A New Method for Modeling the Drying Kinetics of Zataria Multiflora (Avishan Shirazi) Leaves: Superposition Techniques

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Abstract

Drying curves of agricultural products at different air temperatures and velocities are often identical in shape, but shifted along the abscissa. The shift distance for each curve measured relative to a chosen reference curve is called shift factor. This allowing that the drying curves shifted horizontally along the time axis through a time multiplier (shift factor), until a smooth master curve is created. The master curves can be used to address air temperature and velocity effect on the drying kinetics through the use of the shift factors. The purpose of the present work was to test the validity of this method, time-temperature-superpositioning technique (TTST), in order to model the effect of air temperature and velocity on drying kinetics of Avishan (Zataria Multiflora L.) leaves. The drying data at three temperatures (30, 40, and 50°C) as well as three air velocity levels (0.5, 0.8 and 1.2 m/s) were used for the modeling. The results showed that the TTST was adequate to generate a moisture ratio master curve for Avishan leaves. The resulting master curve represented by a two-term model and its validity to predict the moisture ratio of Avishan leaves was compared with a regression model. The prediction errors for the TTST were 44.7% - 243.2% less than the regression model. An Arrhenius equation was sufficiently capable of explaining the temperature dependence of the shift factors.

Keywords: Avishan leaves, drying, modeling, master curve, superposition technique

Introduction

Zataria multiflora Boiss (Lamiaceae) is one of the valuable medicinal plants grown extensively in Iran, Pakistan and Afghanistan (Hosseinzadeh et al., 2000). This plant with the local name of Avishan Shirazi (in Iran) is practically useful for anesthetic, tonic, digestant, tranquilizer, antiseptic, diuretic, laxative, antispasmodic and for treatment of gastrointestinal infection (Khalili and Vahidi, 2006; Ramezani et al., 2006). In the term of food consumptions, the Avishan leaves, after being plucked from the plant bush, go through drying process followed by grinding. Dried leaves have a strong and pleasant aroma and are extensively used as flavor ingredients in a number of foods in Iran.

One of the most important aspects of drying technology is the modeling of the drying process (Manjeet, 1984). Some theoretical, empirical, and semi-theoretical drying models that have been widely used for modeling the drying kinetics of food products are presented in form of models, namely, Fick, Page, Logarithmic, and Two-Term models (Kashaninejad et al., 2003). Although all the above mentioned models have been successful in explaining the drying kinetics of agricultural products, none of them can be used over a wide range of foods and
drying conditions. The drying kinetics is greatly affected by air temperature, air velocity, material size, drying time, and etc. (Akpinar and Bicer, 2005; Park et al., 2002). Each of them may have varying degrees of effect on drying process which must be considered during the drying process. However, all the mentioned above models are just related to drying time and do not include the interaction effect of other related parameters. Thus, it is important to researchers to find a model that incorporates a large number of variables. In this study, a novel method; called time-temperature superposition technique; is proposed to include the effect of air temperature and air velocity into the drying models. The time-temperature superposition technique (TTST) is one of the most useful extrapolation techniques with a wide range of applications. It has been used by many researchers for modeling the effect of temperature and moisture content on mechanical properties of materials (Waananen and Okos, 1999, Khazaei and Mann, 2004). Khazaei et al.(2008) reported that this method could be successfully used for modeling the effect of air temperature and slices thickness on drying kinetics of tomato slices. However, a review of literature found no more studies on using the TTST for modeling of drying data for agricultural products. Moreover, it was found no published paper on hot air drying of Avishan leaves.

The objectives of this study were (1) to determine the effects of drying air temperature and air velocity on drying kinetics of Avishan leaves, (2) to fit the experimental data to four thin-layer drying models and estimate the constants, and (3) to calculate the effective diffusivity and activation energy, for drying of Avishan leaves. The other objective of this study was to evaluate the applicability of the superposition principle to the prediction of the moisture ratio of Avishan leaves at different air temperatures and air velocities.

**Methodology of Superposition Technique**

It can be found from previous studies that drying curves of agricultural products at different temperatures are often identical in shape, but shifted along the abscissa (Akpinar, 2006; Kashaninejad). This implies that the drying behaviour at one temperature can be related to that at another temperature by a change in the time scale. In other words, the effect of temperature on drying kinetics is equivalent to extension or reduction of the effective time. The similarity of the drying curves allowing that the drying data measured at different temperatures can horizontally shifted in such a manner that they join a choosing reference curve to form a smooth curve called master curve. Therefore, drying data measured at several different temperatures can be combined on a single curve, which is equivalent to data measured at a fixed temperature over an extended drying period. The action of shifting is termed "superpositioning" when the curves coincide to form the master curve. This is called the time-temperature superposition principle. In fact, the technique of superposition is based on the principle of time-temperature correspondence, which uses the equivalence between drying time and temperature for the drying function.

To illustrate the shifting process more clearly two individual drying curves are considered in Fig 1 in a semi-logarithmic scale; the same procedure is applicable to the other curves at different temperatures. Let $M(t)$ be the drying function at some reference temperature of $T_r$ and $M(t)$ be the drying function at temperature of $T$. An arbitrary point, $P_t$, on $M(t)$ is chosen at: $P_t = [\log(t)], M_t]$. Point $P_t$ on $M(t)$ is accordingly moved to $P_{tr}$ at: $P_{tr} = [\log(t_{tr}), M_t]$. Where $\log(t) − \log(t_{tr}) = \Delta(t) = \log a_{tr}$. Therefore:
The shift distance measured relative to the curve for reference temperature \( T_R \) is called the shift function and designated as \( \Delta(t) \). At reference temperature, the shift function \( \Delta(t) = 0 \). The \( t_{ir} \) is the individually shifted time-value of data point \( t_i \), shifted over \( \log(a_{iT}) \), such that it exactly matches the reference curve. Therefore, each points of \( \log(t_i) \) and \( \log(t_{ir}) \) on drying curves at the same moisture content can be written as (Waananen and Okos, 1999; Khazaei and Mann, 2004):

\[
M(\log(t_i))_T = M(\log(t_{ir}) + \log(a_{iT})_T) \quad i = 1, 2, 3, \ldots, p
\]

The time-temperature superposition principal in its simplest form implies that the drying behavior at one temperature can be related to that at another temperature only by a change of time scale. Thus, the drying function of product at any temperature \( T \) and any drying time can be estimated using the drying data at \( T_R \) over an extended time scale \( t' = t a_T \); where (Corcione et al., 2005):

\[
M(t)_T = M(t.a_T)_{T_R}
\]
Hence it could be pointed out that \( t \) units of time at temperature \( T \) is equivalent to \( t' = a_r \) units of time at drying temperature of \( T_R \). The new independent variable \( t' = a_r \) is called reduced or pseudo time (Jazouli et al., 2005; Khazaei and Mann, 2004). A single “master curve” may be obtained by applying the shifting procedure to a series of drying curves at different temperatures. Here is demonstrated that the temperature dependence of the temperature-shift factor \( a_r \) may be described by an Arrhenius expression. Manjeet, (1984), concluded that the drying rate of agricultural product is proportional to the difference in moisture content between the material to be dried and the equilibrium moisture content, \( dM/dt = -k(M_e - M) = f(M) \). Previous studies have also reported that the drying rate is strongly related to air temperature. Typically the drying rate increases with increasing temperature. Therefore, the drying rate as a function of moisture content and air temperature may be expressed as follows:

\[
\frac{dM}{dt} = f(M).U(T)
\]  \hspace{1cm} (6)

Previous studies have reported that the effect of temperature on the drying kinetics of agricultural products could be expressed using the Arrhenius-type relationship (Doymaz et al., 2006). Therefore, the \( U(T) \) function in (Eq. 6) may be expressed as follows:

\[
U(T) = A \exp \left( -\frac{E_a}{RT_a} \right)
\]  \hspace{1cm} (7)

Integrating from (Eq. 7) at constant temperature and taking the natural logarithm, (Eq. 8) is obtained:

\[
\log \int \frac{dM}{f(M)} = \log U(T) + \log(t)
\]  \hspace{1cm} (8)

Considering that the left-hand side of the (Eq. 8) is a unique function of \( M \), a new function \( F(M) \) can be introduced as follows: \( F(M) = \log U(T) + \log(t) \). Analysis of this equation indicates that the same value of \( F(M) \) can be carried out for different pairs of air temperatures and drying times as indicated in (Eq. 9):

\[
F(M) = \log U(T_1) + \log(t_1) = \log U(T_2) + \log(t_2)
\]  \hspace{1cm} (9)

Consequently: \( \log(t_1) - \log(t_2) = \log U(T_2) - \log U(T_1) \). In other words, for any two drying curves \( \log[U(T_2) - \log U(T_1)] \) is constant. Considering the drying curves for two different temperatures \( T_1 \) and \( T_2 \), the argument \( M(t) \) of the function \( F(M) \) as a function of \( \log(\text{drying time}) \) will have the same functional form, however the curve for the temperature \( T_2 \) will be displaced from that of the temperature \( T_1 \) by a constant factor \( a_r \). That means, all curves of \( M(t) \) versus \( \log(\text{time}) \) at different temperatures can be superposed by simply shifting each curve along the \( \log(\text{time}) \) axis relative to the curve at an arbitrary reference temperature by a shift factor \( a_r = [\log(t_R) - \log(t)] \). This yield the following equation:
\[ a_T = \log(t_R) - \log(t) = \log(U(T) - \log(U(T_R)) \tag{10} \]

By combining the Eqs. (7) and (10) gave the following relationship:

\[ \log(a_T) = \frac{E_a}{R} \left( \frac{1}{T} + \frac{1}{T_R} \right) \tag{11} \]

Equation 11 can be used to obtain the activation energy \( E_a \) of the drying process via the shift factor values (Kumar and Gupta, 2003).

**Materials and Methods**

**Plant Material and Experimental Procedure**

Fresh Avishan leaves were used in the drying experiments. The initial moisture content of Avishan leaves was 53% wet basis (w.b.), 1.13 g H2O/g DM (g water/g dry matter). The hot-air dryer used in this study consists of an adjustable centrifugal blower, air heating duct, humidity generator, sample platform, and measurement instruments of temperature, air velocity and humidity.

The drying experiments were performed to determine the effect of air temperatures at 30, 40, and 50°C and air velocities at 0.5, 0.8, and 1.2 m/s. Moisture losses of the sample was determined by weighing the sample tray periodically. Three replicated tests were conducted for each drying condition and mean moisture contents from those three tests as a function of drying time were reported.

**Mathematical Modeling**

**Time–Temperature- Superposition Method**

From this study, a total of nine average drying curves were drawn for three air velocity level and three drying air temperatures. The drying data were plotted as moisture ratio versus log(time). All of the nine curves were combined on a single master curve using the TTST in two steps. At first, The separate curves measured at different temperatures, but at a common air velocity, were shifted on the log-time axis to a reference temperature of 40 °C. For each temperature level the time-temperature shift factor \( T_a \) was determined according to the procedure described in previous section.

At second step, the three developed master curves, for air velocities of 0.5, 0.8, and 1.2 m/s, were shifted again to a reference air velocity of 0.8 m/s to construct a final single master curve with the shift factor of \( a_v \). The final single master curve was used to estimate moisture ratio of Avishan leaves at air temperatures of 30°C to 50°C and air velocities of 0.5 to 1.2 m/s, \( Mr(t',T,V) = Mr(t a_v a_T) \). In the final master curve, the new time scale is represented by the reduced time of \( t' = t a_T a_v \).
Results and Discussion

Drying Curves

The changes in the moisture contents (d.b.) of Avishan leaves with drying time at different air temperatures and at air velocities of 1.2 and 0.5 m/s are shown in Fig. 2. Similar trends were obtained for air velocity of 0.8 m/s. Air temperature had a significant effect (P = 0.01) while air velocity had a small effect on drying time (Fig. 2). The average times required to reach to a moisture content of 0.16 g H2O/g DM were 560, 225, and 130 min at air temperatures of 30ºC, 40ºC, and 50ºC, respectively.

The maximum significant effect (P = 0.01) of air velocity on drying time of Avishan leaves was observed at air temperature of 50ºC (Fig. 3). Increase in air velocity from 0.5 to 1.2 m/s, caused a significant (P = 0.01) decrease in the drying time for about 12%, 38% and 47% at air temperatures of 30ºC, 40ºC and 50ºC, respectively.

The changes in the drying rates of Avishan leaves with moisture content showed that drying rate decreases continuously with drying time and decreasing moisture content. No constant-rate drying period was found and all the drying operations were seen to occur in the falling rate period. It means that diffusion is dominant physical mechanism governing moisture movement in the Avishan leaves.

Calculation of Effective Diffusivity and Activation Energy

The effective diffusion coefficient, $D_e$, of Avishan leaves was derived from the Fick’s 2nd law in slab geometry (Eq. 12) (Sacilik, 2007). In this equation, the moisture ratio $M_r$ was reduced to $M_t/M_o$ because $M_e$ was relatively small compared to $M_o$ as assumed by Sacilik (2007).

$$\ln \left(\frac{M}{M_o}\right) = \ln\frac{8}{\pi^2} - \left(\frac{\pi^2 D_e t}{H^2}\right)$$

(12)

Where $H$ is the thickness of the leaves (m). The mean values of diffusion coefficients, computed for all the air temperatures and velocities, are given in Table 1. The diffusivity values increased about 3.26 times when the air temperature increased from 30 to 50ºC. Air velocity had also a significant increasing effect on water diffusivity for Avishan leaves.
The dependence of diffusion coefficients on temperature was modeled using the Arrhenius equation (Sacilik, 2007). As it is clear from Fig. 4, the linearity of the curves for the three air velocity levels indicates an Arrhenius relationship and allows determining the average activation energy from the slopes of straight lines. The activation energies were determined equal to 51.1, 49.0, and 38.6 kJ/mol for air velocities of 1.2, 0.8, and 0.5 m/s, respectively with a value for $R^2$ of higher than 0.890.

Table 1. Values of effective diffusivity ($\times 10^{-11}$ m²/s) attained for Avishan leaves at various air temperatures and velocities.

<table>
<thead>
<tr>
<th>Air temperature (°C)</th>
<th>Air velocity (m/s)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>30</td>
<td>0.196</td>
<td>0.291</td>
</tr>
<tr>
<td>40</td>
<td>0.284</td>
<td>0.376</td>
</tr>
<tr>
<td>50</td>
<td>0.506</td>
<td>0.978</td>
</tr>
<tr>
<td>Average</td>
<td>0.329</td>
<td>0.548</td>
</tr>
</tbody>
</table>

Mathematical Modeling

Superposition Technique

Figure 5a shows variation in moisture ratio $M_r$ versus log(time) at different air temperatures for air velocity of 0.8 m/s. Similar trends were observed for other air velocities. It is evident from Fig. 5a that drying curves of Avishan leaves at different temperatures had the same general shape, allowing for smooth horizontal shifting along the time axis thereby forming a single master curve (Fig. 5b). Using reference temperature of $T = 40$°C the “master curves” for each air velocity level were obtained (Fig. 6). For example, both the original and shifted moisture ratio data at air velocity of 0.8 m/s are presented in Figs. 5a and 5b. Similar master curves generated for the other two air velocity levels (Fig. 6). The values of time-temperature shift
factor $a_t$ of different temperatures, used to shift the drying curves, are given in Table 2 for different air velocity levels. Figures 5b and 6 show that the drying curves at different air temperatures can be well described by a single master curve as a function of reduced time of $t' = t \cdot a_t$. Master curves in term of reduced time $t \cdot a_t$ can be used to address temperature effect on the drying kinetics through the use of time-temperature-shift factors that combines the effect of drying time and air temperature into a single value of reduced time $t'$.

At the second step of shifting the drying curves, the three generated master curves (Fig. 6) were superposed again to generate a single master curve (Fig. 7). The curve related to the air velocity of 0.8 m/s was taken as the reference curve and the other master curves were shifted by superposition until a single master curve was achieved (Fig. 7). The corresponding air velocity-shift factors $a_v$ are plotted versus air velocity in Fig. 8. The relationship between air velocity-shift factor $a_v$ and air velocity was determined as follows:

$$a_v = 0.6549 + 0.4622V$$

$R^2 = 0.983$ (13)

Again, the amount of shifting at each air velocity required to form the final master curve, describes the air velocity-dependency of the material. The curve fitting using the Two-Term

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### Table 2. Temperature shift factors ($a_T$) for Avishan leaves at temperatures of 30, 40 and 50°C dried at different air velocities.

<table>
<thead>
<tr>
<th>Air temperature (°C)</th>
<th>Air velocity (m/s)</th>
<th>0.5</th>
<th>0.8</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.5</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1.43</td>
<td>1.65</td>
<td>1.49</td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 3. Effect of air velocity on drying behavior of Avishan leaves at air temperature of 50°C.  
Fig. 4. Arrhenius-type relationship between the effective diffusivity and absolute temperature at different air velocities.
model \( (Mr = a \exp(-k_o t) + b \exp(-k_i t)) \) yields the following equation for the final single master curve of moisture ratio as a function of \( t' = t a_r a_v \): \[
Mr(t, T, V) = Mr(t a_r a_v) = 0.5965 \exp(-0.0288 t a_r a_v) + 0.3487 \exp(-0.0038 t a_r a_v) \quad R^2 = 0.983 \quad (14)
\]

Figure 7 shows the master curve from the experimental data as well as the predicted curve from (Eq. 14). It is evident that the measured data generally banded around the predicted data which shows the master curve model (Eq. 14) can completely describe the information contained in the experimental data. The linear adjustment between the measured and the predicted values gave a slope practically equal to 1 (\( Y = 0.9959X +0.0018, R^2=0.996 \)). The average of RMSE between the measured and the predicted data was 0.019 which implies that the generated single master curve (Eq. 14) could be used to predict the drying behavior of Avishan leaves for air temperatures of 30 to 50°C and air velocities of 0.5 to 1.2 m/s. This implies that the drying kinetics which is both air temperature and air velocity dependent, in addition to being time-dependent, can be reduced to a simple time dependency (Eq. 14) over an extended time scale.

According to (Eq. 14), in order to obtain the moisture ratio of Avishan leaves at a desired air temperatures and velocities we need the corresponding shift factors \( a_r \) and \( a_v \) which are obtained from Table 2 and Fig. 8, respectively and the \( Mr \) values for the corresponding \( t a_r a_v \) values which are obtained by either the master curve is shown in Fig. 7 or (Eq. 14). The values of \( a_r \) and \( a_v \) at any temperature in the range of 30-50°C (Table 2) and any air velocity in the range of 0.5 to 1.2 m/s (Fig. 8) could be obtained via the interpolation method.
The horizontal temperature shifting factors $a_T$ (Table 2) agrees with the Arrhenius equation as can be seen in Fig. 9. A plot of log($a_T$) against the reciprocal of the absolute temperature (Eq. 11) gave a straight line, indicating an Arrhenius relationship (Fig. 9). This result implies that temperature-shift factor $a_T$ is an inherent property of a given material and could be determined experimentally. The mean values of activation energies calculated for air velocities of 1.2, 0.8, and 0.5 m/s were 46.86, 42.58, and 36.82 kJ/mole, respectively. These results are in agreement with the values obtained from the water diffusivity method (Fig. 4), 51.1, 49.0, and 38.6 kJ/mol for air velocities of 1.2, 0.8, and 0.5 m/s, respectively. The differences could be related to some assumptions which are applied to Fick’s second law where are at best only partially valid.

**Semi-Theoretical Models**

The curve fitting results for the nine average drying curves showed that the Page model ($Mr = \exp(-kt^n)$) provided an excellent fit to the experimental drying data with a value for $R^2$ >0.99, indicating a good fit. The values of RMSE obtained from this models were less than 0.0301, which were in an acceptable range. Although the Page model could be used for
modeling of the drying behavior of Avishan leaves, but it did not indicate the effect of drying air temperature and air velocity. To account for the effect of the drying variables on the Page model parameters of \( k \) and \( n \) (Eq. 15), the calculated values of \( k \) and \( n \) (for the nine average drying curves) were regressed against those of drying air temperature and velocity as Arrhenius-type equation using multiple regression analysis (Togrul and Pehlivan, 2003). The following results was obtained:

\[
M_r = \exp(-kt^n) \quad (15)
\]

\[
k = 0.09807V^{0.1411} \exp\left(-\frac{18.1271}{T}\right) \quad R^2=0.656 \quad (16)
\]

\[
n = 0.8559V^{-0.02087} \exp\left(-\frac{8.6481}{T}\right) \quad R^2=0.856 \quad (17)
\]

The (Eqs. 15-17) can be used to estimate the moisture ratio of Avishan leaves at any time during the drying process, in the ranges of \( T = 30 \) to 50°C and \( V = 0.5 \) to 1.2 m/s. Similar method has been reported by others researchers to generate a single regression equation to correlate moisture ratio to drying time, air velocity, and air temperature (Togrul and Pehlivan, 2003). The performance of the model is illustrated in Fig 10. The experimental data seem scattered around the computed straight line. The consistency of the model is evident with \( R^2 = 0.992 \) and RMSE = 0.062. However, a comparison between Figs 7 and 10 indicates that the master curve model (Eq. 14) had better moisture ratio prediction accuracies than the single regression model (Eqs. 15-17). The prediction errors (RMSE) for the superposition technique were 44.7%-243.2% less than the conventional regression method.

![Fig. 10. Experimentally determined and predicted moisture ratio data of Avishan leaves using (Eq. 15) to (Eq. 17).](image)

**Acknowledgements**

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References


