Mathematical modeling of thin layer drying kinetics of stone apple slices

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Abstract

This study was conducted to investigate the effect of temperature on hot-air drying kinetics of stone apple (Aegle marmelos correa) slices and to evaluate the best model predicting the drying kinetics along with the colour changes during drying. Stone apple slices were conditioned to remove the mucilaginous material followed by hot-air drying in single layer slices with thickness of 8 mm at different temperatures (40–70°C) in a forced convection dryer. In order to estimate and select the appropriate drying model, six different models which are semi-theoretical and/or empirical were applied to the experimental data and compared. The goodness of fit was determined using the coefficient of determination (R²), reduced chi square (χ²), root mean square error (RMSE) and mean bias error (MBE). Among the models proposed, the semi-empirical logarithmic model was found to best explain thin layer drying behavior of the stone apple slices as compared to the other models over the experimental temperature range. By increasing the drying air temperature, the effective moisture diffusivity values increased from 3.7317E-10 m²/s at 40°C to 6.675E-10 m²/s. The activation energy was calculated using an exponential expression based on Arrhenius equation. The relationship between the drying rate constant and drying air temperature was also established which gave a polynomial relationship. Samples dried at lower temperature had better lightness (higher L* values) compared to those dried at higher temperature. However, the samples dried at 60°C showed a significant overall deviation (∆E*) in colour and may be considered as a limiting temperature for drying of stone apple slices.

Introduction

Stone apple (Aegle marmelos correa) is a wild fruit, which is rich in nutritional as well as medicinal qualities. These fruits are used to manufacture various herbal remedies for diarrhea, intermittent fever, antibacterial and stomach disorder (Baliga et al., 2010; Saradha and Rao, 2010; Samrot et al., 2010). Several studies have been done regarding the formulation and extracts of stone apple fruit (Brijesh et al., 2009; Maity et al., 2009; Raja et al., 2009; Sivaraj et al., 2009) and also its processed form (Joshi et al., 2009) which have been detected to have great curative effects on various diseases. As the storage quality of the whole fruit can’t be maintained for long period of time, improvement in the post harvest processing will enhance the effective utilization of the fruit. The fruit has a hard shell, sticky texture and numerous seeds along with gummy, mucilaginous materials within it, which makes it difficult to be processed manually (Singh and Nath, 2004). That is why the fruit is not very popular as a fresh fruit. As a result, this has become one of the most neglected wild fruits in the region which has the potential to provide an excellent source of income (Mishra, 2000). Since the fruit takes around eleven months to ripe after the tree bears fruit, it is not available to the people throughout the year. It has excellent processing attributes (Roy and Singh, 1978). Therefore there is possibility of stabilization of use of the fruit year round.

Dehydration is the best feasible method for the preservation of stone apple fruit pulp, because it decreases the moisture content which leads to retardation of many chemical and microbiological processes taking place in the fruit and helps in sample preservation (Maskan et al., 2002; Yaldiz et al., 2001; Zhang et al., 2006). The dried powder becomes an important raw material for many processed ready-to-eat food products. Stone apple pulp powder is expected to have a lot of potential in confectionery and fruit beverage industry for preparation of soft drinks, fruit juices, jams, jellies, candies, chocolates, milk-based drinks, ice-creams etc. Further, it offers additional advantages such as less storage space, extended shelf life and ensures availability throughout
the year irrespective of its being a seasonal fruit (Bag 	extit{et al.}, 2009). It is difficult to dry stone apple fruit pulp because it is highly viscous in nature and possess handling problems due to the presence of mucilaginous matter (MacLeod and Pieris, 1981; Shoba and Thomas, 2001; Roy and Singh, 1979). Drying influence physicochemical and quality characteristic of products (Maskan 	extit{et al.}, 2002), thus, modeling of drying kinetic is one tool for process control. Evaluation of drying kinetics as a function of drying conditions could help us in drying simulation for predicting the suitable drying conditions. Many mathematical models have been used to describe the drying process of food products. (Cao 	extit{et al.}, 2004; Gaston 	extit{et al.}, 2004), fruits (Doymaz, 2004a; Velic 	extit{et al.}, 2004; Simal 	extit{et al.}, 2005), vegetables (Doymaz, 2004b).

The present study was therefore undertaken to investigate the thin layer drying characteristics of stone apple slices in a convective dryer. Also the experimental data were fit to the proposed mathematical models in order to estimate the constant parameters for calculating the effective diffusivity and activation energy for drying of stone apple fruit pulp.

**Materials and Methods**

**Conditioning of sample**

Fresh and matured raw stone apple fruits of variety Narendra-bael were procured from the farmers’ field, near the city Bhubaneswar, in the province Orissa, India during the month of November, 2009. It was ensured that the fruits were matured but not ripe, which was judged mostly by personal experience. Colour of hard cover was green, but the internal pulp was yellow unlike the ripe ones where the colour of pulp is generally dark yellow. The whole fruits were washed in running water and cleaned. Since the rind of the raw stone apple is very hard, these were sliced to smaller pieces with uniform thickness of 8 mm. The circular slices of diameter 10-15 mm were obtained which were kept in the water for one hour at a temperature of 27 °C, in a way that all slices were under the water. Because of this, the mucilaginous matter dissolved and the rind also loosened. The seed, mucilaginous matter and rind were removed from the slices using knife and fork. Then the pulp slices were made into smaller pieces with uniform thickness of 8 mm.

**Drying experiment**

The experimental convective tray dryer (IIC, Model TD-12) used in this investigation consisted of a centrifugal blower, an electrical resistance air heating section, the measurement sensors and the data recording system. The air velocity was continuously measured using an anemometer (Lutron AM-4201). The blower and heater of dryer were switched on for 30 minutes for the drying air to reach the stable temperature, which were also the chosen experimental parameters. The slices were dried at four different air temperatures of 40, 50, 60 and 70°C. After attaining desired drying air temperature, samples were loaded onto the drying trays (80 × 60 cm²) in single layer. The trays were removed from the dryer and weighed regularly at 30 min intervals. All the experiments were carried out at 1.1 ± 0.2 m/s air velocity, which was the maximum velocity and was also less than terminal velocity. The drying tests were terminated when the weights of the samples were stabilized up to 2 decimal points, which was assumed to be the stage of dynamic equilibrium. Each experimental run was conducted in triplicate and the average of the results was analyzed. The initial moisture content of fresh slices and the final moisture content of dried samples were determined by hot air oven method at 105°C for 24 h. Moisture content was measured by the gravimetric method using an electronic balance. Precision of the electronic balance was 0.0001 g.

**Drying analysis and evaluation of thin layer drying models**

Based on the initial moisture content from oven drying, the weight loss was used to calculate the moisture content. The drying characteristic curves were plotted after analyzing the experimental data. The moisture content was converted to moisture ratio (MR) using the following equation

\[
MR = \frac{(M_i - M_f)}{(M_o - M_f)} \tag{1}
\]

where \(M, M_o, M_i, M_f\) are the moisture content, kg water/kg dry matter at a given time, beginning of the drying, when the equilibrium is reached, and at time \(t\), min respectively.

As the air humidity in the oven wasn’t constant, the expression was reduced to

\[
MR = \frac{M_i}{M_o} \tag{2}
\]

where \(M_o\) was assumed to be negligible.

In order to estimate and select the appropriate drying model among different semi-theoretical and/or empirical models, mathematical modeling was carried out to describe the drying curve equation of stone apple slices and to determine the parameters of the thin layer drying models by fitting experimental data to the model equation. The thin layer drying
Calculation of moisture diffusivity

Fick’s diffusion equation for particles with slab geometry was used for calculation of effective diffusivity by method of slopes. Since the stone apple slices are having a flat surface geometry and in this case the average thickness of the slices was 8 mm, the samples were considered of slab geometry. The equation expressed as (Lopez et al., 2000):

$$\text{MR} = \frac{8}{\pi} \exp \left( -\frac{E_a}{RT} \right)$$

where MR is the dimensionless moisture ratio, Deff is the effective diffusivity in m²/min, t is the time of drying in mins and L is the slab thickness in metres.

For the calculation of the effective moisture diffusivity at the different temperature conditions, the slope (kₜ) was calculated by plotting ln(MR) versus time according to Equation (8).

$$k_t = \frac{2.303 m}{t}$$

The activation energy for diffusion was estimated using simple Arrhenius equation as given below (Kaleemullah and Kailappan, 2006)

$$D_{eff} = D_0 \exp \left( \frac{-E_a}{RT} \right)$$

where, D₀ is the constant equivalent to the diffusivity at infinitely high temperature (m²/min⁻¹), Eₐ is the activation energy (kJ/mol), R the universal gas constant (8.314 x 10⁻³ kJ/mol) and T is the absolute temperature (K). Ea was determined by plotting ln(Dₑeff) versus 1/T.

Analysis of different quality parameters

The fresh and dried samples of slices obtained from the above mentioned set of experiments were analyzed for colour. The surface colour analysis of the fresh and dried slices was made by using a Hunterlab colorimeter (Colour Flex) to determine colour coordinates (L*, a* and b* values). The L* value is the degree of lightness, a* value is the degree of redness and greenness, and b* value is the degree of yellowness and blueness. The colour change of stone apple samples affected by drying air temperature was characterized by the total colour change (∆E*), which was calculated by Equation 10.

$$\Delta E^* = \sqrt{\left( \Delta L^* \right)^2 + \left( \Delta a^* \right)^2 + \left( \Delta b^* \right)^2}$$

where $\Delta L^* = L^*_0 - L^*$, $\Delta a^* = a^*_0 - a^*$, $\Delta b^* = b^*_0 - b^*$. 

The L*, a* and b* values correspond to the values of stone apple slices samples at different drying temperature, whereas the values of L*, a* and b* obtained by method of slopes. Since the stone apple slices are having a flat surface geometry and in this case the average thickness of the slices was 8 mm, the samples were considered of slab geometry. The equation expressed as (Lopez et al., 2000):

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The L*, a* and b* values correspond to the values of stone apple slices samples at different drying temperature, whereas the values of L*, a* and b*
are related to the fresh slices.

**Results and Discussion**

*Drying characteristics of stone apple slices in a convective dryer*

The total time required for drying at 40, 50, 60 and 70 °C was 840, 720, 600 and 540 mins respectively to reduce the initial moisture content of 160% to 235% d.b. to final moisture content of 6 to 7% d.b. The reduction of total drying time with increasing temperature may be due to increase in vapour pressure within the product with increase in temperature, which resulted in faster migration of moisture to the product surface. The plots in Figure 1 followed the general trend of drying curves as reported for many food materials (Ahmed and Shivhare, 2001; Pal et al., 2008).

At the higher temperature, the drying curve exhibited a steeper slope, thus exhibiting an increase in drying rate. Drying of stone apple slices took place mainly under falling rate period (Figure 2). During this period, the migration of moisture occurred through the mechanism of diffusion. The peak drying rate for stone apple slices was found to be 0.884 g/100g.min at a moisture content of 194% d.b. at 40 °C drying air temperature as compared to 1.456 g/100g.min at 70 °C. The higher drying air temperature produced a higher drying rate and consequently faster reduction in the moisture content and hence the total drying time was reduced. Similar results were reported by Özdemir and Derves (1999).

**Evaluation of model parameters**

The drying data obtained in the experiments were converted to dimensionless moisture ratio (MR). Figure 3 presents the evolution of the moisture ratio as a function of the drying time at different temperatures. It is observed that moisture ratio decreased with time. Difference between moisture ratios increased gradually from beginning to end of drying.

In order to determine the experimental moisture ratio as a function of drying time, the empirical models (Lewis, Page, Modified Page, Henderson and Pabis, logarithmic and Wang and Singh) have been fitted. The estimated parameters and statistical analysis of these models for all the drying condition are presented in Table 2 and 3. The models gave consistently high coefficient of determination ($R^2$) values in the range of 0.991 – 0.998. This indicated that the models could satisfactorily describe the fast drying of stone apple slices. Among the thin layer drying models, the logarithmic model obtained the highest $R^2$ values and the lowest $\chi^2$, RMSE and MBE values in the temperature range of the study.

The accuracy of the established model for the thin layer drying process was evaluated by comparing the predicted moisture ratio with observed moisture ratio. The performance of the model for all the drying temperatures has been illustrated in Figure 4. The
predicted data generally bandaged around the straight line which showed the suitability of the logarithmic model in describing the drying behaviour of stone apple slices. It was determined that the value of the drying rate constant (k) increased with the increase in temperature. This implies that with increase in temperature, drying curve becomes steeper indicating increase in drying rate. The fitting procedure showed that the results of the logarithmic model could be used to predict the drying behaviour of slices at these four drying temperatures only, but these did not indicate the effect of drying air temperature. To account for the effect of the drying air temperature on the constant “k”, “a” and “c” of logarithmic model, these constants were regressed with respect to drying air temperature. Linear and second order polynomial equations were found to be best fitted, for which the R² value was more than 0.90. So it was concluded that the corresponding equations could be used to indicate the effect of drying air temperature on the constants “k”, “a” and “c”. The values of these constants could be calculated at any particular temperature using these equations and in turn moisture ratios can also be estimated. Based on the analysis mentioned above, the accepted logarithmic model constants and coefficients were expressed in terms of the drying air temperature (Absolute) as

\[ a = 0.991T + 0.945 \quad (R^2 = 0.926) \]

\[ k = 1.49E-06T2 - 0.001T + 0.005 \quad (R^2 = 0.990) \]

\[ c = 8E-05T2 - 0.01T + 0.256 \quad (R^2 = 0.943) \]

**Effective moisture diffusivity estimation**

The method of slopes was used to estimate the effective moisture diffusivity of stone apple slices at corresponding moisture contents under different drying conditions. To calculate the effective moisture diffusivity by using the method of slopes, the logarithm of moisture ratio values, ln(MR), were plotted against drying time (t) according to the experimental data obtained at various temperatures and sample amounts. The linearity of the relationship between ln(MR) and drying time (t) was also illustrated in Figure 5 for various temperatures, with the corresponding coefficients of determination (R²). The effective moisture diffusivity values (Deff) of Equation (7) were presented in Table 4 for various temperatures. For comparing the results obtained, no documentary was found in literature for considering the effect of temperature on effective moisture diffusivity of stone apple slices. Effective moisture diffusivity values ranged from 2.239E-08 m²/min or 3.7317E-10 m²/s at 40 °C to 4.005E-08 m²/min or 6.675E-10 m²/s at different temperatures, which are quite similar to the values obtained in other cases such as berberis fruit (Aghbashlo, 2008) and grape leather (Maskan et al., 2002). It can be seen that the values of Deff increased greatly with increasing temperature. Similar variations were also observed during drying of black tea (Panchariya et al., 2002) and aloe (Simal et al., 2000). Activation energy of stone apple slices was found to be 16.1 kJ/mol from the plot of ln(Deff) versus inverse of absolute temperature (Figure 6). The value is within the range.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Logarithmic</th>
<th>Modified Page</th>
<th>Henderson and Page</th>
<th>Wang and Singh</th>
</tr>
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<tbody>
<tr>
<td>40</td>
<td>0.99262</td>
<td>0.99825</td>
<td>0.99296</td>
<td>0.99261</td>
</tr>
<tr>
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<td>0.99822</td>
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<td>0.99296</td>
</tr>
<tr>
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<td>0.99531</td>
<td>0.99296</td>
<td>0.99296</td>
</tr>
<tr>
<td>70</td>
<td>0.99918</td>
<td>0.99928</td>
<td>0.99296</td>
<td>0.99296</td>
</tr>
</tbody>
</table>

**Table 3. Modeling of moisture ratio with drying time during convective drying of stone apple slices at 40, 50, 60 and 70 °C**

<table>
<thead>
<tr>
<th>Model</th>
<th>Temperature (°C)</th>
<th>Temperature (Absolute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.99925</td>
<td>1.5428E-04</td>
</tr>
<tr>
<td>50</td>
<td>0.99156</td>
<td>7.5222E-04</td>
</tr>
<tr>
<td>60</td>
<td>0.99316</td>
<td>1.6718E-04</td>
</tr>
<tr>
<td>70</td>
<td>0.99928</td>
<td>4.8649E-04</td>
</tr>
</tbody>
</table>

**Table 2. Comparison of different drying models with drying coefficients (constants) at different drying temperatures**
15 to 40 kJ/mol of activation energy values reported by Rizvi (1986) for different foods.

Effect of drying air temperature on colour indices of stone apple slices

The colour of the dried samples was measured using Hunterlab colorimeter. Mean surface colour values of dried stone apple powder dried under the different drying air temperatures and under shade are shown in Table 5. From the point of view of colour coordinates L*, a* and b*, there are significant differences between the fresh and dried slices. The comparisons of the values have been done based on change in colour with respect to the colour of the control samples. L* values of raw stone apple pulp are very close to 50 indicating lightness of colour. The samples are getting darker as L* is reducing with temperature. A value of 11.89 for a* for control sample indicated slight reddishness which increased in dried sample with increase in temperature. The yellowness of control sample was high with a b* value of 30.79. With increase in drying air temperature the b* value of the samples decreased tending towards dark yellow colour. In order to have a relative comparison among samples with the combined effect of L*, a* and b*, the square terms of deviation have been taken and the square roots of summation of the deviation for all the samples have been compared. These values are 2.65, 8.76, 16.83 and 22.54 for 40°C, 50°C, 60°C and 70°C respectively. It is observed that there is an increasing order in the values. But the increase at 60°C is quite abrupt and significantly different. Thus 60°C temperature may be considered as a turning point for change in colour and may be a deciding factor for drying air temperature selection (Table 5).

The statistical analysis of AE* values of dried slices indicated that this is lowest for samples dried at lower temperature of 40°C. However, the difference was statistically significant at 60°C. Therefore drying at 50°C may be recommended for better quality of the product.

Conclusion

The following conclusions were drawn from this study. Stone apple slices did not exhibit a constant rate drying period under the experimental conditions used in this study. Predictions by the logarithmic model are in good agreement with the data obtained from the convective drying experiment. The drying rate constant and drying air temperature was established to share a polynomial relationship. Effective moisture diffusivity values ranged from 2.239E-08 m²/min or 3.7317E-10 m²/s at 40°C to 4.005E-08 m²/min or 6.675E-10 m²/s at different temperature. Activation energy of stone apple slices was found to be 16.1 kJ/mol.

Drying stone apple slices down to about 6% (d.b.) moisture content by a convective dryer at 50°C air temperature requires a drying time of about 720 minutes without any significant loss in the surface colour of the slices.

Acknowledgements

The authors are thankful to College of Agricultural Engineering and Technology, Orissa University of Agriculture and Technology, Bhubaneswar, India for providing the infrastructure for the research work.

References


