Drying kinetics of grape seeds

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Drying of grape seeds representing waste products from white wine processing (Riesling), red wine processing (Cab Franc), and juice processing (Concord) was studied at 40, 50, and 60 °C and constant air velocity of 1.5 m/s. Equilibrium moisture content had a significant effect on the normalized drying curve and was determined for each grape seed at each drying temperature. Effective moisture diffusivity ranged between 1.57 and 3.96 × 10⁻¹⁰ m²/s for Riesling seeds, 2.93–5.91 × 10⁻¹⁰ m²/s for Concord seeds, and 3.89–8.03 × 10⁻¹⁰ m²/s for Cab Franc seeds. The temperature dependence of the effective diffusivity followed an Arrhenius relationship, and the activation energies were 40.14 kJ/mol for Riesling seeds, 30.45 kJ/mol for Concord seeds, and 31.47 kJ/mol for Cab Franc seeds. Three thin-layer models were used to predict the drying curves: Page model, Lewis model, and the Henderson–Pabis model. All three models were found to produce accurate predictions compared to the mass average moisture loss for each grape seed variety (percent error less than 10%), and the Lewis model was shown to be an excellent model for predicting all three grape seed varieties (percent error less than 5%).

1. Introduction

In 2005, the US processed over 4 million metric tons (over 80 million metric tons worldwide) of grapes for wine production, and over 0.5 million metric tons of grapes for juice production (USDA, 2006). Grape pomace is the solid waste product leftover from wine and juice processing and generally consists of pulp, skins, and seeds. Depending on the condition of the grape at harvest and the type of press used, 13.5–14.5% of the grapes crushed from wine and juice processing, and 56–80 thousand metric tons (11.2 million metric tons worldwide) of pomace was generated as waste in 2005. This high volume waste product contains valuable components, such as tannins, phytochemicals and oil. Depending on the variety, grape seeds constitute approximately 26% of the pomace.

One product produced from grape pomace waste is grape seed oil, which has the following nutritional properties; cholesterol free, low in saturated fats, contains linoleic acid and high-density lipoprotein, and rich in Vitamin E and antioxidants (Arvanitoyannis et al., 2006). Grape seed oil is a high-quality culinary oil having a high smoke point, 252 °C, making it a good choice for frying and other high temperature food applications. Due to its stability and fluidity properties, grape seed oil spreads and mixes better with food, requiring 50% less than other oils (Arvanitoyannis et al., 2006).

Fresh grape seeds are highly perishable, and dehydration is a useful means to increase the shelf-life of seeds for further use. Cold mechanical pressing of dried seeds is an environmentally friendly method to extract oil where no chemicals are used. Dry seeds with moisture content below 0.10 g/g dry solids are required for a cold press operation, thus dehydration is a critical processing step. There are a limited number of reported studies on drying kinetics of seeds: tomato seeds (Sogi et al., 2003), pumpkin seeds (Sacilik, 2007), and rapeseeds (Pathak et al., 1991). To these authors’ knowledge, drying kinetic studies on grape seeds have not been reported.

The objective of this research is to quantify the drying kinetics of grape seeds to facilitate production of valuable grape seed oil from high volume waste pomace.

2. Materials and methods

2.1. Sample preparation

Grape seeds used in drying experiments were provided from grapes Vitis vinifera of the variety Riesling and Cabernet Franc, representing waste materials from white wine and red wine processing, respectively, and grape seeds from Vitis labrusca of the variety Concord, representing waste material from grape juice processing. Pomace was obtained from New York wineries and grape juice manufacturers, and the seeds were separated using a very efficient separator (turbo finisher/extractor, Bertocchi Inc., ITALY). Riesling
seeds were the smallest seeds of the three varieties, and a 6 mm screen was used to separate the seeds from the pomace. An 8 mm screen was used to separate the seeds from the Cabernet Franc and Concord pomace. After bulk separation, the seeds were washed to remove the remaining pomace. Initial moisture contents of all samples were determined by the oven drying method at 70°C in a vacuum oven (Model 3608, Lab-Line Instrument, Inc.) for 24 h (AOAC, 1990).

2.2. Convective hot air drying

The schematic diagram of the apparatus used for convective hot air drying experiments is shown in Fig. 1. The basic design of the convective drying apparatus is described by Roberts et al. (2002). Samples were suspended beneath an analytical balance (AG204, Mettler Toledo, Inc., Hightstown, NJ) into the oven and within a polycarbonate air-flow cylinder using a fabricated mesh basket. The balance was interfaced to a PC computer by a RS-232 cable, and the weight loss of the samples was recorded on-line every 30 s throughout drying using software for the balance (Balance Link, Mettler Toledo, Inc., Hightstown, NJ). High drying temperatures used in drying seeds prior to oil extraction may have deleterious effects on the final oil quality (Gomes and Caponio, 2001); however, little is known about the extent of thermal damage caused by the drying process prior to oil extraction (Gögüs and Maskan, 2006). Thus, the temperatures used in this study, 40, 50, and 60°C, were in the range of the low end of typical drying temperature. External resistances to mass transfer become important for a Biot number for mass transfer, $Bi_m = \frac{kL}{Dq_s}$, less than 10 (Vaccarezza et al., 1974). In addition, experimental studies of the effect of air velocity on the moisture content of the material during drying can be used to determine whether external resistances are important to mass transfer (Vaccarezza et al., 1974). When convective hot air is equal to or greater than 1 m/s, external resistances become negligible (Jason, 1958). Srikiatden and Roberts (2006) showed that the Biot number for mass transfer for 0.7 cm samples was in the range of $1.44 \times 10^2$ to $9.70 \times 10^4$ using an air velocity above 1.5 and air temperatures between 50 and 70°C. This Biot number for mass transfer is far above 10 below which external resistances become negligible (Jason, 1958). Srikiatden and Roberts (2006) showed that the Biot number for mass transfer for the seed samples will also be above 10 insuring negligible external resistance to mass transfer. Moisture contents at each time interval were calculated from both weight loss data and dry solid weight of the sample, which was determined at the end of drying by the vacuum oven-drying method at 70°C for 24 h (AOAC, 1990).

2.3. Drying analysis

Simplified drying models have been used to quantify drying kinetics of various grains and some seeds (Sogi et al., 2003; Parti, 1993; Bruce, 1985). Three common models are the Page model:

\[ M_t = M_i \left(1 + \frac{N}{N - 1} \left(1 - \frac{M_t}{M_e} \right)^{N - 1}\right) \]

where:
- $M_i$ is the initial moisture content (dry basis), kg H₂O/kg dry solid
- $M_t$ is the moisture content (dry basis), kg H₂O/kg dry solid
- $M_e$ is the equilibrium moisture content (dry basis), kg H₂O/kg dry solid
- $N$ is a constant in the Page model
- $t$ is time, s
- $D$ is the effective moisture diffusivity, m²/s
- $D_0$ is the pre-exponential factor of the Arrhenius equation, min⁻¹
- $K$ is the drying rate constant, min⁻¹
- $E_a$ is the activation energy, kJ/mol
- $A$ is the intercept constant in the Henderson–Pabis model
- $M_e$ is the equilibrium moisture content (dry basis), kg H₂O/kg dry solid
- $N$ is a constant in the Page model
- $R_c$ is the universal gas constant, = 8.314 × $10^{-3}$ kJ/mol K
- $T$ is the absolute temperature, K

Fig. 1. Convective hot-air drying apparatus.
The moisture content is significantly less than the initial moisture content.

Due to fluctuating relative humidity during drying, the equilibrium moisture content can be assumed to be 0 g/g dry solid (Saci-lik, 2007; McMinn, 2006; Doymaz and Pala, 2003; Midilli et al., 2002; Yaldiz and Ertekin, 2001; Diamente and Munro, 1993). This assumption is valid only at the beginning of drying, but as the sample dries the moisture content approaches the equilibrium moisture content. This can significantly affect the slope and linearity of the normalized drying curve, as shown in Fig. 2. Also, if the drying curve is not allowed to continue until it reaches equilibrium and thus the equilibrium moisture content is measured to be too high, the slope is shown to be greater and departs from linearity. As the unaccomplished moisture content reduces by more than 90% (or one log-cycle), the slope of the semi-log plot is particularly sensitive to changes or deviations during the second log reduction. Thus, if the equilibrium moisture content is measured accurately, the slope of the semi-log unaccomplished moisture content graph will be linear throughout drying. Table 1 shows the equilibrium moisture content of each grape seed variety at each temperature and equilibrium relative humidity condition. Initial moisture content for each grape seed variety is also provided in Table 1 and ranges between 0.324 and 0.387 g/g dry-solid (d.s.), which is within the low-end range reported for grape seeds by Rice (1976).

### 3.2. Effective moisture diffusivity and activation energy

Drying of most food materials occurs in the falling rate period (Wang and Brennan, 1992), and moisture transfer during drying is controlled by internal diffusion (Saravacos and Charm, 1962). Fick’s second law of diffusion, as shown in Eq. (1), has been widely used to describe the drying process during the falling rate period for most biological materials (Saravacos and Charm, 1962; Sablani et al., 2000; Saravacos and Maroulis, 2001) as follows:

\[
\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}
\]

where \( D \) is the moisture diffusivity and \( \rho \) is the moisture content. The moisture diffusivity is determined from the slope and intercept of the semi-log plot of moisture content versus time (McLaughlin and Magee, 1998; Ozdemir and Devres, 1999; McLaughlin, 2006):

\[
\text{RMSE} = \left[ \frac{1}{n} \sum_{i=1}^{n} (\text{MR}_{\text{exp}} - \text{MR}_{\text{predict}}) \right]^2
\]

\[
\chi^2 = \frac{1}{N-n} \sum_{i=1}^{n} (\text{MR}_{\text{exp}} - \text{MR}_{\text{predict}})^2
\]

As RMSE and \( \chi^2 \) approach zero, the closer the prediction is to experimental data. Where RMSE and \( \chi^2 \) compare the differences between the predicted moisture ratios to the experimental moisture ratios, relative percent error compares the absolute differences between the predicted moisture contents with the experimental moisture contents throughout drying (McLaughlin and Magee, 1998; Ozdemir and Devres, 1999):

\[
\text{PE} (%) = 100 \left[ \frac{\sum_{i=1}^{n} |\text{MR}_{\text{exp}} - \text{MR}_{\text{predict}}|}{\text{MR}_{\text{exp}}} \right]
\]

The relative percent errors below 10% indicate good fit (McLaughlin and Magee, 1998).

### 3.3. Results and discussion

#### 3.3.1. Equilibrium moisture content

Several papers have suggested that since the equilibrium moisture content is significantly less than the initial moisture content...
Table 2
Effective diffusivities and corresponding activation energies for the three grape seed varieties

<table>
<thead>
<tr>
<th>Grape seed variety</th>
<th>Temp (°C)</th>
<th>$D_{\text{eff}}$ (m²/s) $\times 10^{-10}$</th>
<th>$E_a$ (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riesling</td>
<td>40</td>
<td>1.57</td>
<td>40.14</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cab Franc</td>
<td>40</td>
<td>3.89</td>
<td>31.47</td>
<td>0.9916</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>8.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concord</td>
<td>40</td>
<td>2.93</td>
<td>30.45</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5.91</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$D_{\text{eff}}$ is the effective moisture diffusivity representing the conductive term of all moisture transfer mechanisms. This parameter is usually determined from experimental drying curves (Saravacos and Maroulis, 2001). Based on the assumptions of uniform initial moisture distribution, negligible external resistance, negligible temperature gradients, negligible shrinkage during drying, and constant diffusion coefficient, the analytical solution of the diffusion equations for infinite cylinder is given as the following equation (Crank, 1975):

$$\frac{\partial M}{\partial t} = \nabla [D_{\text{eff}}(\nabla M)]$$

(10)

where $J_{0}(x) = 0$ is the Bessel function of the first kind and zero order, and $M_{r}$'s are the roots of this function. Expansion of Eq. (11) of the first three terms is as follows:

$$MR = M - M_{r} = \sum_{r=1}^{\infty} \frac{4}{r^2 \pi^2} \exp(-D_{\text{eff}}x_r^2t). J_{0}(r_2) = 0$$

(11)

The effective moisture diffusivities for each seed variety are within a range to those reported for hull-less seed pumpkin (Sacliker, 2007).

Table 3
Empirical constants of the Page, Lewis, Henderson–Pabis equations

<table>
<thead>
<tr>
<th>Grape seed variety</th>
<th>Temp (°C)</th>
<th>Page equation</th>
<th>Lewis equation</th>
<th>Henderson–Pabis equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k$ (min⁻¹) $N$ $R^2$</td>
<td>$k$ (min⁻¹) $R^2$</td>
<td>$k$ (min⁻¹) $a$ $R^2$</td>
</tr>
<tr>
<td>Riesling</td>
<td>40</td>
<td>7.42 $\times 10^{-4}$ 0.8328 0.9999</td>
<td>1.42 $\times 10^{-4}$ 0.9991</td>
<td>1.45 $\times 10^{-4}$ 0.9991</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9.14 $\times 10^{-4}$ 0.8628 0.9794</td>
<td>2.83 $\times 10^{-4}$ 0.9938</td>
<td>2.79 $\times 10^{-4}$ 0.9726</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.13 $\times 10^{-3}$ 0.8900 0.9830</td>
<td>4.24 $\times 10^{-4}$ 0.9971</td>
<td>4.24 $\times 10^{-4}$ 0.9704</td>
</tr>
<tr>
<td>Cab Franc</td>
<td>40</td>
<td>2.80 $\times 10^{-3}$ 0.7062 0.9603</td>
<td>2.23 $\times 10^{-3}$ 0.9845</td>
<td>2.19 $\times 10^{-3}$ 0.9588</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>3.42 $\times 10^{-3}$ 0.7149 0.9829</td>
<td>3.06 $\times 10^{-4}$ 0.9824</td>
<td>3.10 $\times 10^{-3}$ 0.9786</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>4.11 $\times 10^{-3}$ 0.7260 0.9946</td>
<td>4.27 $\times 10^{-3}$ 0.9894</td>
<td>4.26 $\times 10^{-3}$ 0.9899</td>
</tr>
<tr>
<td>Concord</td>
<td>40</td>
<td>1.28 $\times 10^{-3}$ 0.7996 0.9916</td>
<td>2.13 $\times 10^{-3}$ 0.9889</td>
<td>2.01 $\times 10^{-3}$ 0.9015</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.38 $\times 10^{-3}$ 0.7412 0.9918</td>
<td>2.47 $\times 10^{-3}$ 0.9955</td>
<td>2.39 $\times 10^{-3}$ 0.9411</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.90 $\times 10^{-3}$ 0.7101 0.9876</td>
<td>3.30 $\times 10^{-3}$ 0.9846</td>
<td>3.21 $\times 10^{-3}$ 0.9377</td>
</tr>
</tbody>
</table>

Table 4
Model prediction evaluation

<table>
<thead>
<tr>
<th>Grape seed variety</th>
<th>Temp (°C)</th>
<th>Page equation</th>
<th>Lewis equation</th>
<th>Henderson–Pabis equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>RMSE $A^2$ ($\times 10^{-10}$) PE</td>
<td>RMSE $A^2$ ($\times 10^{-10}$) PE</td>
<td>RMSE $A^2$ ($\times 10^{-10}$) PE</td>
</tr>
<tr>
<td>Riesling</td>
<td>40</td>
<td>0.0730 0.295 7.16</td>
<td>0.0236 0.058 2.35</td>
<td>0.0256 0.009 2.10</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0393 0.196 5.86</td>
<td>0.0355 0.167 4.28</td>
<td>0.0385 0.188 4.44</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0417 0.188 5.43</td>
<td>0.0217 0.055 2.97</td>
<td>0.0222 0.057 4.64</td>
</tr>
<tr>
<td>Cab Franc</td>
<td>40</td>
<td>0.0528 0.298 7.32</td>
<td>0.0355 0.134 2.88</td>
<td>0.0364 0.140 3.13</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0664 0.539 10.64</td>
<td>0.0293 0.106 4.28</td>
<td>0.0308 0.116 5.78</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0387 0.213 6.56</td>
<td>0.0205 0.047 4.37</td>
<td>0.0212 0.050 4.70</td>
</tr>
<tr>
<td>Concord</td>
<td>40</td>
<td>0.0194 0.041 2.79</td>
<td>0.0452 0.219 4.09</td>
<td>0.0550 0.324 2.65</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0338 0.148 3.41</td>
<td>0.0224 0.055 3.14</td>
<td>0.0292 0.098 2.56</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0346 0.188 3.00</td>
<td>0.0395 0.195 4.98</td>
<td>0.0449 0.240 4.48</td>
</tr>
</tbody>
</table>

where $N_r$ is the Fick number ($D_{\text{eff}}/r^2$). For long drying time when the Fick number, $D_{\text{eff}}/r^2$, is greater than 0.1 or MR is less than 0.6, the first term of the series solution dominates (Crank, 1975; Rizvi, 1986):

$$\ln(MR) = 0.692 - \frac{5.783D_{\text{eff}}}{R} t$$

(13)

The effective moisture diffusivity can be determined from the slope of the normalized plot of the unaccomplished moisture ratio, $\ln(MR)$ vs time, using the following equation:

$$D_{\text{eff}} = -\frac{\text{slope}(r^2)}{5.783}$$

(14)

The activation energy is determined from the slope of the Arrhenius plot, $\ln(D_{\text{eff}})$ vs. $1/T$. Table 2 shows the activation energy for each seed variety, which ranges between 30.45 and 40.14 kJ/mol and corresponds to reported activation energies for food materials (Saravacos and Maroulis, 2001) and similar to the activation energy reported for hull-less seed pumpkin, which was 33.15 kJ/mol (Sacliker, 2007). Thus, the temperature dependence of the three grape

where $k_0$ is the pre-exponential factor of the Arrhenius equation (m²/s), $E_a$ is the activation energy (kJ/mol), $R$ is the universal gas constant (kJ/mol K), and $T$ is the absolute air temperature (K). The activation energy is determined from the slope of the Arrhenius plot, $\ln(D_{\text{eff}})$ vs. $1/T$. Table 2 shows the activation energy for each seed variety, which ranges between 30.45 and 40.14 kJ/mol and corresponds to reported activation energies for food materials (Saravacos and Maroulis, 2001) and similar to the activation energy reported for hull-less seed pumpkin, which was 33.15 kJ/mol (Sacliker, 2007). Thus, the temperature dependence of the three grape varieties.
seed varieties can be represented by the following equations: 

**Riesling:**

\[
D_{\text{eff}} = 7.79 \times 10^{-5} \exp\left(\frac{-4828.51}{T}\right)
\]  

**Cab Franc:**

\[
D_{\text{eff}} = 6.77 \times 10^{-5} \exp\left(\frac{-3785.11}{T}\right)
\]

3.3. Thin-layer drying models

The empirical drying constants for each grape seed variety at each temperature are given in Table 3. The coefficients of determination \((R^2)\) for the drying rate constants of all three thin-layer drying models for three grape varieties were above 0.96 for all values, with all but two being above 0.98. These high coefficients of determination are due to the highly linear plots of the unaccomplished moisture content, which are perhaps due to accurate equilibrium moisture contents. The drying rate constants for all three thin-layer models and for all three grape seed varieties were similar to those of hull-less seed pumpkin (Sacilik, 2007), and the drying rate constants for all three grape seed varieties in Page’s model were similar to those of tomato seeds (Sogi et al., 2003). The drying constants for the Lewis and Henderson–Pabis models were similar, which can be explained by the intercept constants for the Henderson–Pabis model being close to 1. An interesting physical characteristic comparison of all three seed varieties was the obvious softness of the Cab Franc seeds, perhaps as a result of being in a fermentation environment. Also, the drying rate constant and the effective diffusivity values for Cab Franc seeds were the highest. Extraction of phytochemicals from seeds occurs during fermentation of red wines (Kovac et al., 1992), and after 5–7 days of fermentation, seed coat cuticle is dissolved by ethanol produced and extraction of tannins predominates (Zoecklein, 2006). This removal of the cuticle during fermentation may result in softening of the seeds and allow moisture to be removed at a greater rate during drying. In contrast, Concord seeds were from grape juice processing and do not undergo fermentation, and Riesling seeds are from white wine processing where the skins and seeds are removed prior to fermentation (Boulton et al., 1999). Therefore, Concord and Riesling seeds were not exposed to ethanol, so their cuticles remained intact resulting in their rate of moisture loss being less than that of the Cab Franc seeds.

Table 4 shows the results of the RMSE, \(\chi^2\), and PE for the three thin-layer drying models for each seed variety. Overall, the three models provided good predictions, where the percent error ranged between 4.98% and 2.35% using the Lewis model, between 5.78% and 2.10% using the Henderson–Pabis, and between 10.49% and 2.79% using the Page model. Fig. 3 shows the drying curves of each grape seed variety at each temperature and the corresponding Lewis Model prediction. For drying predictions of Riesling and Cab Franc seeds, the Lewis model was a better fit based on moisture ratio goodness of fit analysis (lower RMSE and \(\chi^2\)) and moisture content fit analysis (lower PE). For Concord seeds, the Page model was a better fit model, though all three thin-layer models had an error below 5%.

4. Conclusion

This study showed that the drying of grape seeds can be accurately predicted using the thin-layer models of either the Page, Lewis, or Henderson–Pabis models. The Lewis model proved to be an overall better prediction model for drying of each grape seed variety. The moisture transfer can be described by diffusion, where the effective diffusivities were within ranges of other seeds, and the temperature dependence of the effective moisture diffusivities was shown to follow an Arrhenius relationship. This study also showed the importance of the equilibrium moisture content on the slope and linearity of the normalized unaccomplished moisture content curve in determining the drying rate constants.
Drying grape seeds is an essential in both stabilizing the seeds for preventing microbial and chemical degradation and producing the seeds in a form suitable for oil extraction. Seeds from grape and wine processing plants are contained within waste pomace. From a practical standpoint, drying the pomace and the seed together may not be a promising practice due to the extensive energy requirement to remove the added significant moisture load from the pomace. Also, from preliminary experience, it is much more difficult to separate dry pomace from dry seeds particularly since the ratio of pomace to seeds is very high and re-wetting was required. By separating the pomace first, drying of the seeds is preferred where separating a small amount of dry pomace, or chaffe, is much easier. This study provides information to dry high volume and highly valuable seed waste from wineries and grape juice manufactures to produce grape seed oil.

References