Modeling of thin layer drying kinetics of grape juice concentrate and quality assessment of developed grape leather

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Abstract: Studies on modeling of thin layer drying kinetics of grape juice concentrate were conducted using pilot scale convective dryer. Experiments were conducted in temperature range of 55-75^{0}C and drying bed thickness of 3-7 mm, to attain desired moisture content (14±1% db). Different thin layer drying models like newton, page, logarithmic, two term, two term exponential and midilli models were fitted to the experimental data of convective dehydration and their adequacy of fit was investigated. All the samples witnessed falling rate period drying irrespective of the selected temperature and thickness. The effective moisture diffusivity and activation energy were found in range of 7.18-2.56 m^2/sec and 26.07-21.59 kJ/mole respectively for 3-7 mm drying bed thickness. Among the various models investigated, two term exponential model was found to be best fitted model for depicting the drying kinetics of grape juice concentrate. The quality properties such as total sugars, non enzymatic browning (NEB), protein, titrable acidity, texture (cutting force), color change, water activity and overall acceptability of dried grape leather were determined and data were analyzed as per ANOVA. The grape leather developed at 55^{0}C drying temperature witnessed maximum acceptability irrespective of the drying bed thickness.

Keywords: convective drying, drying kinetics, drying models, grapes, quality parameters

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1 Introduction

Grape *(Vitis vinifera)* is among the important fruits consumed by human beings since ancient (Ghasemzadeh et al., 2008). The major varieties of grapes grown in India are Thomson Seedless, Sonaka, Anab-e-Shahi, Perlette, Bangalore blue, Pusa seedless, Beauty seedless, etc (Anonymous, 2009). Grapes can be eaten raw or used for making jam, juice, jelly, vinegar, drugs, wine, grape seed extracts, raisins, and grape seed oil (Shikhamany, 2007). More than 70% of the total production is harvested in March-April. But as cold storage facilities are currently inadequate, there are frequent market gluts. The preservation/drying of grapes in the form of raisins or leather are a major profit making business. Traditionally, fruit puree is prepared by adding cane sugar or jaggery in the ratio of 1:2 or 1:4 to the puree, spreading the puree on bamboo mats and drying the puree in the sun (Tandra, 1979). The traditional process was improved by mechanizing the extraction, blending and drying of the puree in a hot air drier. Fruit leather is the term used for the products prepared by dehydration of fruit puree (Raab and Oehler, 1976).

Fruit leathers can be made from wide variety of fruits such as apple, apricot, banana, blackcurrant, cherry, grape, mango, peach, pear, pineapple, plum, raspberry, strawberry, papaya, sweet potato, chiku, jackfruit and durian (Lodge, 1981; Chan and Cavaletto, 1978; Che Man and Raya, 1983; Chauhan et al., 1993; Che Man and Taufik, 1995; Irwandi and Che Man, 1996).

Drying is one of the oldest methods of food preservation and it represents an important aspect of food processing. Food drying reduces the water activity of

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the foodstuffs in order to extend the shelf life thereby preventing its spoilage. This maintains the product quality thereby reducing losses and making them available at the time of shortage, off-season use and for places which are far away from production site (Santos and Silva, 2008). It is a complicated process involving simultaneous heat and mass transfer. The required amount of energy to dry a particular product depends on many factors, such as initial moisture content, desired final moisture content, drying air temperature, relative humidity and velocity (Karim and Hawlader, 2005).

Thin-layer drying models contributes to understanding of drying phenomenon of agricultural products which fall mainly into three categories, namely theoretical, semi-theoretical and empirical (Panchariya et al., 2002). The theoretical approach is concerned with diffusion or simultaneous heat and mass transfer equations whereas semi-theoretical approach is concerned with approximated theoretical equations. Empirical equations are easily applied to drying simulation as they depend only on experimental data (Afzal and Abe, 2000). The principle of modeling is based on a set of mathematical equations that can adequately characterize the system. In particular, the solution of these equations must allow prediction of the process parameters as a function of time at any point in the dryer based only on the initial conditions (Günhan et al., 2005). The objective of this research was to determine the thin-layer drying characteristics of grape juice concentrate, to observe the effect of drying process parameters such as drying air temperature and drying bed thickness, to calculate effective diffusivity and activation energy and to estimate the effect of drying process parameter on physical, chemical or sensory quality of developed product which will provide enough information to build a commercial impingement drying system for development of value added product i.e. grape leather.

2 Materials and methods

2.1 Preparation of grape juice concentrate

Grapes (var. Thomson seedless) were procured from the local fruit market of Ludhiana, Punjab, India and were sorted by its uniform size, color and physical damage. The grapes were thoroughly washed and wiped with a muslin cloth. The hot water blanching of grapes were carried out for 28 seconds for negative peroxidase test. The cleared juice (TSS 19-21^{0}B) was obtained by crushing and pressing in the juicer and filtered through the muslin cloth. The clarified grape juice was boiled for 3–5 min in order to inactivate enzymes to prevent color change. The total juice was divided into two fractions: first fraction contains 3/4 part of juice which was boiled to obtain concentrated juice and simultaneously glucose was added with constant stirring in order to raise the juice TSS to 40^{0}Brix. The scum formed on the surface of the juice during boiling was removed. Whereas, the left fraction (1/4 part of juice) was added with the wheat starch and mixed properly by stirring. Both the fractions were them mixed together and boiled again to raise the TSS of the juice to 40^{0}Brix. The starch and glucose was added at levels of 4 g/100 g and 6 g/100 g of the juice respectively. The density of developed grape juice concentrate was 1.2 g/cm^3.

2.2 Drying of grape concentrate

The convective dehydration of grape juice concentrate was carried out at different levels of thickness and temperatures by spreading on the trays. The thickness of the grape concentrate was selected based on the amount of grape concentrate in g/mm and was calculated as the product of tray area and grape concentrate density. The samples were convectively dehydrated in hot air tray drier to final moisture content (14±1 % db) to form end product, grape leather. The weight of the samples was recorded at regular intervals till the desired moisture content was achieved.

2.3 Experimental design

The grape concentrate of 40^{0}Brix and density 1.2 g/cm^3 was convectively dried for development of grape leather in tray drier by varying the process variables i.e. thickness (3-7 mm) and temperature (55-75^{0}C) and dried to desired moisture content (14±1 %db). The experiments were designed in completely randomized design (CRD). Three replications of each experimental combination were taken. The data were statistically analyzed using factorial experiment in completely randomized design by using computer software package

(Cheema and Singh, 1990). The least significant difference was calculated at 5% level of significance.

2.4 Drying characteristics for grape juice concentrate

The mechanism of drying rate is very useful in understanding the mechanism of moisture movement within the food as well as the transport of moisture from the food to the surrounding air. To study the drying behavior at different drying air temperature, percentage moisture content and drying rates were calculated. The drying curves (moisture content v/s time) were plotted to observe the effect of process variables. Corresponding to the drying curves, the drying rate curves (drying rate v/s moisture content) were also plotted.

The drying rates were calculated from the drying data by estimating the change in moisture content, which occurred in each consecutive interval and was calculated as given by Brooker et al. (1997).

$$\frac{dM}{dT}=\frac{(M_i-M_{i+1})}{(t_{i+1}-t_i)} \quad (1)$$

where, dM/dT = drying rate, moisture loss per hour (% db /min)

2.5 Mathematical modeling of drying kinetics

The semi-theoretical and empirical models were 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. Moisture ratio (MR) is the ratio of the moisture content at any given time to the initial moisture content (both relative to the EMC). 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).

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)

2.6 Effective moisture diffusivity during drying

The mechanism of moisture movement within a hygroscopic solid during the falling-rate period is represented by effective moisture diffusion phenomenon (which includes liquid diffusion, vapor diffusion, vaporization–condensation, hydrodynamic flow and other possible mass transfer mechanisms) and represents an overall mass transport property of water in the material. During drying, it can be assumed that diffusivity, explained with Fick's diffusion equation, is the only physical mechanism to transfer the water to surface (Dadali et al., 2007; Dincer and Dost, 1995; Wang et al., 2007). Effective moisture diffusivity, which is affected by composition, moisture content, temperature and porosity of the material, is used due to the limited information on the mechanism of moisture movement during drying and complexity of the process (Abe and Afzal, 1997). For the effective moisture diffusivity determination, grape concentrate thickness was assumed to be infinite slabs. When the plot of logarithm of moisture ratio (lnMR) versus drying time is linear, the moisture diffusivity assumes an independent function of moisture content. In this case, the change of moisture content can be described by the following equation (Crank, 1975):

$$MR=\frac{M_t-M_e}{M_0-M_e}=\frac{M_t}{M_0}=\frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n+1)}\exp\left[-\frac{(2n+1)^2\pi^2D\,t}{4L^2}\right] \quad (2)$$

where, MR = Moisture ratio; M_0 = Moisture content (% db) of sample at 0 time; M_t = Moisture content (%db) of sample at t time; M_e = Equilibrium Moisture content (% db) of sample.

Since the top surface of grape concentrate thickness was only exposed to hot air, the length (L), in Equation (1) was the thickness of the slabs. For long drying times; $n = 1$, then Equation (2) can be written as:

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

Further simplified to straight line equation

$$In(MR)=In\left(\frac{8}{\pi^2}\right)-\left(\frac{D_{eff}\cdot\pi^2}{4L^2}\cdot t\right) \quad (3)$$

The effective moisture diffusivity was calculated using the method of slopes. When logarithm of MR values v/s drying time was plotted in accordance with

Equation (3), straight lines were obtained at all temperatures and sample thickness was investigated. Linear regression analysis was employed to obtain values of diffusion coefficients for different drying conditions from the slope of the straight lines obtained.

2.7 Activation energy

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

$$D_{eff} = D_0 \exp\left(\frac{-E_a}{R_g T_{abs}}\right) \quad (4)$$

Equation (4) can be rearranged in the form of:

$$In(D_{eff}) = In(D_0)\frac{-E_a}{R_g T_{abs}} \quad (5)$$

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

2.8 Adequacy of fit of various empirical models

Modeling the drying behavior of different agricultural products often requires the statistical methods of regression and correlation analysis. Linear and nonlinear regression models are important tools to find the relationship between different variables, especially for which no established empirical relationship exists. Regression analysis was conducted to fit the mathematical models by the statistical package for social sciences (SPSS version 7.5). The determination coefficient (R^2) and plots of residuals were the primary criterions for selecting the best equation to define the drying curves. In addition to R^2, the goodness of fit was determined by various statistical parameters such as reduced chi-square (χ^2), means bias error (*MBE*), root mean square error (*RMSE*) and mean deviation modulus (*P*) and was defined by the given below equations (Gomez and Gomez, 1983).

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

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

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

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

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

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, 2003; Sacilik et al., 2006).

2.9 Quality analysis

Total sugars (%) were determined by using phenol-sulphric acid method (Dubois et al., 1956). Non enzymatic browning (NEB) as optical density (OD) of alcoholic extract of sample was determined by Ranganna (1986). Titrable acidity was analyzed by using reagents i.e. 90% alcohol, 0.1N NaOH solution and phenolphthalein indicator (AOAC, 2000). Protein content of the grape leather was estimated by the Kjeldhal method (AOAC 2000). Texture of the samples was determined with the help of Texture Analyzer TA-Hdi in terms of cutting force (g-f). The color of initial grape juice concentrate and developed grape leather was measured by using Miniscan XE plus Hunter lab colorimeter (Hunter Associates Laboratory, Inc., Reston, Va., U.S.A.) and total color change was determined by formulae as given below:

Total color difference (ΔE) = $[(L_0-L_1)^2+(a_0-a_1)^2+(b_0-b_1)^2]^{1/2}$

where, L_0, a_0 and b_0 represents the respective readings of initial sample and L_1, a_1 and b_1 represents the respective readings of final sample.

Water activity of develop product was measured by hygrometer (Hydro Lab). Overall acceptability of developed product was evaluated in terms of appearance, color, taste, texture, flavor and overall acceptability on a nine point hedonic scale. Semi-trained panels of ten judges were selected for the evaluation. Overall acceptability was evaluated as an average of color, appearance, taste, flavor and texture score and is expressed in percentage. Three replications of each test was conducted and the statistical analysis of the data was done at level of 5% significance by using univariate analysis of variance (UNI-ANOVA) in general linear model using Statistical Package for Social Sciences (SPSS, version 7.5).

3 Results and discussion

The grape juice concentrate was dried by varying drying bed thickness and drying air temperature using completely randomized design (CRD). Several drying parameters were evaluated based on the moisture kinetics throughout drying process in a laboratory tray dryer. The detailed description of the study is given below:

3.1 Effect of drying air temperature and thickness on drying behavior of grape juice concentrate

The initial moisture content of grape concentrate was 150% (db) and was reduced to final moisture content of 14±1% (db) for the moisture content at or below 15%, which not only restricts the growth of micro-organism but also reduces the reduction rate of deteriorative reactions significantly (Karel et al., 1994). The drying temperature, drying bed thickness and their interaction significantly affected the drying time at 5% level of significance (Table 2). In order to attain the desired moisture content of developed grape leather, the maximum drying time of 645 minutes (dried at 55^{0}C and 7 mm drying bed thickness) and minimum drying time of 210 minutes (dried at 75^{0}C and 3 mm drying bed thickness) was observed (Table 2). The drying time was decreased by 42% (on average) with increase in temperature irrespective of thickness (Figure 1). This might be due to the fact that high temperature causes larger water vapor pressure deficit, one of the driving forces for the outward moisture diffusion process, during drying (Prabhanjan et al., 1995). Similar behaviours were observed by Vergara et al. (1997) for osmotically dehydrated apples, Moyls (1981) for apple purees drying and Salgado et al. (1994) for sugar beet root and sugar beet pulp, Maskan and Gogus (1998) for mulberry.

It was also observed that with an increase in drying bed thickness of grape juice concentrate increases the drying time by almost 50% irrespective of drying air temperature. It might be due to the fact that with increase in bed thickness the distance for the moisture increases.

Table 2 Average drying time (minutes) required for development of grape leather

Temperature/^{0}C (A)	Drying bed thickness (B)				
	3 mm	4 mm	5 mm	6 mm	7 mm
55	330 (5.00)	420 (5.00)	510 (10.00)	555 (13.23)	645**(15.00)
60	300 (4.51)	360 (2.89)	425 (8.66)	525 (15.00)	615 (13.23)
65	270 (5.00)	315 (3.61)	390 (5.00)	450 (12.58)	525 (5.00)
70	240 (0.00)	285 (5.00)	315 (5.00)	375 (5.00)	450 (13.23)
75	210*(4.58)	240 (3.61)	270 (8.66)	330 (6.56)	375 (7.75)
CD (5%)	A= 6.16, B= 6.15, AB=13.17				

Note: #Mean of N = 3 replications; values in parenthesis are the standard deviation based on N = 3 replications; * Minimum drying time, ** Maximum drying time.

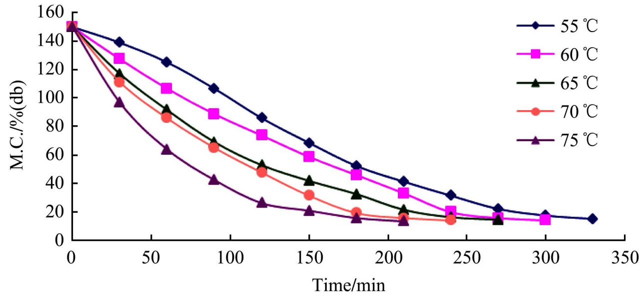

Figure 1 Effect of drying air temperature on drying time at different temperature at 3 mm drying bed thickness of grape juice concentrate

From Figure 2 and Figure 3, it can be seen that with advance in drying time, the moisture content showed reducing trend irrespective of drying air temperature and drying bed thickness. The drying time to remove first moisture was 55%, 60%, 67%, 63% and 71% at 3 mm thickness of grape concentrate at temperature 55^{0}C, 60^{0}C, 65^{0}C, 70^{0}C and 75^{0}C respectively of the corresponding total drying time, that is, 63% on the average. Similarly the time until the moisture up to 0.5 was 58%, 59%, 55% and 54% (on average) for 4, 5, 6 and 7 mm thickness of grape concentrate at temperature 55-75^{0}C.

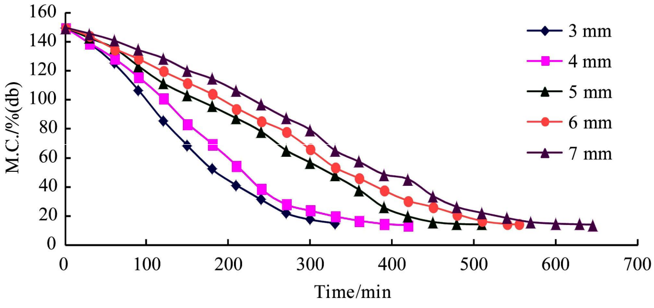

Figure 2 Effect of drying bed thickness of grape juice concentrate on drying time at drying temperature (55°C)

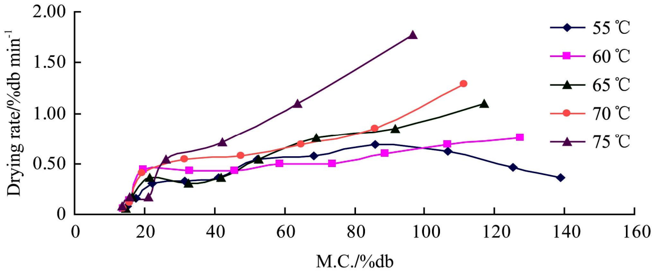

Figure 3 Drying rate curves for grape juice concentrate at constant thickness for different temperature

3.2 Analysis of drying rate

The drying rate is the function of temperature. The initial drying rate of grape juice concentrate at 55^0C for 3-7 mm drying bed thickness was 0.37, 0.36, 0.24, 0.20 and 0.14 %/min respectively which were reduced to 0.08. 0.03, 0.01, 0.02 and 0.02 %/min at the end of the drying process respectively. Similarly the drying rate was observed for temperature ranged from 60-75^0C. It is also clear from Figure 4 that the drying rate increased with the increase in drying air temperature irrespective of drying bed thickness. It was also observed that the drying rate was higher at the beginning of drying than at the end of drying process. This reduction in the drying rate at the end of drying process might be due to reduction in moisture content and also due to decrease in the rate of migration of moisture from inner surface to outer surface at the final stage of drying resulting in lower drying rates (Rajkumar et al., 2007).

Non-existence of a constant rate period was observed for all the samples irrespective of drying air temperature and drying bed thickness. Similar results were reported for apple puree (Moyls, 1981) and apple slabs (Roman et al., 1979) either at high temperatures. This 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 leatherier is generated to resist moisture movement freely (Maskan et al., 2002). Furthermore, addition of starch to grape juice during preparation of grape juice concentrates results addition of augmented hydrophilic interaction in the system (Maskan et al., 2002).

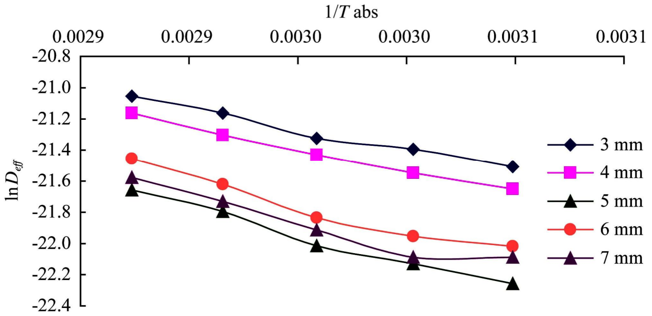

Figure 4 Effect of drying air temperature on average effective diffusivity

3.3 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 effective moisture diffusivity was calculated using the method of slopes. When logarithm of MR values vs drying time were plotted in accordance with Equation (2), straight lines were obtained at all temperatures and drying bed thickness. Linear regression analysis was employed to obtain values of diffusion coefficients for different drying conditions from the slope of the straight lines obtained. Values of D_{eff} for selected drying conditions along with correlation coefficient for grape juice concentrate are presented in Table 3.

Table 3 Average effective moisture diffusivity (m^2/sec) for grape juice concentrate

Temperature /°C	Drying bed thickness									
	3 mm		4 mm		5 mm		6 mm		7 mm	
	$D_{eff}\times10^{-10}$	R^2	$D_{eff}\times10^{-10}$	R^2	$D_{eff}\times10^{-10}$	R^2	$D_{eff}\times10^{-10}$	R^2	$D_{eff}\times10^{-10}$	R^2
55	4.56	0.98	3.96	0.98	3.10	0.95	2.74	0.96	2.56	0.96
60	5.11	0.98	4.38	0.96	3.53	0.96	2.92	0.97	2.56	0.94
65	5.48	0.99	4.93	0.99	3.96	0.98	3.29	0.94	3.04	0.97
70	6.45	0.99	5.60	0.97	4.93	0.98	4.08	0.97	3.65	0.96
75	7.18	0.98	6.45	0.99	5.66	0.99	4.81	0.99	4.26	0.98

Note: *Mean of $N=3$ replications.

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 effective diffusivity increased with the increase in temperature due to the increase in the vapor pressure inside the sample. These values are within the range 10^{-9}-10^{-11} m^2/sec for drying of food materials and comparable with the reported values of 1-3×10^{-11} m^2/sec for air drying of apricots (Abdelhaq and Labuza, 1987), sun drying of differently treated grapes 10.4-9.9×10^{-11} m^2/sec (Mahmutoglu et al., 1996) and hot air drying of mulberry 2.32×10^{-10}-2.76×10^{-9} m^2/sec (Maskan and Gogus, 1998).

3.4 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}) v/s the reciprocal of the absolute temperature (1/T) as presented in Figure 5 and a straight line with a negative slope is obtained which implies that the diffusivity of the samples decreases linearly with increase in (1/T) during convective dehydration. The activation energy along with the D_0 and R^2 is presented in Table 4. The value of E_a shows the sensitivity of the diffusivity against temperature. These values are in the range or close to the E_a values reported (15-40 kJ/mol) by Rizvi (1986) for various foods.

Table 4 Activation energy and coefficients of arrhenius model for grape juice concentrate for different temperature range (55-75^{o}C)

Drying bed thickness	E_a/kJ mole^{-1}	D_0/m^2 sec^{-1}×10^{-6}	R^2
3 mm	21.59	1.23802	0.98
4 mm	23.18	1.91844	0.99
5 mm	29.10	9.07488	0.99
6 mm	27.60	6.45923	0.96
7 mm	26.07	4.5929	0.94

3.5 Validation of various drying models for convective drying process

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 were determined. The result showed that the 'k' value decreased with increase in the drying bed thickness and air temperature irrespective of all models. All the models showed the higher R^2 value >0.90 except for the midilli model for drying bed thickness less than 5 mm layer of grape juice concentrate (R^2<0.70). The error terms χ^2, *MBE*, *RMSE* and *P*% were ranged from 0.00007-0.033249912, -0.49797-0.054074, 0.006251-0.148885 and 2.532404-55.29784 for all models at temperature 55-75^{0}C.

Further, the average of each error terms was done of all thickness at particular temperature. From that the error term χ^2 was varied from 0.000232-0.001088 for two tem exponential term, 0.00028-0.001082 for page model, 0.000681-0.001402 for log model, 0.002167-0.006151 for two term model and rest model have higher range. Among these models, the average value of χ^2 for logarithmic model (0.001025) was 0.8098 times higher than two term exponential model (0.00083). Similarly, the MBE value was found lower than -0.00028, 0.000399, 0.0042822 (average values) for two term exponential model, logarithmic model and page model respectively. The average RMSE value of logarithmic model (0.024514) was 0.918717 times higher than page model (0.024514). The minimum average *P*% was found for two term exponential model (7.813847) followed by page model (8.134548). Thus these were indicating that two term exponential model, logarithmic model and page model are fitted well to the experimental data. The same results were supported by the distribution of residuals (%) v/s *MR* showing random pattern for all the models (Figure 5). Thus among all these models, two term exponential model was the best one to predict the moisture transfer of grape juice concentrate owing to the lowest average values of χ^2 (0.00083), *MBE* (-0.00028) and *P*%(7.813847). The plot for predicted and experimental *MR* v/s time for the best fitted model i.e. two term exponential is presented in Figure 6. Similar results could be also obtained at other temperatures and thickness. Thus, the two term exponential model was found to be the best fitted model for describing the drying kinetics of grape juice concentrate for development of grape leather. Regression coefficients and statistical parameters of best fitted convective drying models are listed in Table 5.

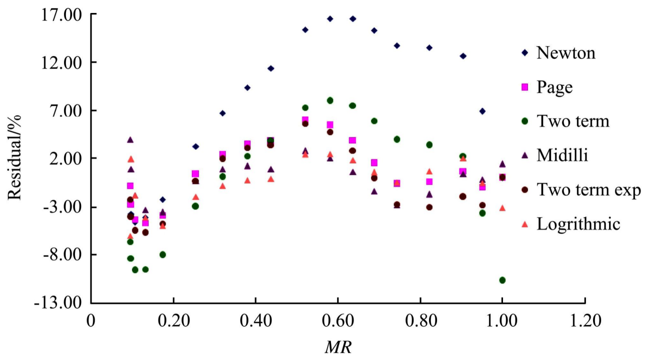

Figure 5 Model adequacy using plot of residuals for grape concentrate at 55°C at 3 mm

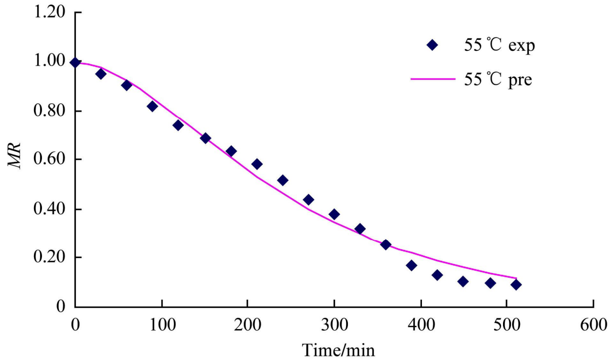

Figure 6 Fitting of two tem exponential model for grape concentrate at 55°C at 3 mm

Table 5 Regression coefficients and statistical parameters of best fitted convective drying model (Two term exponential model)

Temperature/^{0}C	Thickness/mm	*k*	*a*	R^2	χ^2	*MBE*	*RMSE*	*P*%
55	3	0.0091	2.0227	0.99906	0.00014	-0.00191	0.01069	2.77
	4	0.0079	2.0426	0.99501	0.00066	-0.00341	0.02392	7.79
	5	0.0055	2.0112	0.98635	0.00139	-0.00635	0.03513	13.69
	6	0.0050	2.0442	0.98936	0.00113	-0.00760	0.03186	11.15
	7	0.0046	2.1243	0.98877	0.00132	-0.00775	0.03477	12.41
60	3	0.0095	1.7822	0.99523	0.00045	-0.00257	0.01927	7.16
	4	0.0079	1.9331	0.98433	0.00155	-0.00669	0.03622	6.37
	5	0.0064	1.9899	0.98484	0.00160	-0.00873	0.03744	6.80
	6	0.0055	1.9883	0.99456	0.00052	-0.00475	0.02156	6.65
	7	0.0046	2.0627	0.98829	0.00131	-0.00661	0.03455	13.91
65	3	0.0099	1.4271	0.99904	0.00007	-0.00022	0.00746	3.67
	4	0.0096	1.8475	0.99584	0.00052	-0.00230	0.02075	4.77
	5	0.0074	1.8510	0.99394	0.00068	-0.00412	0.02410	7.02
	6	0.0058	1.9249	0.98254	0.00168	-0.00703	0.03836	7.45
	7	0.0056	2.0447	0.99250	0.00166	-0.00965	0.03646	7.85
70	3	0.0121	1.5304	0.99764	0.00028	-0.00035	0.01485	6.48
	4	0.0109	1.8337	0.98890	0.00132	-0.00165	0.03283	11.42
	5	0.0098	1.9045	0.99325	0.00073	-0.00245	0.02466	6.81
	6	0.0074	1.9125	0.98743	0.00128	-0.00591	0.03318	11.58
	7	0.0067	2.0603	0.98896	0.00128	-0.00738	0.03349	11.03
75	3	0.0203	0.4938	0.99831	0.00016	0.00152	0.01103	5.94
	4	0.0124	1.6123	0.99915	0.00012	-0.00035	0.00970	5.06
	5	0.0113	1.7610	0.99952	0.00009	-0.00022	0.00837	3.71
	6	0.0100	1.9190	0.99794	0.00027	0.00074	0.01492	5.12
	7	0.0085	2.0529	0.99565	0.00052	-0.00311	0.02115	6.45

In order to take into account the effect of temperature on the constants of the two tem exponential model namely, k and a (listed in Table 5), the regression analysis was used to set up the relations between these parameters. Thus, the regression equations of these parameters against temperature are listed in Table 6.

3.6 Quality analysis

Total sugars of grape leather developed at different temperature-drying bed thickness combinations varied from 29.57% to 31.54% (Table 7). A decreasing trend was observed due to caramelization of total sugars at higher temperatures caused by maillard reactions. The % total sugars decreased with decrease in drying temperature irrespective of drying bed thickness. The variation in drying bed thickness showed minimum change in % total sugars at constant temperature of drying. The analysis of variance showed that drying temperature and drying bed thickness have significant effect on % total sugars. However, the temperature witnessed the higher effect on % total sugars at 5% level of significance (Table 7) The total sugars of mango ranged from 7.84% to 7.88% was reported (Rajkumar and Kailappan, 2006).

Table 6 Regression equations of coefficients of selected model

Thickness /mm	Model equation	R^2
3	$k=2\times10^{-7}T^4-4\times10^{-5}T^3+0.0035T^2-0.1364T+2.012$ $a=-0.0001T^4+0.0369T^3-3.523T^2+148.66T-2340$	$R^2=1$
4	$k=2\times10^{-7}T^4-5\times10^{-5}T^3+0.0046T^2-0.2029\mathrm{T}+3.3282$ $a=-2\times10^{-5}T^4+0.0055T^3-0.5219T^2+21.784T-337.05$	$R^2=1$
5	$k=-2\times10^{-7}T^4+5\times10^{-5}T^3-0.0051T^2+0.2163T-3.4163$ $a=-5\times10^{-5}T^4+0.0121T^3-1.1665T^2+49.883T-794.18$	$R^2=1$
6	$k=-1\times10^{-7}T^4+4\times10^{-5}T^3-0.0036T^2+0.1575T-2.552$ $a=-6\times10^{-6}T^4+0.0016T^3-0.1552T^2+6.6925T-105.18$	$R^2=1$
7	$k=8\times10^{-8}T^4-2\times10^{-5}T^3+0.0021T^2-0.0901T+1.4786$ $a=-3\times10^{-6}T^4+0.0008T^3-0.0696T^2+2.7655T-38.299$	$R^2=1$

The value of non-enzymatic browning of grape leather ranged from 0.19 to 0.45 (Table 7). An increased trend was observed for non-enzymatic browning due to caramelization of total sugars at higher temperatures resulting more the browning of the product. It has been stated that the change in the brightness of dried samples can be taken as a measurement of browning (Tijskens et al., 2001). The non-enzymatic browning increased with increase in drying temperature irrespective of drying bed thickness. The analysis of variance showed that drying temperature and drying bed thickness has significant effect on non-enzymatic browning. The temperature witnessed the higher effect on non-enzymatic browning at 5% level of significance (Table 7)

Table 7 Effect of drying air temperatures and drying bed thickness on some chemical properties of developed grape leather

Temperature /^{0}C, (T)	Thickness /mm (Th)	Total sugars	Non enzymatic browning	Protein	Titrable acidity	Texture (cutting force)	Total color change	Water activity*	Overall acceptability
55	3	31.31	0.193	1.425	6.272	108.7	4.952	0.386	100.00
	4	31.31	0.206	1.385	6.272	117.4	5.337	0.357	100.00
	5	31.43	0.211	1.375	6.4	355.9	5.851	0.33	100.00
	6	31.43	0.216	1.325	6.4	582.2	6.474	0.397	100.00
	7	31.54	0.221	1.275	6.528	859.9	7.245	0.346	100.00
60	3	30.96	0.201	1.225	5.76	119.3	5.493	0.355	100.00
	4	31.08	0.213	1.175	5.632	142.8	6.228	0.365	100.00
	5	31.08	0.219	1.125	5.76	378	7.220	0.322	100.00
	6	31.19	0.23	1.11	5.888	630.4	8.798	0.417	88.89
	7	31.19	0.239	1.00	5.76	870.1	10.690	0.363	88.89
65	3	30.73	0.217	1.11	5.12	141.1	6.269	0.343	100.00
	4	30.61	0.223	0.985	5.376	196.8	7.256	0.401	100.00
	5	30.73	0.235	0.975	5.12	416.6	8.511	0.367	88.89
	6	30.85	0.257	0.965	5.248	641.2	9.966	0.358	88.89
	7	30.96	0.271	0.95	5.376	922.7	11.631	0.387	88.89
70	3	30.38	0.225	0.895	4.48	170.8	7.292	0.331	100.00
	4	30.50	0.252	0.885	4.608	233.6	8.536	0.419	88.89
	5	30.61	0.281	0.875	4.48	460.8	9.988	0.409	77.78
	6	30.61	0.307	0.85	4.864	682.6	11.550	0.339	88.89
	7	30.73	0.321	0.835	4.736	990.6	13.247	0.379	77.78
75	3	29.69	0.352	0.845	4.224	193.2	8.557	0.333	88.89
	4	29.57	0.382	0.82	4.096	390	9.974	0.351	77.78
	5	29.69	0.406	0.825	3.84	502	11.627	0.397	66.67
	6	29.80	0.417	0.79	3.84	720.5	13.440	0.375	66.67
	7	29.80	0.452	0.785	3.84	1012.4	15.455	0.421	66.67
Sum of squares, T		24.88	0.37	2.75	52.79	241707.95	299.930	2.05×10^{-3}	5489.35
Sum of squares, Th		0.611	3.63×10^{-2}	7.83×10^{-2}	0.197	625.55×10^4	250.721	9.73×10^{-3}	17.49
R^2		0.994	0.977	0.980	0.982	0.993	0.992	0.180	0.976

Note: * indicates non significant effect of drying temperature and thickness on water activity.

Protein content of 1.38% was observed in fresh grape concentrate. The protein content of grape leather was ranged from 1.43% to 0.79% (Table 7). The protein content decreased with increase in drying air temperature. It might be due to denaturizing effect of the protein content at high temperatures. The analysis of variance showed that drying temperature and drying bed thickness have significant effect on protein content. The temperature witnessed the higher effect on protein content at 5% level of significance (Table 7).

A titrable acidity in grape leather ranged from 3.64% to 6.27%. It was also noticed that temperature had negative correlation with titrable acidity. The variation in drying bed thickness showed minimum change in % titrable acidity at constant temperature of drying. Drying temperature and drying bed thickness had significant effect on % titrable acidity whereas, the temperature showed higher influence on % titrable acidity at 5% level of significance (Table 7).

Texture analysis of the product revealed that cutting force for grape leather ranged from 108.70 to 1012.40 gf (Table 7). Texture became more gummy and sticky at higher levels of temperatures. The cutting force increased with increase in drying temperature irrespective of drying bed thickness. The variation in drying bed thickness also showed change in cutting force at constant temperature of drying. The analysis of variance showed that drying temperature and drying bed thickness have significant effect on cutting force. However, the drying bed thickness witnessed the higher effect on cutting force at 5% level of significance (Table 7).

The color values L, a and b for initial grape juice concentrate was ranged from 45.16-39.72, 10.16-8.27 and 21.83-19.48 respectively. After drying, total color change ranged from 4.95-15.45 over a temperature range of 55^{0}C to 75^{0}C. The total color change increased with advance in air drying temperature irrespective of drying bed thickness. The maximum color change was observed at higher temperatures due to maillard reactions and caramelization of sugars. Air drying temperature had maximum significant effect on color change (p<0.05) (Table 7).

The water activity of grape leather was varied from 0.33-0.42 (Table 7). The water activity for all samples were the same as all samples were dries to the desired moisture content of 14 %db. The grape leather had low water activity; hence, it can be stored for longer time period. The non significant effect of temperature and thickness on the water activity was observed for all samples as dependent on the final moisture content of grape leather (Table 7).

The sensory quality of grape leather was evaluated on nine point hedonic scale for various attributes namely appearance, color, texture and taste; whereas the overall acceptability was determined as an average of all the attributes and was expressed in percentage. The overall acceptability ranged from 100% to 66.67%. The drying temperature showed significant effect on overall acceptability (Table 7). The % overall acceptability decreased with increase in drying temperature irrespective of drying bed thickness. The drying bed thickness showed non significant effect (p<0.05) on overall acceptability showing minimum change in % overall acceptability at constant drying temperature. The leather formed at 55^{0}C and 60^{0}C witnessed higher values of overall acceptability. The grape leather prepared at higher temperatures showed comparatively poor appearance, hard texture and sticky in nature. This led to lower sensory scores for the products developed at higher temperatures. The analysis of variance showed that drying temperature and drying bed thickness have significant effect on % overall acceptability. Thus, the leather prepared at 55^{0}C was evaluated as the best quality product.

4 Conclusions

The study of development of grape leather and drying of grape juice concentrate revealed that the drying temperature and drying bed thickness influenced drying time for development of grape leather. All samples dried in the falling rate drying period. Fick's model of water diffusion fitted all experimental data with acceptable correlation coefficients. Diffusivity values followed Arrhenius-type temperature dependence. The two tem exponential showed higher adequacy of fit between experimental and predicted data for grape juice concentrate which were supported by the distribution of residuals (%) v/s *MR*. The best quality product of grape leather was found to be at 55^{0}C for all drying bed thickness.

Nomenclature

dM/dT = drying rate, moisture loss per hour (% db /min)

M_i = Moisture content (% db) of sample at time t_i

M_{i+1}= Moisture content, (%db) of sample at time t_{i+1}

MR = Moisture ratio

D = Effective moisture diffusivity (m^2/sec)

D_0 = constant in Arrhenius equation in m^2s^{-1}

Ea = Activation energy in kJ. mol^{-1}

T = Temperature in ºC

R = Universal gas constant in kJ. $mol^{-1}K^{-1}$

$MR_{\exp,i}$ = Experimental dimensionless moisture ratios

$MR_{pre,i}$ = predicted dimensionless moisture ratios

n = Number of observations

z = Number of constants

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