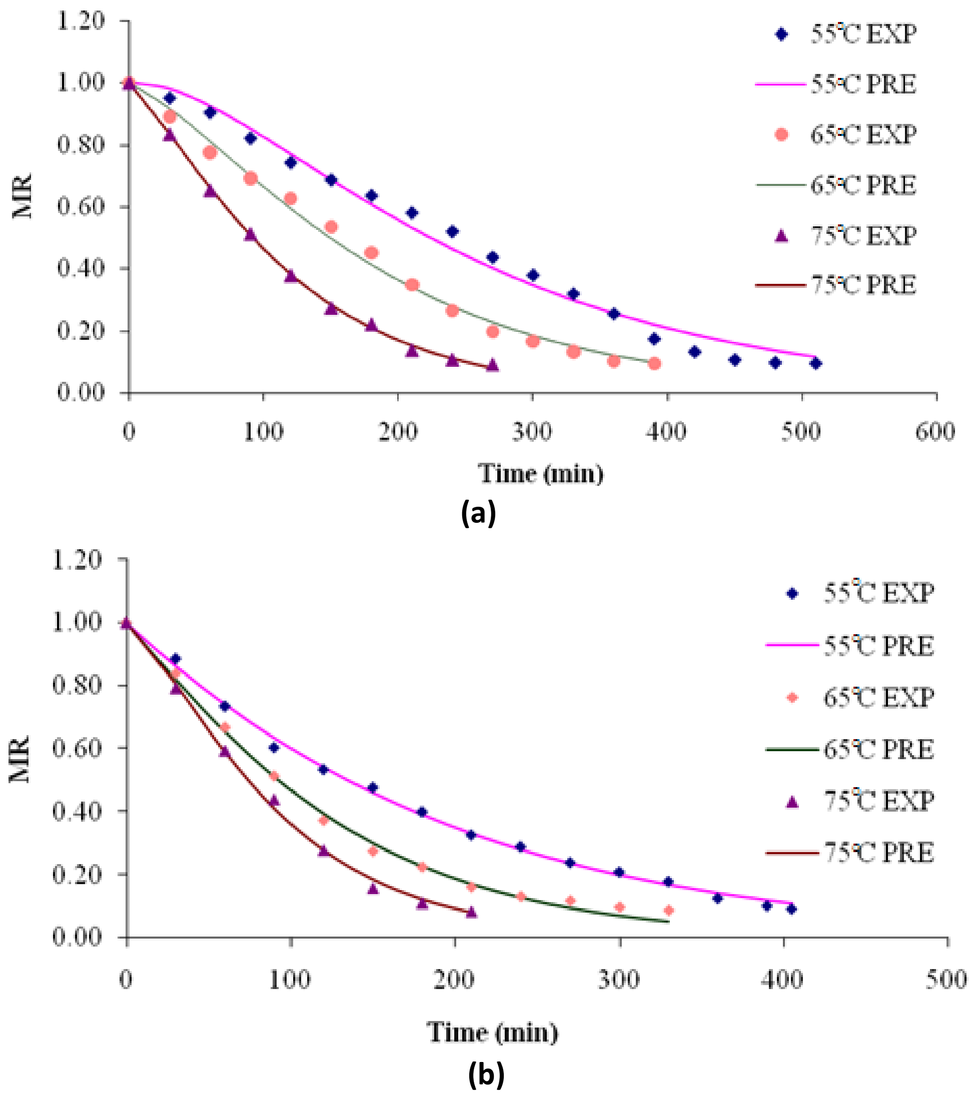

Figure 3. Fitting of two tem exponential model (a) non foamed grape concentrate (b) foamed grape concentrate.

represented in Table 6. The increasing trend for rate constant 'k' was observed for non foamed and foamed grape concentrate. Figure 6 shows the best fitted zero model with an increase in a values which is accentuated when the treatment temperature increases for grape concentrate color trend in the plane a and b.

For non foamed grape concentrate, the relative visual yellow color (b values) decreased during heat treatment while '*b'* value was increased for foamed grape concentrate because the temperature increased the color variation showed a clearer tendency, describing a shift from the yellow to red hues. It was observed that the first-order kinetic model fitted well to parameter b for both grape concentrate (Figure 7). The rate constant increased with the higher heating temperatures (Table 6). This could be explained by the assumption that high temperature accelerated the carotenoid isomerization which led to the loss of yellowness (Chen et al., 1995; Singleton et al., 1961), non-enzymatic Maillard browning and formation of brown pigments (Maskan, 2001; Yadollahinia, 2006).

Effect of drying air temperature on color values ΔE, Hue and Chroma of grape concentrate

Total color difference(s) increases with time and treatment temperature. The zero-order kinetic model fitted well to ΔE for both grapes concentrates (Figure 8). The same order of reaction was found by Pagliarini et al. (1990) in milk and by Barreiro et al. (1997) in double concentrated tomato paste. The estimated statistical

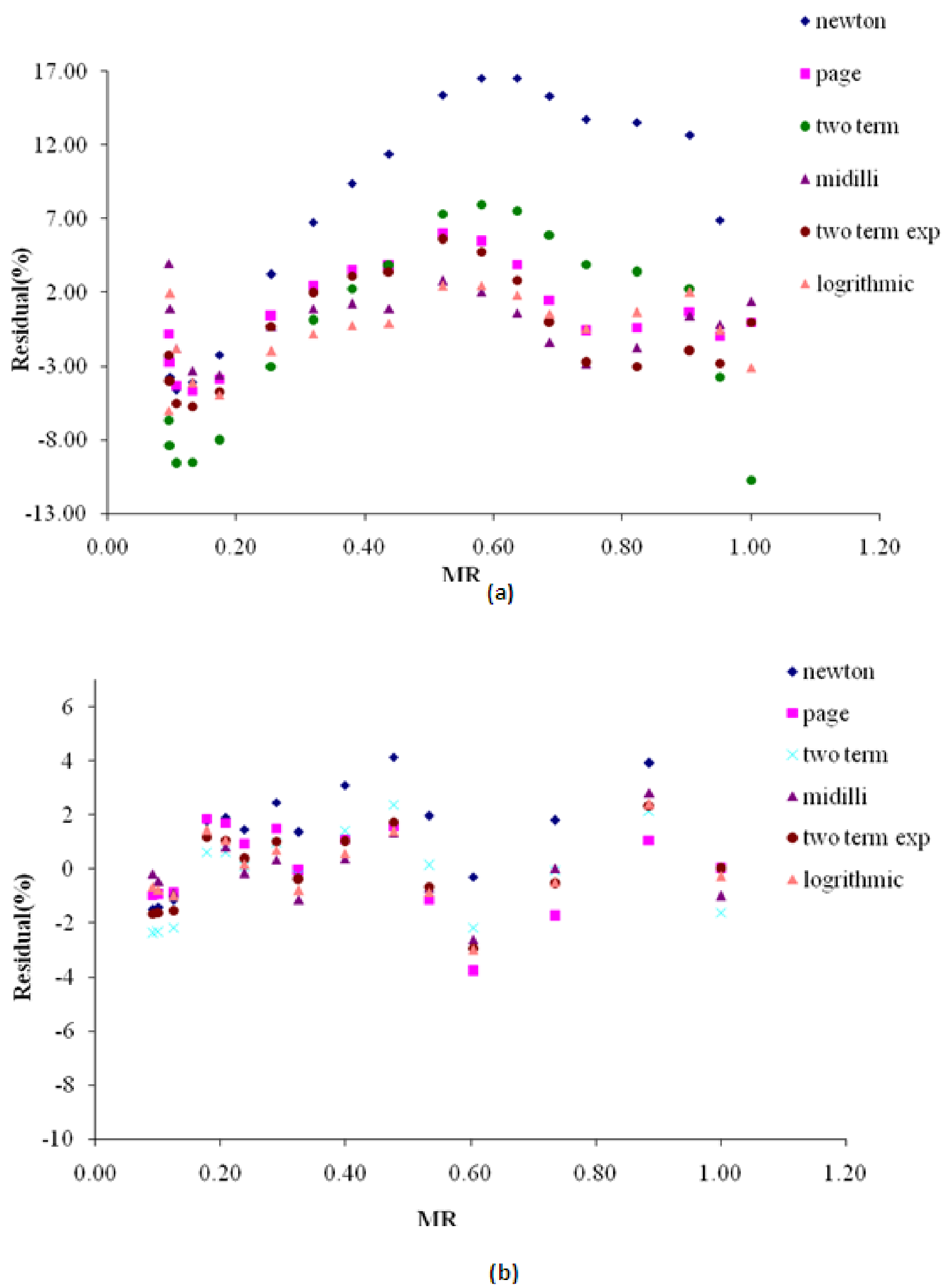

Figure 4. Model adequacy using plot of residuals at 55 °C at 5 mm for (a) non foamed grape concentrate (b) foamed grape concentrate.

coefficients and rate constants are presented in Table 6. In this current study, it was observed that the total color change (ΔE) was found minimum for foamed grape concentrate as compare to non foamed grape concentrate. Similarly, the rate constants of hunter values L, a, b simultaneously ΔE had lower values than the non foamed grape concentrate. This implies that with increase in air temperature, the degradation rate of color becomes faster for non foamed grape concentrate as a result of high energy transferred to the inside of food material and resulted that the better retention of color for foamed grape concentrates.

The hue angle decreased as a function of drying time in non foamed and foamed grape concentrate. It suggested reduction of green (when Hue >90°) to orange- red (when Hue < 90°) color (Waliszewaki et al., 1999). The zero order model was found as the best fitted model for grape concentrates (Figure 9).

The Chroma values was decreased for non foamed concentrate and increased for foamed grape concentrate

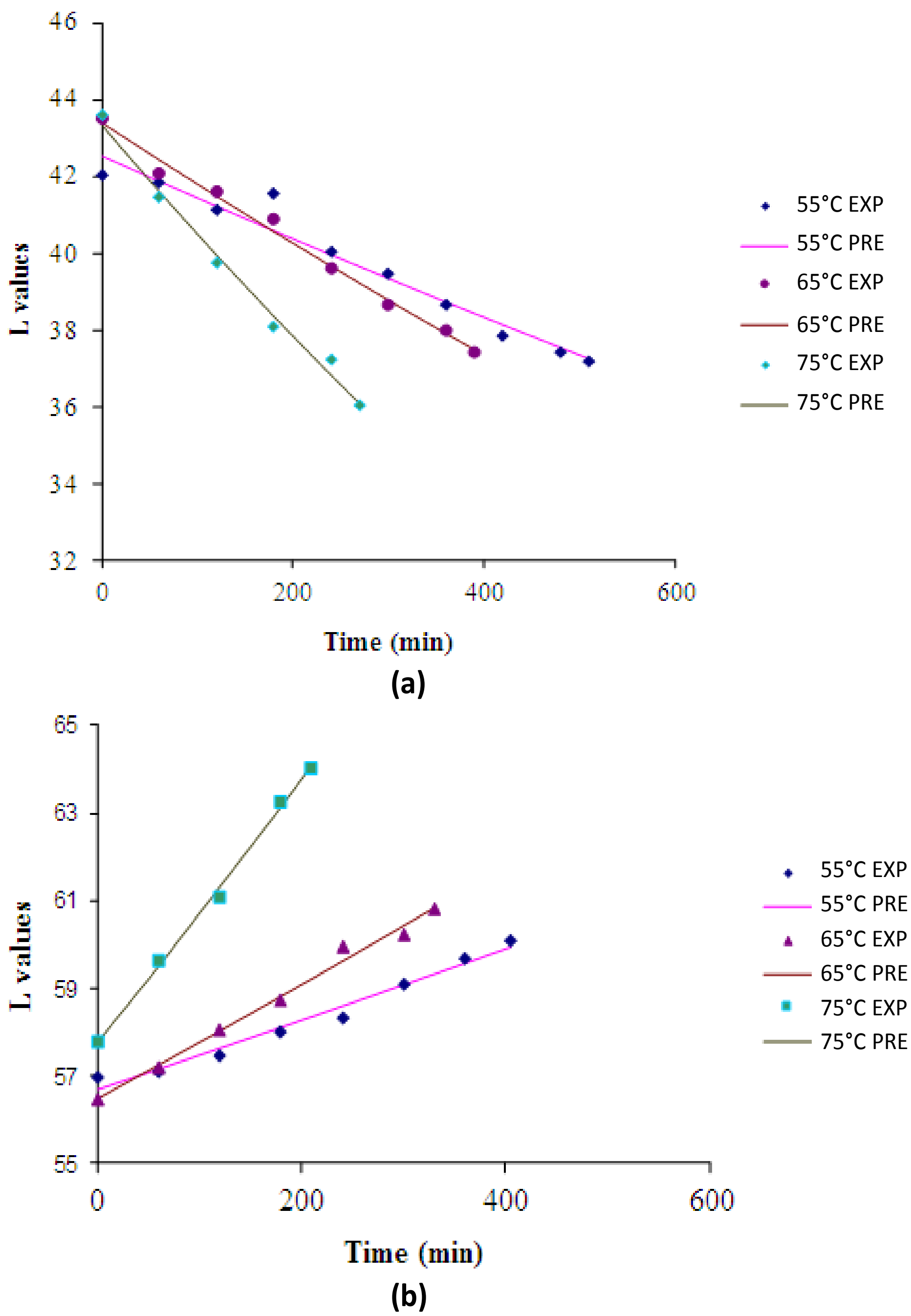

Figure 5. Kinetics of change in *L* value as a function of drying time at various air temperatures for first order model for (a) non foamed grape concentrate (b) foamed grape concentrate.

during drying process and closely followed b values (Figure 10). The Chroma values indicated degree of saturation of color and are proportional to strength of color. Little change was found in Chroma between fresh and dried samples of both type of grape concentrates. This indicated the stability of yellow color in dried samples. Several investigators (Fernando and Cisneros, 2007; Lee and Coates, 1999) reported similar observations.

The first order model was the best fitted one for Chroma values and estimated rate constants and R^2 were reported in Table 6.

Effects of temperature on the rate constant

Effect of temperature on color degradation rate constants

Table 6. Rates of color change in response to treatment time were described as zero and first-order reaction kinetics depending on the specific parameter.

Parameter	Model	Parameter	Non foamed grape concentrate			Foamed grape concentrate		
			C_1	k_1 (min^{-1})	R^2	C_1	k_1 (min^{-1})	R^2
L	N = 1	55	42.42	-0.0003	0.9562	56.68	0.0001	0.9765
		65	43.40	-0.0004	0.9904	56.48	0.0002	0.9904
		75	43.34	-0.0007	0.9910	57.79	0.0005	0.9972
			C_0	k_0 (min^{-1})	R^2	C_0	k_0 (min^{-1})	R^2
a	N = 0	55	9.49	0.0048	0.9666	5.29	0.0038	0.9970
		65	9.21	0.0126	0.9755	5.91	0.0076	0.9807
		75	10.05	0.0224	0.9734	6.06	0.0167	0.9168
			C_1	k_1 (min^{-1})	R^2	C_1	k_1 (min^{-1})	R^2
b	N = 1	55	20.59	-0.0002	0.9538	17.29	0.0002	0.9817
		65	20.81	-0.0005	0.9843	17.62	0.0003	0.9838
		75	20.48	-0.0012	0.9808	17.60	0.0009	0.9715
			C_0	k_0 (min^{-1})	R^2	C_0	k_0 (min^{-1})	R^2
E	N = 0	55	0.19	0.0119	0.9939	0.23	0.0094	0.9860
		65	0.08	0.0216	0.9938	0.07	0.0166	0.9939
		75	0.57	0.0409	0.9834	0.10	0.0382	0.9927
			C_0	k_0 (min^{-1})	R^2	C_0	k_0 (min^{-1})	R^2
Hue	N = 0	55	55.94	-0.0066	0.9787	57.14	-0.0008	0.9752
		65	56.77	-0.0216	0.9507	57.03	-0.0023	0.9495
		75	56.03	-0.0518	0.9823	56.97	-0.0050	0.7542
			C_1	k_1 (min^{-1})	R^2	C_1	k_1 (min^{-1})	R^2
Chroma	N = 1	55	22.64	-0.0001	0.9419	18.08	0.0002	0.9906
		65	22.58	-0.0001	0.9718	18.58	0.0004	0.9865
		75	22.55	-0.0002	0.9894	18.62	0.0010	0.9768

is shown in Figure 11. Dependence of the rate constant on temperature obeyed the Arrhenius relationship (R^2 > 0:90) (Equation (8)). The computed values of the activation energy (Ea) and frequency factor (k_0) are reported in Table 7.

Effects of temperature on the rate constant

Effect of temperature on color degradation rate constants is shown in Figure 11. Dependence of the rate constant on temperature obeyed the Arrhenius relationship (R^2 > 0:90) (Equation (8)). The computed values of the activation energy (Ea) and frequency factor (k_0) are reported in Table 7.

Higher activation energy signified greater heat

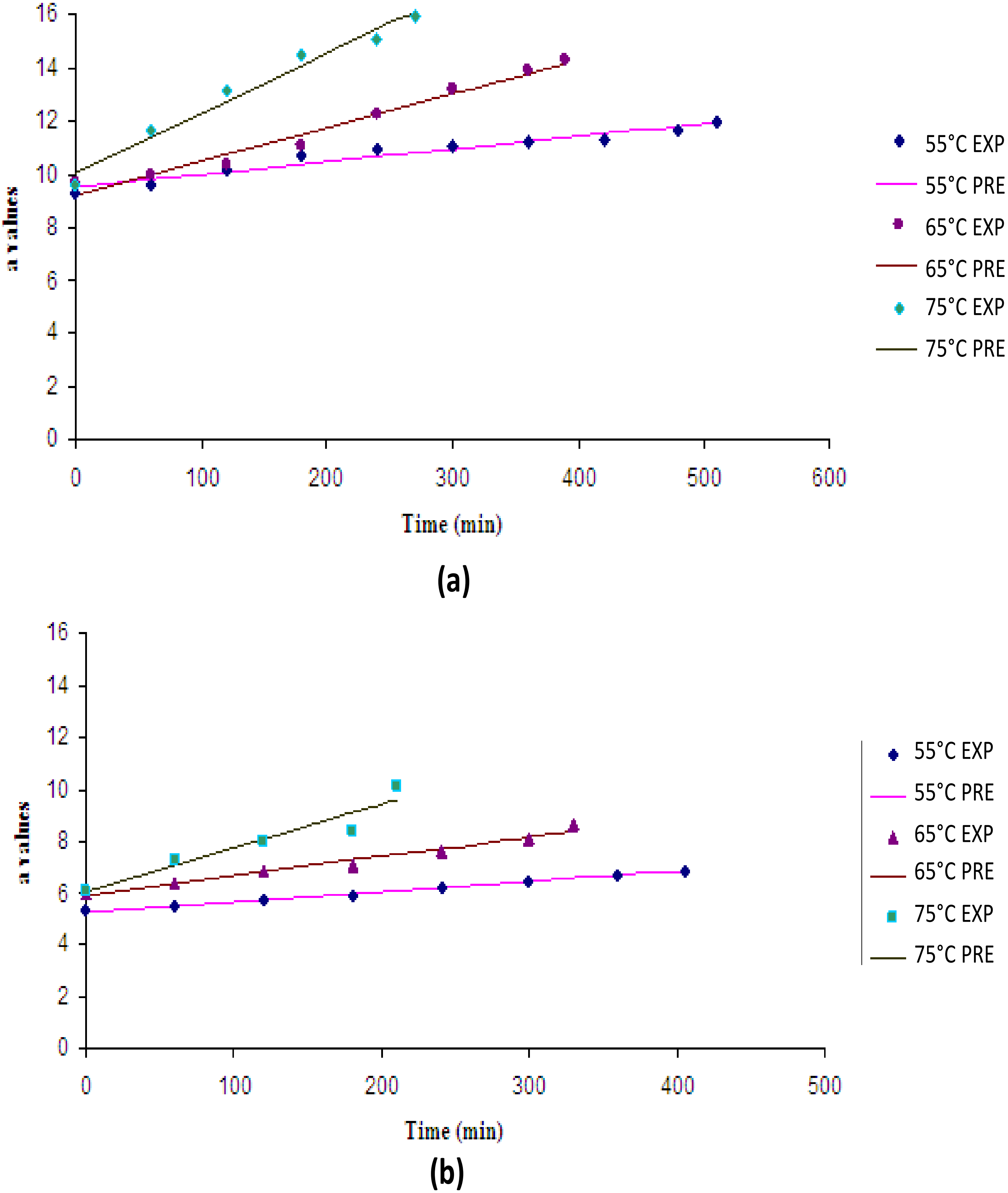

Figure 6. Kinetics of change in *a* value as a function of drying time at various air temperatures for zero order model for (a) non foamed grape concentrate (b) foamed grape concentrate.

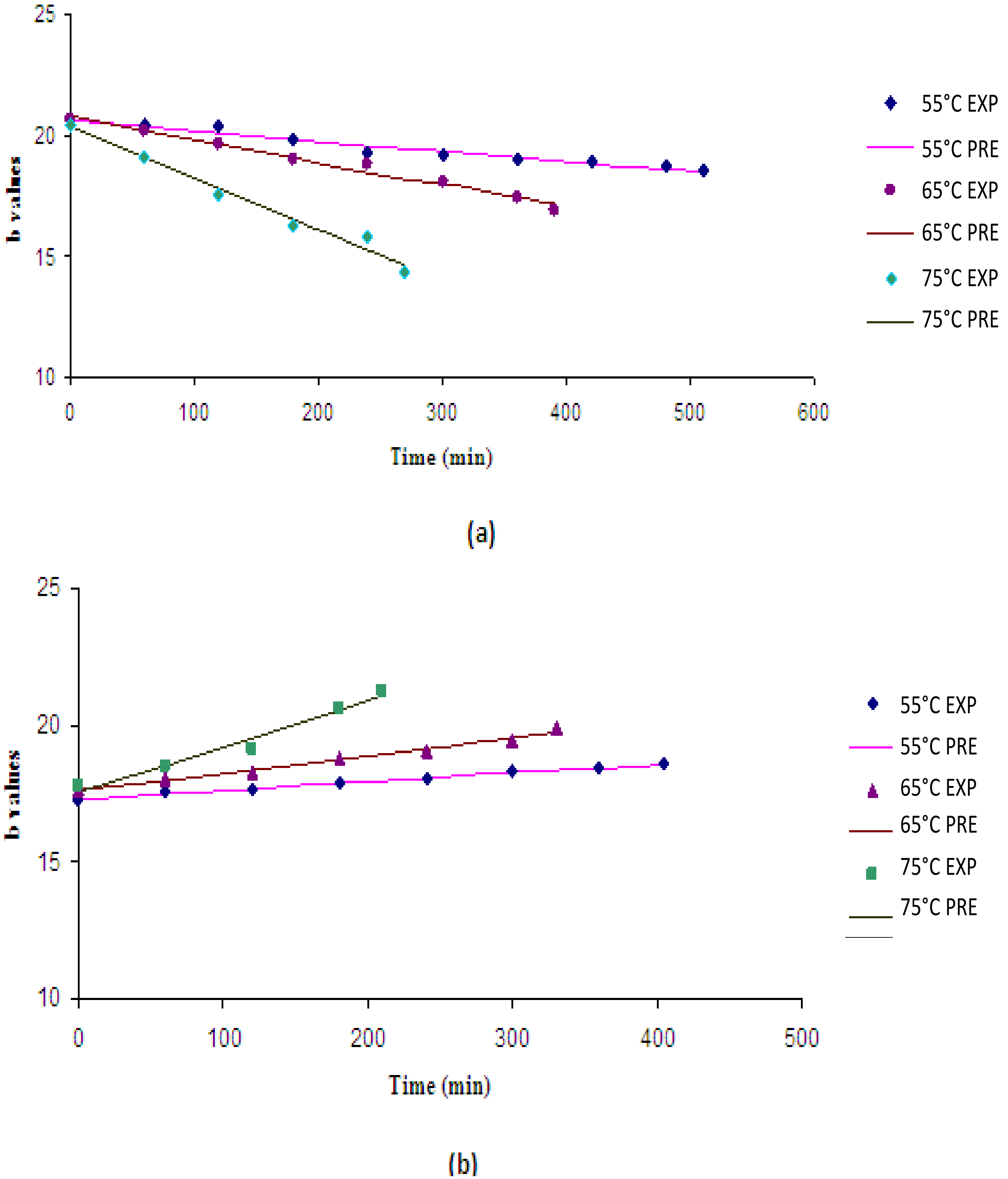

Figure 7. Kinetics of change in *b* value as a function of drying time at various air temperatures for first order model for (a) non foamed grape concentrate (b) foamed grape concentrate.

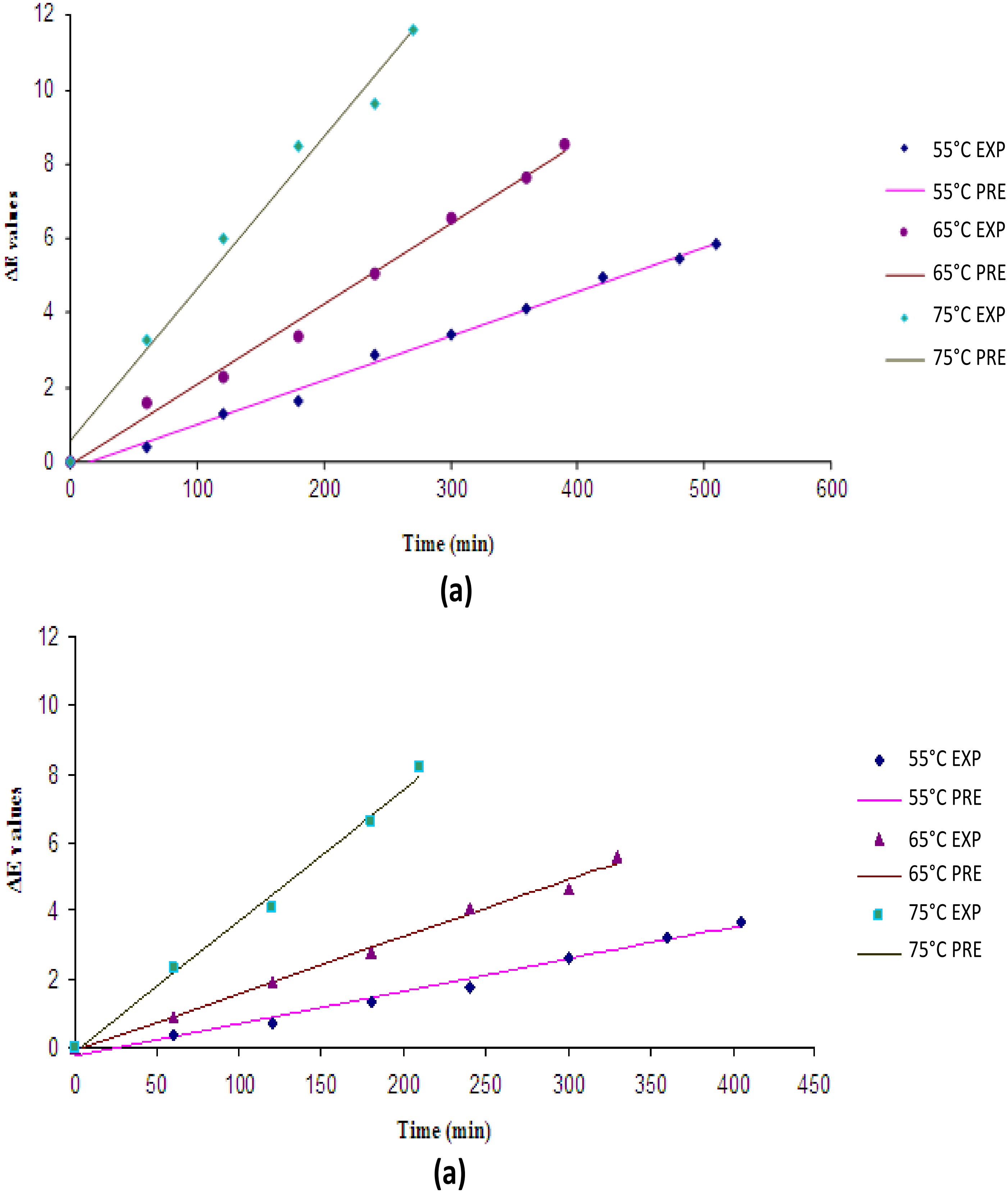

Figure 8. Kinetics of change of ΔE value as a function of drying time at various air temperatures for zero order model for (a) non foamed grape concentrate (b) foamed grape concentrate.

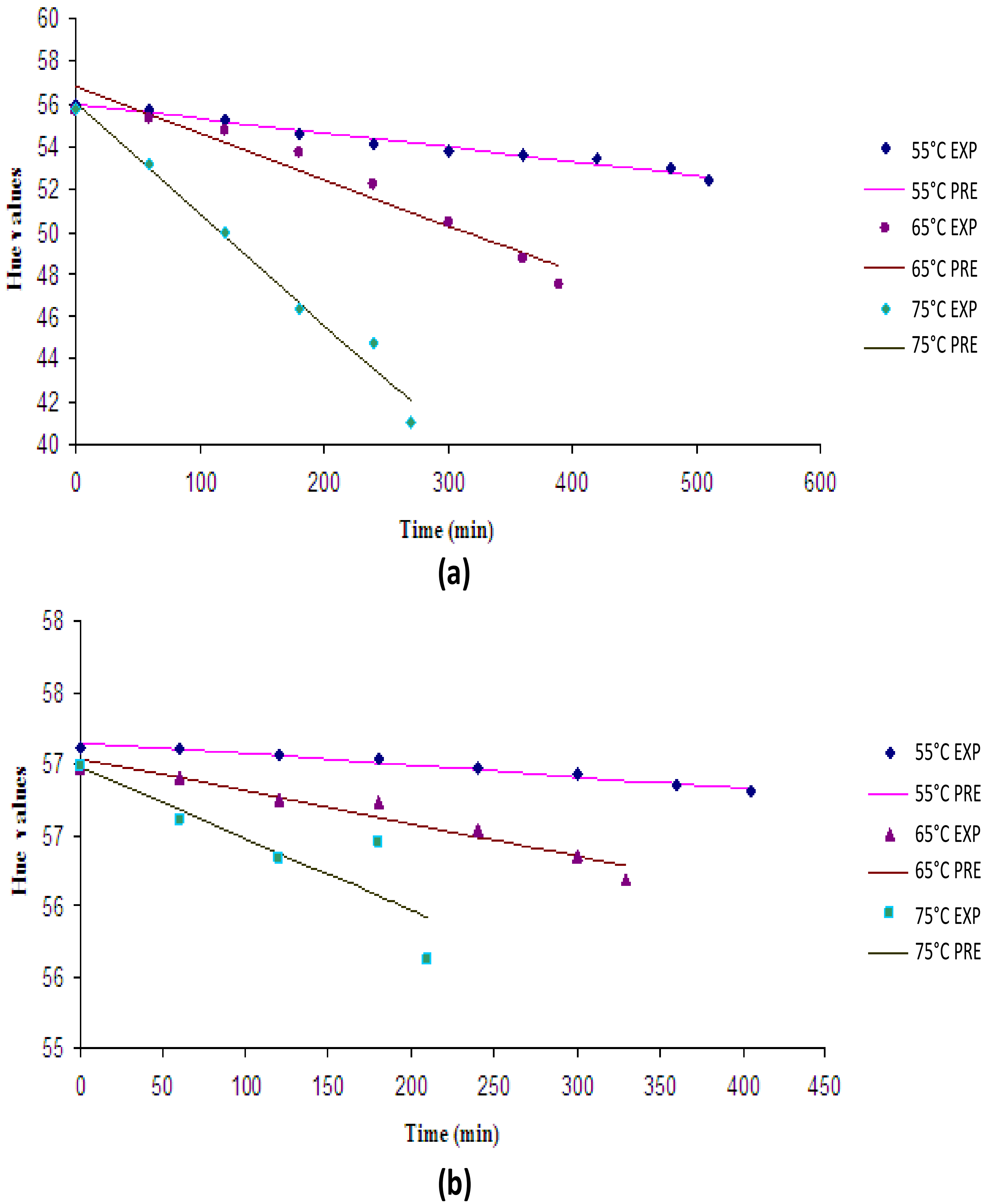

Figure 9. Kinetics of change in Hue value as a function of drying time at various air temperatures for zero order model for (a) non foamed grape concentrate (b) foamed grape concentrate.

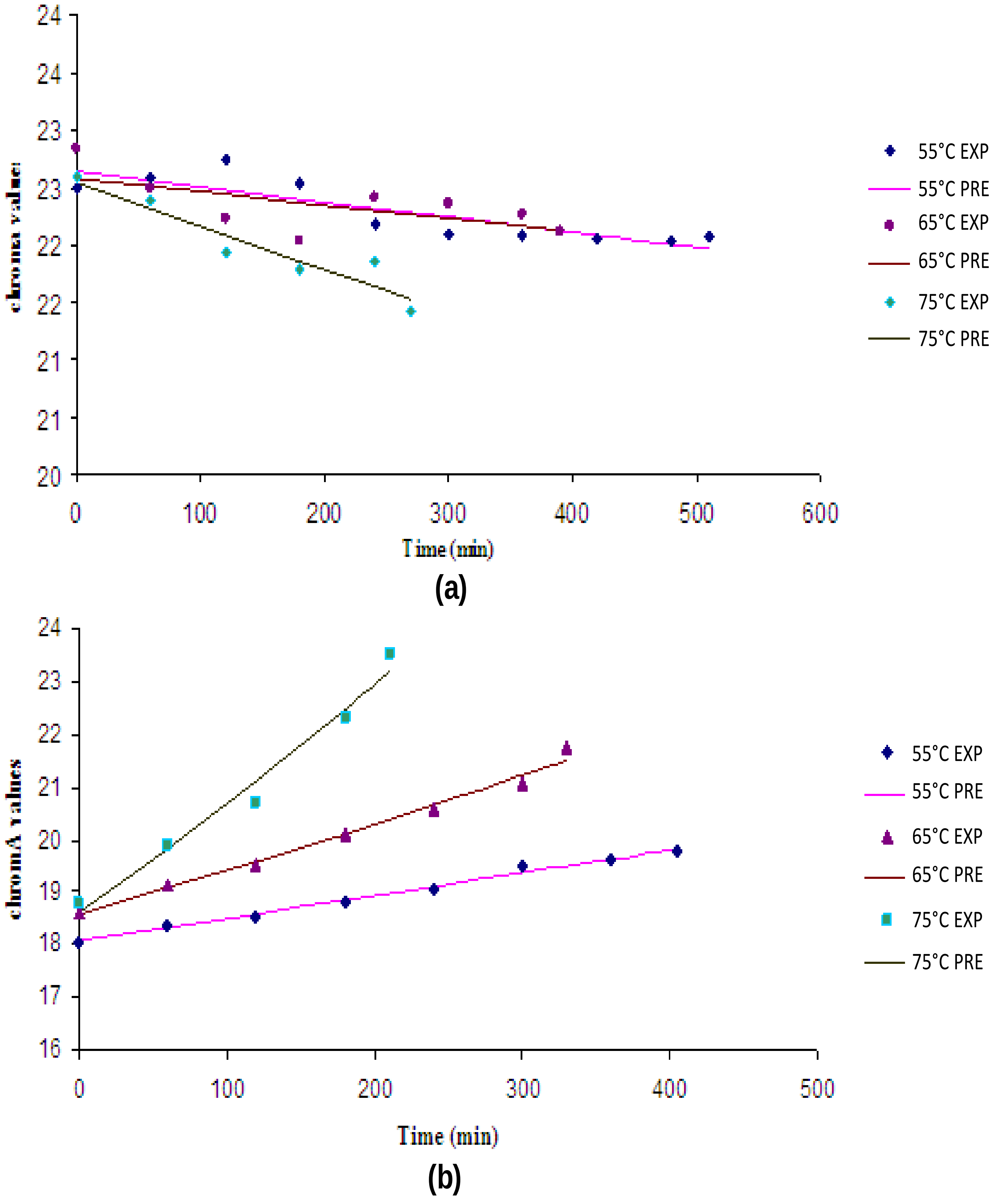

Figure 10. Kinetics of change in Chroma value as a function of drying time at various air temperatures for first order model for (a) non foamed grape concentrate (b) foamed grape concentrate.

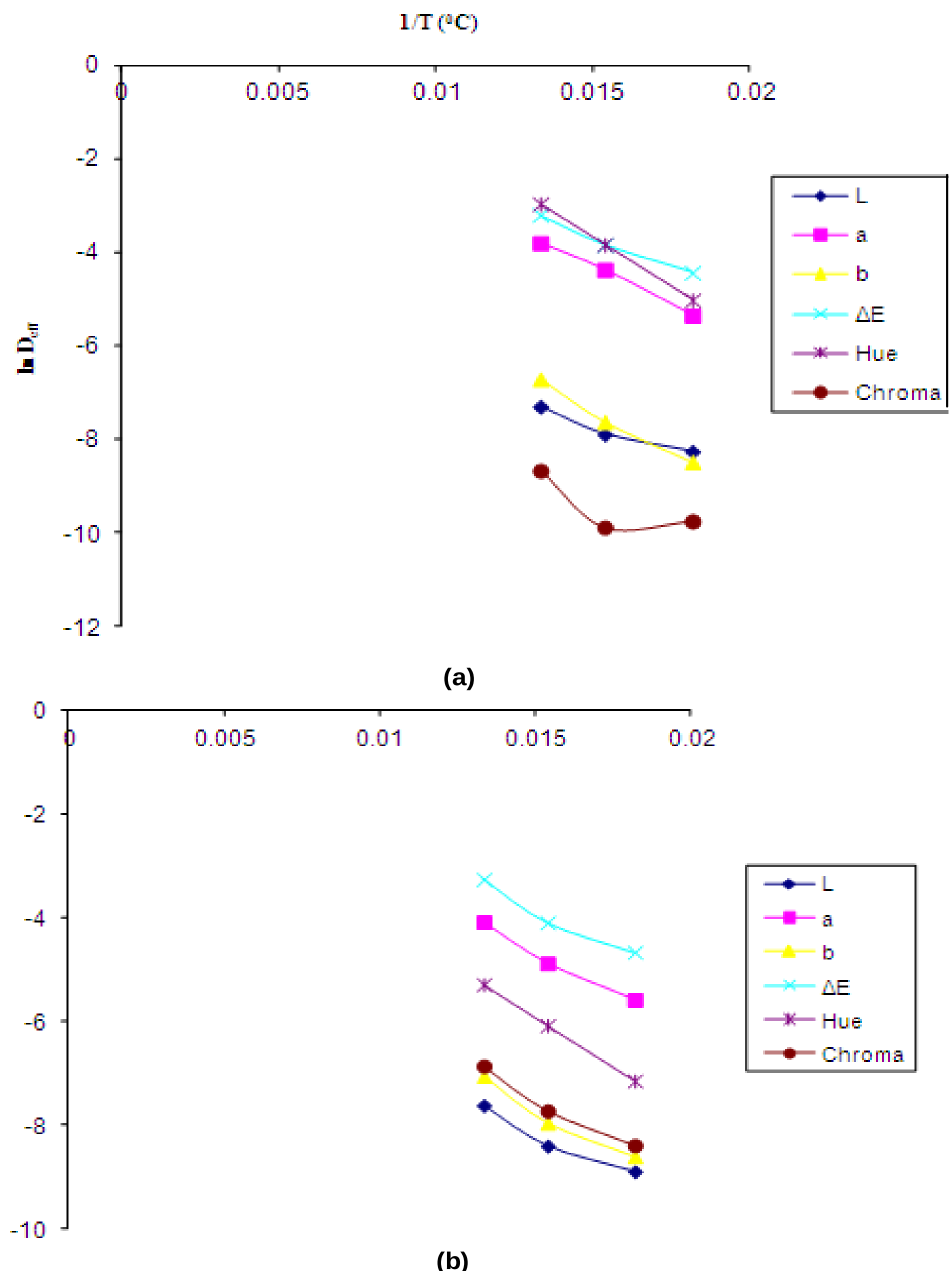

Figure 11. Effect of drying air temperature on average effective diffusivity over temperature range 55 to 75°C for (a) Non foamed grape concentrate (b) Foamed grape concentrate.

Table 7. Arrhenius equation parameters for different studied parameters in grape concentrate.

Parameter	Model	Non foamed grape concentrate			Foamed grape concentrate		
		k_0 (min^{-1})	E_a (kJ/mole)	R^2	k_0 (min^{-1})	E_a (kJ/mole)	R^2
L	n = 1	0.008	1613.249	0.951	0.014	2136.033	0.953
a	n = 0	1.666	2667.796	0.996	0.912	2532.694	0.984
b	n = 1	0.141	3000.356	0.988	0.052	2614.088	0.966
ΔE	n = 0	1.127	2095.710	0.988	1.550	2366.746	0.962
Hue	n = 0	14.863	3529.044	0.990	0.828	3181.435	0.990
Chroma	n = 1	0.002	1719.252	0.573	0.060	2580.250	0.973

sensitiveness of visual color degradation during thermal processing (Chutintrasri and Noomhorm, 2007). Comparing the activation energy between the parameters, the Hue followed by b values has higher activation energy for both type of grape concentrate. Pear puree (Ibarz et al., 1999) with a higher Ea value over the lower temperature range for yellowness (b value) was 102.1 KJ/mol was observed. Comparing the activation energy with grape concentrate, juice, the Ea for Hunter b of grape concentrate was much higher than that found for peach puree. This could be due to the fact that more pulp was contained than peach puree. The results from this study indicated that the measurement of color degradation in grape concentrate for greater temperature sensitivity of visual color during processing was Hue and b value based on their Ea estimates. The relationship between ln k and 1/T for Hue and b in the temperature range of 55 to 75°C could be represented by:

For Hue values

ln k = -424.47 (1/T) + 2.6989 R^2 = 0.99 (Non foamed grape concentrate)
ln k = -382.66 (1/T) - 0.189 R^2 = 0.99 (Foamed grape concentrate)

For b values

ln k = -360.88 (1/T) - 1.9561 R^2 = 0.9884 (Non foamed grape concentrate)
ln k = -314.42 (1/T) - 2.9547 R^2 = 0.9656 (Foamed grape concentrate)

Therefore, Hue and b value may be suggested as an on-line quality control parameter for processing of grape concentrate and its related products like grape leather to monitor processing effects on color change.

Conclusion

Based on the study, it was observed that the time taken for drying of foamed grape concentrate was less than non-foamed during convective drying process. The drying rate constant '*k*' value increased with increase drying air temperature for both grape concentrate. The more activation energy for foamed samples was observed during thermal processing. The retention of visual color may be measured by Hue and b values, where the rate constant increased with an increase in the temperature and thus can be selected as online quality parameter during the processing of the grape leather.

Nomenclature: dM/dT = drying rate, moisture loss per hour (% db /min); **Mi** = Moisture content (% db) of sample at time ti; **Mi+1** = Moisture content, (%db) of sample at time ti+1; **MR** = Moisture ratio; **D** = Effective moisture diffusivity (m^2/s); ***D0*** = constant in Arrhenius equation in m^2s^{-1}; ***Ea***= Activation energy in kJ.mol^{-1}; ***T*** = Temperature in °C; ***R*** = Universal gas constant in kJ.$mol^{-1}K^{-1}$; ***MRexp,*I** = Experimental dimensionless moisture ratios; **MRpre,*I*** = predicted dimensionless moisture ratios; ***n*** = Number of observations; ***z*** = Number of constants.

Conflict of Interests

The authors have not declared any conflict of interests.

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