Influence of temperature, air velocity and ultrasound application on drying kinetics of grape seeds

Gabriela Clemente,¹ Neus Sanjuán,¹ Juan Andrés Cárcel,¹ and Antonio Mulet¹

¹Agro-Food Processes Analysis and Simulation Group (ASPA). Food Technology Department. Universitat Politècnica de València, C/ Camí de Vera, s/n, Valencia 46022, Spain

*Corresponding author. Tel.: +34 963 87 91 48; Fax: +34 963 87 98 39
E-mail address: gclemen@tal.upv.es

ABSTRACT

The objective of this study was to determine the influence of temperature, air velocity and ultrasound application on the drying kinetics of grape seeds. The drying kinetics were determined at 1.0, 1.5, 2.0 and 3.0 m/s and at 40, 50, 60 and 70ºC. At 1.0 and 1.5 m/s, the experiments were carried out with and without ultrasound application. To establish the influence of the variables on the drying kinetics, the results were modeled by means of both the Peleg and a diffusion model. The activation energy was determined (Arrhenius’ equation). For an air velocity of over 1.5 m/s, it was determined that the external resistance to mass transfer was negligible. No influence of ultrasound application was observed, probably due to the fact that grape seeds are very hard and have a low level of porosity.

Keywords: Grape seeds; Ultrasound; Air velocity; Effective diffusivity; activation energy
INTRODUCTION

Spain is the European country which has the largest surface area dedicated to grape cultivation with 1.113 million hectares, 97.4% of which are for the wine industry\textsuperscript{[1]}.

By weight, around 13\% of the grapes processed in the wine industry end up as a by-product after pressing. The by-product is called grape pomace and it consists of skins, seeds and stems\textsuperscript{[2]}. According to the literature\textsuperscript{[3, 4]}, the seeds are a rich source of polyphenols and oil. The oil from grape seeds is free from cholesterol and is low in saturated fats. It also has linoleic acid, high density lipoproteins, E vitamin and antioxidants. Thus, it is an oil with interesting nutritional properties.

The by-product must be stabilised before extracting the compounds of interest and, to this end, drying is the most commonly used process. Drying stabilizes the raw material by reducing its water content and it also decreases the amount of solvent used in subsequent extraction processes\textsuperscript{[5]}. Convective drying, using air at different temperatures and velocity, is the most commonly used drying system. The initial moisture content of grape seeds is around 0.82 kg water/kg dry matter and usually drops by between 0.02 and 0.07 kg water/kg dry matter. Convective air drying is a highly demanding operation. Thus, in order to reduce energy consumption it is necessary to determine the influence of the process conditions on the dehydration kinetics. In addition, process conditions have an influence on the quality of the final product.

One important operating condition is temperature. The dehydration rate increases when the temperature rises due to the fact, under these conditions, the water molecules increase their mobility. Nevertheless, an increase in temperature may affect compounds which are of interest.

The air drying velocity is another important process condition. It influences the external resistance to heat and mass transfer. Thus, if the external resistance is negligible, an increase in the air drying velocity will not influence the drying kinetics. For that reason, from an energy point of view, it is important to establish a threshold value for air velocity when a particular product is dehydrated\textsuperscript{[6, 7]}.

Another process condition which may be taken into account is the relative humidity of the drying air. This parameter, together with temperature, determines the drying potential of the air. When the air has a high temperature and a low relative humidity, its drying potential will be high. In convective drying, room air is heated until it reaches the temperature sought for the drying process. In this operation, the drying potential of air is increased because its temperature rises and its level of relative humidity falls.
Recently, the application of high intensity ultrasound during air drying has been considered as an intensification technology. Ultrasound is mainly applied in food processes due to the effects it exerts on heat or mass transfer operations[8]. Ultrasonic waves are transmitted in a relatively easy way in liquids. For that reason, most of the ultrasonic applications reported in literature are found in liquid–liquid and liquid–solid systems[9]. Some examples of these applications can be found in the literature[8]. In gas-solid systems, like convective air drying, the high impedance mismatch and the high ultrasonic energy attenuation in air make the transmission of ultrasound from the transducer to the air and from the air to the solid difficult[10]. Nevertheless, some studies can be found in literature into high intensity ultrasound-assisted convective air drying[10, 11, 12, 13, 14]. In some cases, it has been found that over 70% less time is needed for the drying process[14]. Nevertheless, as the effects of ultrasounds are product and drying variables (temperature, air velocity) dependent, the drying gains should be considered case by case. So far, all this research is laboratory scale and no ultrasound application has been found in the industrial drying of food products.

Power ultrasound assisted convective drying (acoustic drying) may constitute a means of improving the dehydration rate without significantly heating the material[8]. The application of ultrasound during convective air drying increases the kinetics of dehydration, affecting both the internal and the external resistance[8]. As regards internal resistance, when ultrasound travels across a medium, it produces alternating cycles of expansions and contractions (sponge effect), helping the water to leave easily and diminishing the internal resistance to mass transfer[15]. These effects are product dependent, and the texture of the material is a key parameter. Ozuna et al.[16] found that the sponge effect was more intense in soft products. It seems that the expansions and contractions would be diminished in hard products due to the fact that their solid matrix moves with difficulty.

The influence of ultrasound on the external resistance to mass transfer could be linked to the generation of differential pressures and the microstirring at the interfaces[8]. Although these effects are not observed, if internal resistance prevails, as consequence no change will be found in the mass transfer coefficient identified.

It is essential to model the drying kinetics in order to carry out the engineering design of the drying processes and evaluate the effects of the variables considered. In the literature, research can be found into modeling the drying of different grain food, for example, soya bean[17], rice[18] or corn[19]. These models can be theoretical or empirical. The theoretical models, for example the diffusion model, are based on the understanding of the phenomenon under study, whereas the empirical models, for example Peleg’s model, are based on empirical approximations which are product of the observation or experimentation. For that reason, theoretical models are more
complicated from a mathematical point of view. Empirical models are easy to solve and sometimes the results provided are good enough for the purpose sought. In general, the simplest model is always recommended in order to facilitate its solution and use in real time for control or optimal operation management[7].

In the literature, there is scarce research into the influence of the drying conditions on the dehydration process of grape seeds and the effect of ultrasounds on a hard product is lacking. Thus, the aim of this work was to determine the influence of temperature, air velocity and the application of ultrasounds on the drying kinetics of grape seeds, in order to provide a sound basis for industrial process management.

MATERIALS AND METHODS

Raw material

Grape pomace from the wine processing of red grapes (Vitis vinifera var Bobal) was collected from a winery located in Requena (Valencia, Spain). It was packed in a plastic film, in order to avoid moisture loss until its constituents were separated, and refrigerated at 2 ± 0.2 ºC. The separation of skins, seeds and stems was performed manually. After separation, grape seeds were again plastic wrapped and refrigerated at 2 ± 0.2 ºC until the determination of the drying kinetics.

The initial moisture content of grape seeds was determined by drying them at 70 ºC under vacuum conditions until constant weight was reached[20].

Determination of experimental drying kinetics

The experimental drying kinetics were obtained in triplicate at 1.0, 1.5, 2.0 and 3.0 m/s air velocity and 40, 50, 60 and 70ºC air temperature. All these temperatures were under the smoke point of the grape seed oil[4]. The relative humidity at the air inlet for all the drying kinetics was 71.4 ± 6.0 %. When the air was heated, this value 1 falls to 15.0 ± 8.9 %. In order to determine the influence of ultrasound application, the drying kinetics were obtained in triplicate at 1.0 and 1.5 m/s with and without ultrasound application (30.8 kW/m³). When ultrasounds were applied, their intensity measured as Sound Pressure Level was 154.1 dB and the electroacoustic efficiency was around 60-70 %. For experimental drying kinetics determination, the convective dryer described previously by Cárcel at al.[11] was used (Figure 1). This equipment is a pilot scale convective dryer modified to apply power ultrasound. The dryer has remote control temperature and air velocity and the weight of
the sample was monitored periodically during the drying period. Grape seeds were placed into the drying chamber on a perforated parallel plate support, in order to guarantee that the hot air affects the entire surface of the seeds. In each experiment, 22.3 ± 2.3 g of grape seeds were used. The drying was carried out in stationary bed.

**Figure 1.** Convective dryer. (1) Fan; (2) Heating; (3) Anemometer; (4) Pneumatic three-way valve; (5) Temperature probe Pt-100; (6) Coupling material; (7) Elevator; (8) Ultrasonic transducer; (9) Braces; (10) Parallel plate support; (11) Scale; (12) Impedance matching unit; (13) Digital watimeter; (14) Generator of power ultrasound; (15) Computer-controller.

**Modelling of experimental drying kinetics**

Two models were used to model the experimental drying kinetics: Peleg’s model and a simplified model based on Fick’s second law.

**Peleg’s model**

Peleg’s model[^21] has been used satisfactorily to model the dehydration of grain food products[^22]. It is shown in equation 1.

\[
X = X_0 - \frac{t}{k_1 + k_2 t}
\]  

(1)

The constant, \(k_1\), is a kinetic parameter. Sopade et al.[^23] proposed describing the effect that temperature has on \(k_1\) by means of the Arrhenius equation and the activation energy can be assessed as follows (equation 2).
\[ \frac{1}{k_1} = \frac{1}{k_p} \exp \left( \frac{-E_a}{9RT} \right) \]  \hspace{1cm} (2)

From equation 2, the activation energy can be identified from the slope of the fitted straight line by plotting $1/k_1$ versus $\ln(1/T)$.

**Diffusion model**

As no constant drying rate period was observed, the initial moisture content and critical moisture content were considered equal; thus, only the falling drying rate was considered in the model\cite{24}. Shrinkage and external resistance were not considered in this model. Seeds were considered to be homogeneous, isotropic and spherically shaped. The governing equation (equation 3), the initial equation (equation 4) and the boundary conditions (equations 5 and 6) are shown:

\[ \frac{\partial X_i}{\partial t} = D_e \left( \frac{\partial^2 X_i}{\partial r^2} + \frac{2}{r} \frac{\partial X_i}{\partial r} \right) \]  \hspace{1cm} (3)

\[ X_i(r,0) = X_0 \]  \hspace{1cm} (4)

\[ X_i(R,t) = X_e \]  \hspace{1cm} (5)

\[ \frac{\partial X_i}{\partial r}(0,t) = 0 \]  \hspace{1cm} (6)

The equilibrium moisture content was calculated by means of Peleg’s model (equation 7).

\[ X_e = X_0 - \left( \frac{1}{k_2} \right) \]  \hspace{1cm} (7)

The diffusion model was solved by using the method of the Separation of Variables and the effective diffusivity was identified by means of an optimization method\cite{25,24}. The objective function was the squared differences between the experimental and calculated values of the average moisture content. The minimization of the objective function was performed using the tool Solver from Microsoft Excel.

The influence of temperature on the effective diffusivity was assessed by means of the Arrhenius equation (equation 8).

\[ D_e = D_0 \exp \left( \frac{-E_a}{9RT} \right) \]  \hspace{1cm} (8)
Evaluation of the quality of fit

The goodness of fit for the two models was assessed by means of the explained variance\(^{[26]}\). Additionally, both a t-test and a Lilliefors test were performed at the 5% significance level for both models and also for the Arrhenius equation. The t-test served to evaluate whether the data in the residual vector are random and have a normal distribution with mean 0 and unknown variance, against the alternative that the mean is not 0. The Lilliefors test was used to test the assumption that the residual vector comes from normal distributions. The “ttest” function and “lillietest” function of the software Matlab\(^{®}\) R2011\(^{[27]}\) were used to perform the t-test and the Lilliefors test, respectively.

The result of the t-test was a confidence interval \((C_i)\). There was a 95% probability of the residual vector mean being in the confidence interval.

In the Lilliefors test, the statistical value \((kstat)\) and the critical value \((critval)\) were the results. If \(kstat\) was lower than \(critval\), there was a 95% probability of the normality of the residuals being established.

RESULTS AND DISCUSSION

Experimental drying kinetics

In Figures 2, 3 and 4 some experimental drying kinetics are plotted in order to illustrate the effect of temperature, air velocity and ultrasound application. Each of the represented experimental drying kinetics is the average of the three replications for each of the experimental conditions. The time interval measurements were the same for all the experiments, which allowed the data obtained on the three replicates to be averaged.

As can be observed in Figure 2, in the range considered, when the temperature rises the drying kinetics also increases. This result coincides with what has been found in other studies\(^{[28,29]}\).
**Figure 2.** Experimental drying kinetics at different temperatures and an air velocity of 1 m/s (without ultrasound application)

**Figure 3.** Experimental drying kinetics at different air velocities and a temperature of 40ºC (without ultrasound application)

**Figure 4.** Experimental drying kinetics at 40 ºC and 1m/s with and without ultrasound application
The influence of drying air velocity is assessed in Figure 3. When the air velocity increases from 1 m/s to 1.5 m/s, less time is needed to attain a given moisture content. Nevertheless, for an air velocity of between 1.5 and 3 m/s, this parameter is only observed to have a slight influence on drying kinetics. It seems that the external resistance to mass transfer is negligible for an air velocity of over 1.5 m/s. Similar results have been found by other authors when studying different agro-food products: broccoli, turmeric or meat, where different velocity thresholds were observed depending on the product.

Figure 4 shows that, under the experimental conditions 1 in this study, there was no influence of ultrasound application on the dehydration kinetics.

**Modelling**

Modelling was carried out for all the drying kinetics separately and, after that, the average and standard deviations were calculated for the parameters obtained from each model.

Table 1 shows the results for the parameters of Peleg’s model. The percentage of explained variance for all the drying kinetics was over 98%, thus the agreement between the experimental and calculated values can be considered a good one. As regards the t-test, the 0 is contained in every confidence interval for all the drying kinetics. As to the Lilliefors test, the statistical value is lower than the critical value for all the experimental conditions. Thus, the residuals followed a normal distribution and their mean was 0, with a significance level of 5%. As an example, in Figure 5 a comparison between two experimental drying kinetics and Peleg’s model results are shown. The same behavior was observed for all the other drying conditions.

![Figure 5](image.png)

**Figure 5.** Comparison between modeled by Peleg’s model and experimental drying curves for two drying conditions (40°C, 1.5 m/s, without ultrasound and 70°C, 1.5 m/s, with ultrasound)
Table 1. Results for the parameters of Peleg’s model, sd (standard deviation), var (explained variance)

<table>
<thead>
<tr>
<th>Sample</th>
<th>k₁ ± sd</th>
<th>k₂ ± sd</th>
<th>var (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 m/s without US</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>4470 ± 61</td>
<td>2.09 ± 0.21</td>
<td>99.6</td>
</tr>
<tr>
<td>50 °C</td>
<td>3006 ± 85</td>
<td>1.90 ± 0.52</td>
<td>90.7</td>
</tr>
<tr>
<td>60 °C</td>
<td>2100 ± 49</td>
<td>1.77 ± 0.01</td>
<td>99.5</td>
</tr>
<tr>
<td>70 °C</td>
<td>1818 ± 68</td>
<td>1.55 ± 0.25</td>
<td>97.7</td>
</tr>
<tr>
<td>1.5 m/s without US</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>4049 ± 72</td>
<td>1.79 ± 0.32</td>
<td>99.5</td>
</tr>
<tr>
<td>50 °C</td>
<td>2450 ± 172</td>
<td>1.70 ± 0.02</td>
<td>95.0</td>
</tr>
<tr>
<td>60 °C</td>
<td>1652 ± 37</td>
<td>1.51 ± 0.16</td>
<td>99.8</td>
</tr>
<tr>
<td>70 °C</td>
<td>1328 ± 136</td>
<td>1.46 ± 0.02</td>
<td>95.8</td>
</tr>
<tr>
<td>2 m/s without US</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>3424 ± 149</td>
<td>1.81 ± 0.11</td>
<td>99.7</td>
</tr>
<tr>
<td>50 °C</td>
<td>2317 ± 85</td>
<td>1.72 ± 0.03</td>
<td>99.8</td>
</tr>
<tr>
<td>60 °C</td>
<td>1427 ± 115</td>
<td>1.58 ± 0.02</td>
<td>99.7</td>
</tr>
<tr>
<td>70 °C</td>
<td>1162 ± 9</td>
<td>1.42 ± 0.03</td>
<td>90.1</td>
</tr>
<tr>
<td>3 m/s without US</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>2646 ± 48</td>
<td>1.96 ± 0.12</td>
<td>99.8</td>
</tr>
<tr>
<td>50 °C</td>
<td>1496 ± 45</td>
<td>1.80 ± 0.01</td>
<td>99.9</td>
</tr>
<tr>
<td>60 °C</td>
<td>1137 ± 78</td>
<td>1.61 ± 0.02</td>
<td>91.4</td>
</tr>
<tr>
<td>70 °C</td>
<td>843 ± 122</td>
<td>1.50 ± 0.11</td>
<td>99.9</td>
</tr>
<tr>
<td>1 m/s with US</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>4400 ± 40</td>
<td>1.70 ± 0.19</td>
<td>95.5</td>
</tr>
<tr>
<td>50 °C</td>
<td>3018 ± 28</td>
<td>1.66 ± 0.15</td>
<td>99.4</td>
</tr>
<tr>
<td>60 °C</td>
<td>2076 ± 20</td>
<td>1.61 ± 0.14</td>
<td>99.2</td>
</tr>
<tr>
<td>70 °C</td>
<td>1789 ± 24</td>
<td>1.46 ± 0.10</td>
<td>98.1</td>
</tr>
<tr>
<td>1.5 m/s with US</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>3792 ± 195</td>
<td>1.60 ± 0.14</td>
<td>98.6</td>
</tr>
<tr>
<td>50 °C</td>
<td>2152 ± 249</td>
<td>1.56 ± 0.01</td>
<td>98.8</td>
</tr>
<tr>
<td>60 °C</td>
<td>1707 ± 31</td>
<td>1.51 ± 0.14</td>
<td>98.7</td>
</tr>
<tr>
<td>70 °C</td>
<td>1117 ± 102</td>
<td>1.45 ± 0.09</td>
<td>99.6</td>
</tr>
</tbody>
</table>
As expected, the kinetic parameter $k_1$ decreased when the temperature rose. It can also be observed that the values for $k_1$ were similar regardless of whether ultrasounds were applied or not. Thus, it seems that the application of ultrasounds has no influence on the drying kinetics under the drying conditions considered in this study.

For all the drying kinetics, the equilibrium moisture content calculated by means of Peleg’s model was $0.05 \pm 0.02$ kg water/kg dry matter. This low equilibrium moisture content value indicates that the relative humidity of the drying air did not influence the drying kinetics.

After modeling the experimental results by means of the diffusion model, the results shown in Table 2 were obtained. There is a good agreement between the experimental and calculated values. The explained variance was higher than 90.5% for all the drying kinetics and the residuals followed a normal distribution, with a mean of 0 and a significance level of 5%.

Figure 6 represents an example of the comparison between calculated by means of diffusion model and experimental drying curves for two experimental drying conditions. The agreement between experimental and calculated values was good for all the drying conditions considered.

![Graph comparing experimental and calculated drying curves](image)

**Figure 6.** Comparison between modeled by diffusion model and experimental drying curves for two drying conditions (40°C, 1.5 m/s, without ultrasound and 70°C, 1.5 m/s, with ultrasound)

The effective diffusivity values obtained are in the range reported by Saravacos and Maroulis\cite{31} for agro-food products, which is between $1 \cdot 10^{-11}$ and $1 \cdot 10^{-8}$. The values also coincide with others found in literature for grape seeds\cite{29}.
**Table 2.** Effective diffusivity ($D_e$), standard deviation (sd) and explained variance (% var) for the different drying conditions

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1 m/s</th>
<th></th>
<th></th>
<th>1.5 m/s</th>
<th></th>
<th></th>
<th>2 m/s</th>
<th>3 m/s</th>
<th></th>
<th></th>
<th>Without US</th>
<th>Without US</th>
<th>Without US</th>
<th>Without US</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature</strong></td>
<td><strong>($D_e \pm sd) \times 10^{10}$ m$^2$/s</strong></td>
<td><strong>% var</strong></td>
<td><strong>($D_e \pm sd) \times 10^{10}$ m$^2$/s</strong></td>
<td><strong>% var</strong></td>
<td><strong>($D_e \pm sd) \times 10^{10}$ m$^2$/s</strong></td>
<td><strong>% var</strong></td>
<td><strong>($D_e \pm sd) \times 10^{10}$ m$^2$/s</strong></td>
<td><strong>% var</strong></td>
<td><strong>($D_e \pm sd) \times 10^{10}$ m$^2$/s</strong></td>
<td><strong>% var</strong></td>
<td><strong>($D_e \pm sd) \times 10^{10}$ m$^2$/s</strong></td>
<td><strong>% var</strong></td>
<td><strong>($D_e \pm sd) \times 10^{10}$ m$^2$/s</strong></td>
<td><strong>% var</strong></td>
</tr>
<tr>
<td>40 °C</td>
<td>0.55±0.02</td>
<td>95.5</td>
<td>0.51±0.04</td>
<td>96.0</td>
<td>0.68±0.04</td>
<td>96.6</td>
<td>0.65±0.08</td>
<td>95.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>0.78±0.03</td>
<td>93.2</td>
<td>0.75±0.08</td>
<td>90.7</td>
<td>1.08±0.04</td>
<td>94.2</td>
<td>1.01±0.05</td>
<td>93.7</td>
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<tr>
<td>60 °C</td>
<td>1.18±0.12</td>
<td>95.8</td>
<td>1.19±0.04</td>
<td>91.0</td>
<td>1.55±0.04</td>
<td>96.3</td>
<td>1.43±0.12</td>
<td>95.5</td>
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</tr>
<tr>
<td>70 °C</td>
<td>1.56±0.14</td>
<td>92.9</td>
<td>1.48±0.23</td>
<td>90.8</td>
<td>1.87±0.05</td>
<td>95.2</td>
<td>1.85±0.13</td>
<td>92.3</td>
<td></td>
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</tr>
</tbody>
</table>

**Influence of temperature**

As expected, there was an influence of the temperature on $k_1$ and $D_e$ as can be seen in Tables 1 and 2, respectively. This influence was assessed in terms of the Arrhenius equation (equation 2 for Peleg’s model and equation 8 for the diffusion model). Table 3 shows the activation energy and the
pre-exponential values obtained. Regarding to t-test and Lilliefors test, the residuals followed a normal distribution, with a mean of 0 and a significance level of 5% when the Arrhenius equation was used for the calculation of $E_a$ from both models (the diffusion and Peleg’s). Figure 7 shows the values of $k_1$ calculated by the Arrhenius equation versus $k_1$ from Peleg’s model. The fit between the $D_e$ from the diffusion model and from the Arrhenius equation is represented in Figure 8. The correlation coefficient was 0.99 and 0.97 respectively; thus, the Arrhenius equation satisfactorily described the influence of temperature on the drying kinetics.

Table 3. Activation energy ($E_a$, kJ/mol) obtained by means of both models considered. CI (Confidence Interval, 95%). Pre-exponential factors, $D_0$ (diffusion model) and $k_p$ (Peleg’s model)

<table>
<thead>
<tr>
<th></th>
<th>Peleg’s model</th>
<th>Diffusion model</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ ± CI (kJ/mol)</td>
<td>$k_p$</td>
<td>var (%)</td>
<td>$E_a$ ± CI (kJ/mol)</td>
<td>$D_0$ ($m^2/s$)*10^5</td>
</tr>
<tr>
<td>1 m/s</td>
<td>with US</td>
<td>27.8 ± 4.3</td>
<td>0.094</td>
<td>97.1</td>
<td>31.6 ± 4.9</td>
</tr>
<tr>
<td></td>
<td>without US</td>
<td>27.4 ± 5.1</td>
<td>0.113</td>
<td>96.7</td>
<td>32.2 ± 8.6</td>
</tr>
<tr>
<td>1.5 m/s</td>
<td>with US</td>
<td>34.8 ± 8.2</td>
<td>0.005</td>
<td>94.8</td>
<td>30.3 ± 4.1</td>
</tr>
<tr>
<td></td>
<td>without US</td>
<td>33.0 ± 5.6</td>
<td>0.012</td>
<td>95.1</td>
<td>31.8 ± 6.0</td>
</tr>
<tr>
<td>2 m/s</td>
<td>without US</td>
<td>34.0 ± 4.7</td>
<td>0.007</td>
<td>96.7</td>
<td>28.8 ± 5.4</td>
</tr>
<tr>
<td>3 m/s</td>
<td>without US</td>
<td>33.5 ± 5.8</td>
<td>0.006</td>
<td>94.3</td>
<td>24.4 ± 5.2</td>
</tr>
</tbody>
</table>

Figure 7. Values of $k_1$ calculated by Arrhenius equation versus $k_1$ from Peleg’s model for all the temperatures under study
As can be observed in table 3, the $E_a$ values were not significantly influenced by air velocity. According to Ramallo et al.\cite{32}, the activation energy values for agro-food products range from 15 to 95 kJ/mol. Thus, the values in table 3 are in the range reported by these authors. They are also similar to the values found in literature for some products, for example 30.45 kJ/mol for grape seeds\cite{29} or 30.37 kJ/mol for aloe vera\cite{33}.

No significant differences can be observed between the values of $E_a$ given by Peleg’s model or those provided by the diffusion model. Using Peleg’s model to calculate the activation energy offers the advantage that it is easier from a mathematical point of view and, as can be seen in Table 3, the results are comparable with those obtained using the diffusion model.

**Influence of air velocity**

Figure 9 shows the influence that air velocity has on effective diffusivity at 70ºC (no ultrasound application). Similar results were obtained for the other temperatures under study.

**Figure 8.** Values of $D_e$ calculated by Arrhenius equation versus $D_e$ from diffusion model for all the temperatures under study
Figure 9. Influence of air velocity on drying kinetics at 70ºC (no ultrasound application)

For an air velocity between 1.0 and 1.5 m/s, an increase in this parameter leads to a significant increase in effective diffusivity. For an air velocity of over 1.5 m/s, the effective diffusivity is not affected by air velocity. The diffusion model considered in this research work did not take into account the external resistance to mass transfer; thus, calculated $D_e$ included both resistances to mass transfer (internal and external). The effect of an air velocity of between 1.0 and 1.5 m/s on $D_e$ can be attributed to the influence of external resistance to mass transfer for these air velocities. If external resistance is not borne in mind when it is important, the values of $D_e$ can be underestimated\textsuperscript{[7]}. Thus, Figures 3 and 9 seem to indicate that for an air velocity of over 1.5 m/s, the external resistance to mass transfer is negligible when grape seeds are dehydrated. This threshold matches others found in literature\textsuperscript{[34,5,7]}.

Because the models considered described the drying kinetics reasonably well, they can be used to analyze the effects of ultrasounds.

Influence of ultrasound application

Tables 1 and 3 show that, at a particular temperature and for a specific air velocity, there is no significant difference between parameters $k_1$ (Table 1) and $D_e$ (Table 3) obtained for drying kinetics with and without ultrasound application. The activation energy ($E_a$) was not influenced by ultrasound application either.
Ozuna et al.\textsuperscript{16} have identified a relationship between the textural properties of vegetables and how the drying process is affected by the application of ultrasound at 40\textdegree{C} and 1 m/s. This effect was dependent on the ultrasonic power applied: the higher the power, the larger the identified effective diffusivity. Nevertheless, the improvement brought about by the effect of ultrasound on the effective diffusivity was closely correlated with the hardness of the product. These authors found that, when ultrasounds were applied over a wide power range, they only exert a slight influence on the drying kinetics in vegetable products with high levels of hardness. Working on lemon peel and carrot, García-Pérez et al.\textsuperscript{10} dehydrated both products at 40 \textdegree{C} and 1 m/s and found that for the former any power of ultrasound influenced the drying kinetics, whereas for the latter, this influence was detected only from a threshold power value. It seems that ultrasound is less effective on the internal resistance of hard products. Thus, the mechanical compressions and expansions ("sponge effect") produced by ultrasound application, which enhanced the water removal, were more intense in soft products.

According to Milani et al.\textsuperscript{35}, the hardness of the grape seeds is 45.83 N, a higher value than for carrot\textsuperscript{16}. For vegetable products with this level of hardness, ultrasound application should show no influence on drying kinetics when applied at 30.8 kW/m\textsuperscript{3}\textsuperscript{16}, which is the maximum power of the equipment used in this research. Thus, the high level of hardness of the grape seeds would explain the fact that ultrasound has no influence on the drying kinetics under the experimental conditions considered.

Figure 9 shows that, at an air velocity of under 1.5 m/s, external resistance affects drying kinetics. As a consequence, ultrasounds should enhance drying kinetics by affecting external resistance. Nevertheless, this was not the case; this could be linked to the interaction of acoustic energy with the product. Apparently, there is a large reflection of the acoustic energy impinging on the product, which could be due to the great mismatch of acoustic impedance (air – seed) and to the smooth external layer of the seeds. This effect merits further investigation. Apparently, there is not only a phenomena linked to applied power, but also to product characteristics.

CONCLUSION

The experimental drying kinetics of grape seeds were modelled using both Peleg’s model and the diffusion model. The results obtained are similar to others in literature. There was an observed increase in the drying kinetics when the temperature rose. The activation energy was calculated by means of the two models considered. The value ranged between 27.4 and 34.8 kJ/mol. No significant
differences in the values of $E_a$ were found for any of the drying conditions considered. Peleg’s model had the advantage of being mathematically simple and, consequently, useful for real-time applications.

For an air velocity of 1.5 m/s or higher, the external resistance to mass transfer does not influence the dehydration process under the experimental conditions used in this research. As a consequence, in order to save energy, this threshold should not be exceeded.

Under the experimental conditions considered, ultrasound application had no influence on the dehydration kinetics of grape seeds. This may show that the physical characteristics, hardness and low porosity, of the grape seeds may influence the reflection of the acoustic waves reaching the products. This should be investigated further.

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NOMENCLATURE

$D_e$ effective diffusivity, m$^2$s$^{-1}$

$D_0$ pre-exponential factor, m$^2$s$^{-1}$

$E_a$ activation energy, kJmol$^{-1}$

$k_1$ Peleg’s model parameter, s(kg water/kg dry matter)$^{-1}$

$k_2$ Peleg’s model parameter, (kg water/kg dry matter)$^{-1}$

$k_p$ pre-exponential factor

$t$ time, s

$T$ temperature, K

$X$ mean moisture content, db

$X_{cal}$ calculated mean moisture content, db

$X_e$ equilibrium moisture content, db

$X_{exp}$ experimental mean moisture content, db
$X_f$    local moisture content, db

$X_0$    initial moisture content, db

$r$    length co-ordinate, m

$R$    radius of the seeds, m

$\mathbb{R}$    constant of perfect gases (8.31), JK$^{-1}$mol$^{-1}$

$\Psi$    dimensionless moisture content, $\Psi = (X - X_e)/(X_0 - X_e)$

REFERENCES


