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Research Article

Freeze-drying kinetics and diffusion modeling of hawthorn

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ABSTRACT

This study tests freeze-drying (FD) technology (Scanvac Coolsafe model, Labogene brand) to preserve hawthorn fruit. First, 100g hawthorn slices were frozen and then freeze-dried. Kinetic models were applied, and hawthorn's moisture ratio and weight loss were noted after every two hours during the 14-hour freeze-drying process. Matlab program is used to perform a total of eight kinetic drying models. Results show that the root mean square error was 0.011063, the highest determination coefficient was 0.9987, the least chi-square was 1.959×10^{-4}, and the effective diffusivity was $2.33742\times10^{-10} m^2/s$. The diffusion approach is the best among the eight models.

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INTRODUCTION

Hawthorn (Crataegus) is a member of the Rosaceae plant family and can be found in Europe, Asia, and North America [1]. It is frequently found in Turkey, and ripen hawthorn fruit can be dark purple, yellow, or green. Mid-autumn marks the time it ripens [2]. Studies have shown that hawthorn can protect against hypotension, cardiovascular problems, and hypercholesterolemia [3]. As a result, it is utilized as a medication to lower blood cholesterol and enhance cardiovascular function [5]. When examined with an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), it was found that the Turkish wild variety contains significant amounts of sodium, potassium, magnesium, calcium [2]. Aside from these main elements, hawthorn also contains lipids, vitamins, carbs, proteins [6, 7], antioxidants, bioactive compounds, and micronutrients [8]. Biomaterial drying is heat-sensitive, which is true for vegetables, fruits, and other functional foods. When they go through oxidation, thermal decomposition, or long processing time, they undergo deterioration and enzymatic browning. They need specific drying techniques to prevent deformation and deterioration, which extends their shelf life as a drying consequence [6, 7]. Aroma, texture, and color are the main food-quality criteria that make them suitable for consumption, but the drying process might alter such properties depending on the moisture in the dried products. Freeze-drying is needed when a product's ' biological value needs protection [7, 9] because it first freezes the water-rich foods and then treats them using a low-temperature condenser or

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a vacuum. The frozen sample is supplied with heat using conduction. Ice vaporizes through sublimation during primary drying, and the water vapors transfer to the condenser through the vacuum. Then, secondary drying starts with the desorption of water bound to the ice-free sample [10-12]. Acar et al. [13], Liapis et al. [14], Sadikoglu et al. [15] and Sadikoglu and Liapis [16] have mentioned freeze-drying and its steps in detail. According to a few studies, freeze-drying technology is effective for dehydrating products consisting of aromatic compounds like saffron and coffee, which need aroma, flavor, and taste preservation [17, 18] Freeze-drying or lyophilization preserves heat-sensitive serums, pharmaceuticals, biotechnological products, bacterial cultures, teas, fruits, their juices, milk, meat, and vegetables [15, 19]. It is used despite the high cost of freeze drying because it is the only available option to treat heat-sensitive substances for better quality. Since freeze-drying extends a 'product's shelf life, reduces its weight, saves storage space, and does not need cooling; therefore, it is quite useful [20]. Despite the fact that hawthorn is a common fruit with established health benefits, its effective diffusivity, kinetic model, or moisture content have not been determined during the freeze-drying process, which preserves a food's nutritional value better than all other conventional drying methods. To fill this research gap, we selected a frozen hawthorn sample and used a Scanvac Coolsafe device for drying it. Later, we calculated the effective diffusivity and obtained hawthorn's weight loss during freeze-drying using graphs and an empirical model. Freeze-dried fruits have been the subject of numerous experiments. In a study, Krmac et al. [7] found the moisture content (MR) in freeze-dried strawberries (5mm and 7mm thick slices) by determining the weight loss. In another study, Marques and Freire [6] assessed the freeze-drying kinetics of fruits, applying Van Meel, Page, and Chen and Douglas models. They declared the Page Model as the best among the explanatory models for experimental findings. Conducting the same experiment on saffron, Acar et al. [17] froze and dried the samples by applying freeze-drying and sun-drying. After chemical examination, it was found that freeze-drying assures better quality. In an experiment on dehydrating banana puree, For the purpose of producing banana powder, Wang et al. [19] applied vacuum-belt drying (VBD), freeze-drying (FD), and air drying (AD). In order to identify the dried banana powder, they employed gas chromatography-mass spectrometry (GC-MS) and separated it using solid-phase micro-separation (SPME). After statistical analysis, they recommended FD and VBD as preferable procedures rather than AD because they maintain flavor. Apinya et al. [21] conducted a study to assess energy consumption through infrared-assisted freeze-drying (IRAFD) and drying kinetics for making banana chips. According to their findings, compared to freeze-drying, IRAFD significantly reduced drying time (70% time or maximum 213 minutes). They identified the most appropriate drying model using drying kinetics and diffusion models. Slices of kiwi fruit measuring 5.03 x 0.236 mm were used as samples in a study by Maskan et al. [22] to examine the drying qualities of the fruit using hot air, microwaves, and a combination of the two. After the experiment, they studied the samples and calculated their rehydration capacities, shrinkage, and drying rates. They claimed that both microwave drying and the use of both hot air and microwaves accelerated drying and cut down on drying time. Comparing with hot air drying, microwave drying caused more kiwi to shrink. When they combined hot air with a microwave, they observed lower shrinkage than other drying procedures. When microwave drying was applied to dry kiwi slices, the researchers observed lower rehydration capacity and a rapid water absorption rate. In this study, we selected hawthorn for obtaining freeze-dried fruits. Since hawthorn fruit grows in Northern Hemisphere [1], it easily spoils like other water-rich and carbohydrate-rich fruits [6]. Drying is an old food-preserving technique which stops deterioration of the dried food quality. Traditional hot air-drying requires more temperature and a long drying time to remove excess water from the sweet fruit, which seriously damages the fruit flavor, color, density, nutrients, and rehydration capacity [23]. This leads to poor product quality besides long drying duration and limited energy efficiency. When conventional heating is applied, it leads to low heat transfer to the inner part of the fruit because fruits have low thermal conductivity. It is feasible to use freeze-drying (FD) alone or combined with other methods to lessen the quality issues. In the case of freeze-drying, a fruit sample stiffens when it freezes because liquid movement stops inside it; therefore, it results in a crispier product when hot air is used for drying [21]. Thus, our study determines a suitable kinetic drying model for hawthorn freeze-drying and calculates its weight loss.

MATERIALS AND METHOD

We performed the experiment seven times using 100g samples of hawthorn for this experimental study. The fruit was put in the containers, as shown in Figure 1, and was cut into slices that were 5 mm thick. All seven hawthorn samples were placed in a deep freezer in a sliced form a day before conducting experiments in order to get frozen samples.

Figure 1. Hawthorn.

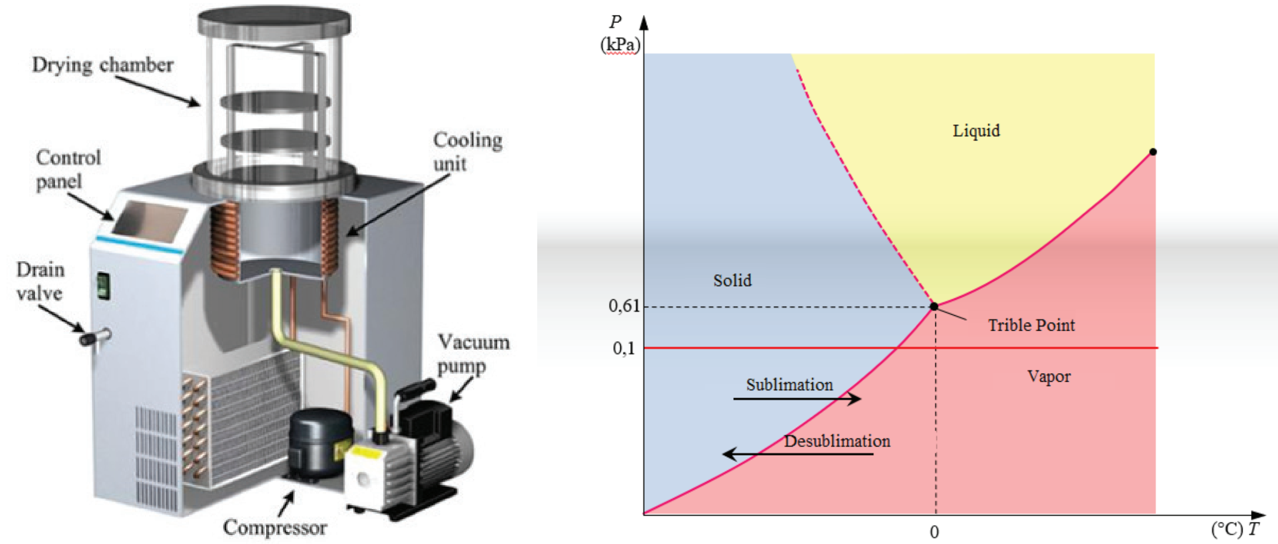

Figure 2. Schematic diagram and logic freeze-drying of the freeze-drying device.

For freeze-drying, we used Labogene Scanvac Coolsafe in the trials. This device can effectively dry materials at condenser temperatures as low as -55°C. The vacuum pump equipment power was $4x10^{-4}$mbar, and the experiments were performed by decreasing the required vacuum pressure up to 0.01 kPa. Figure 2 depicts the freeze dryer used in the studies in schematic form. The theory behind freeze-drying is sublimation. The product freezes in the moisture inside when it is frozen.

The fundamental freeze-drying procedure uses sublimation and relies on raising the temperature of the frozen object while decreasing pressure. Vacuum pumps reduce the inner drying cell pressure, while the internal temperature of the freezing chamber is maintained by a compressor. Before starting the freeze-drying apparatus, the control panel was adjusted extensively, and the necessary time, pressure, and temperature parameters were adjusted. For 14 hours, each sample was frozen and dried. Temperature and time values are displayed in Figure 3. All the samples were first frozen at -15°C before drying. The drying process continued for the first hour at a temperature and pressure of -40°C and 0.01kPa, respectively. After that, while maintaining a constant pressure, the temperature was -30°C for three hours, -20°C for two hours, -10°C for two hours, 0°C for two hours, 5°C for two hours, and 10°C for another hour, respectively. As a result, the freeze-drying process was completed after 14 hours.

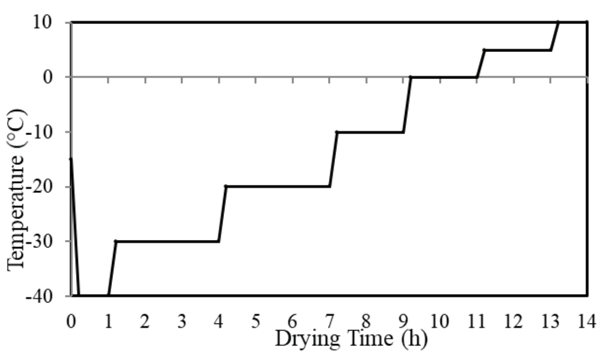

Figure 3. Temperature values as a function of drying time.

For this investigation, we prepared 7 distinct samples to measure weight loss. The sample is placed in the device and removed two hours later. Every two hours, the sample weight is measured using a precision scale with a 0.001 g resolution. The second sample is positioned on the apparatus using the same drying settings. After four hours, the sample is removed and the weight loss is calculated. Other hawthorn samples can be used for this procedure, and at the end of the sixth, eighth, tenth, twelve, and fourteenth hour, the samples are placed in an oven for almost an hour. The sample is later taken out of the drying oven and placed for roughly 15 minutes in a curved glass with more silica gel. The hawthorn sample is then weighed on a precision scale. Even after the freeze-drying process has been finished, this technique removes moisture from the product. This allows for the precise and valuable assessment of the substance's moisture content.

RESULTS AND DISCUSSION

Using a sensitive weight scale, the time-dependent mass loss was measured to calculate the moisture content. The product's dry portion comprised the remaining 25.324g of the 100g package, which had 74.676g of moisture. After two-hour intervals of freeze-drying, the weight loss curve of the hawthorn samples is shown in Figure 4. Figure 5 is a pie chart that displays the percentages of the product mass for the moisture content and dry content.' "

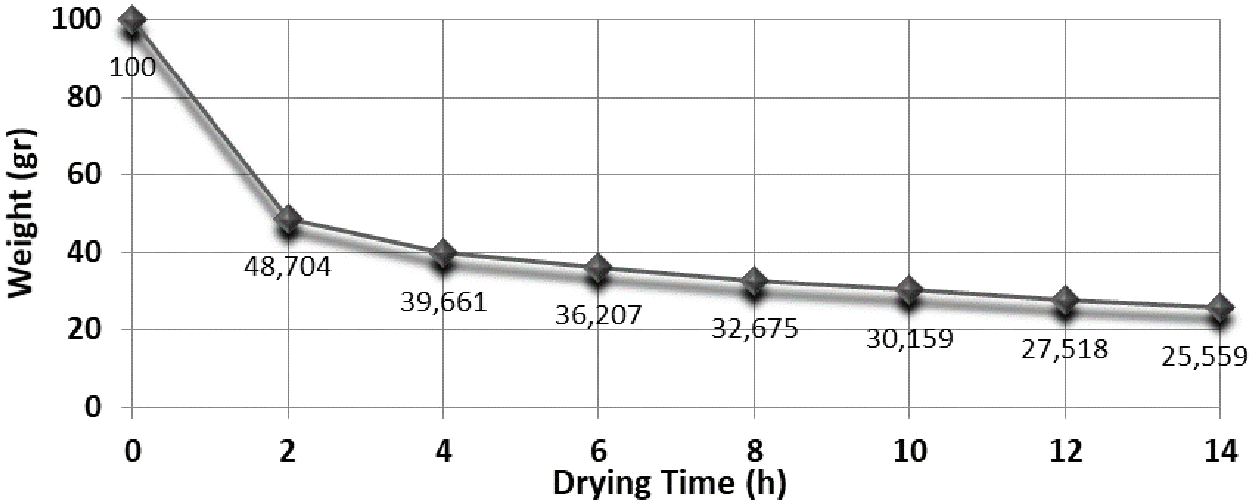

Figure 4. Weight loss of hawthorn samples over time.

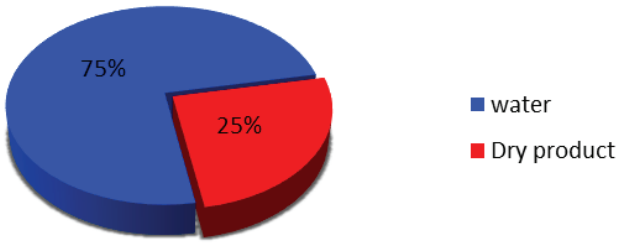

Figure 5. Moisture content and the dry product percentages.

Empirical models can be used in many situations and for various materials, but their application is limited because of the numerous parameters and intricate structures in their equations. Additionally, because the parameters of semi-empirical models are only connected to pertinent products, their application has also been constrained. The drying ratio can be determined without using complicated mathematics. Only experimental specimens under the given experimental conditions are valid for constructed equations. In semi-empirical models, the logarithmic drying equation is frequently used [24]. The moisture ratio (MR), which is a time-based and non-dimensional function because the hawthorn sample changes with time, is calculated using Equation 1.

$$MR = \frac{M_t - M_d}{M_0 - M_d} \tag{1}$$

In this case, M_0, M_t, and M_d represent primary, intermediate time (t), and final equilibrium moisture contents. To make it practical, Equation 1 is simplified for M_t/M_0 [25]. Here, MR is displayed in Equation 1's left side at various t moments. Using the following equation, we can determine the drying ratio (DR):

$$DR = \frac{M_{t+dt} - M_t}{dt} \tag{2}$$

DR, $M_{t+dt,}$ and M_t represent the drying ratio, moisture content for time t+dt, and moisture content at t time period, respectively [17,25]. Figure 6 shows results of 14-hour freeze-drying, and the curve depicts how the moisture ratio of the dried hawthorn samples varied with drying time.

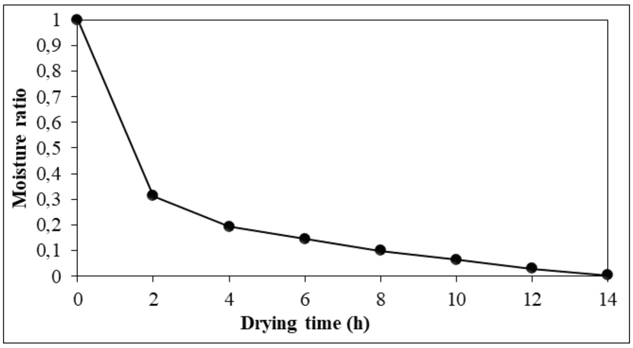

Figure 6. Hawthorn MR curve (drying time: 14 hours).

The rate of drying for frozen hawthorn slices is shown in Figure 7. During the first two hours of the freeze-drying procedure, the drying rate is noticeably higher due to the samples' high surface moisture content. However, the samples' surface moisture content (MC) starts to dry up more slowly because the freeze-dryer's temperature falls to -30°C during the second and third two-hour periods. As the freeze dryer's plate temperature rises during the fourth two-hour session, the drying rate then gradually accelerates. Later, as the freeze-drying process finishes, the drying rate steadily decreases. Figures 7 and 8 illustrate how the drying rate decreases when the sample's moisture level is low.

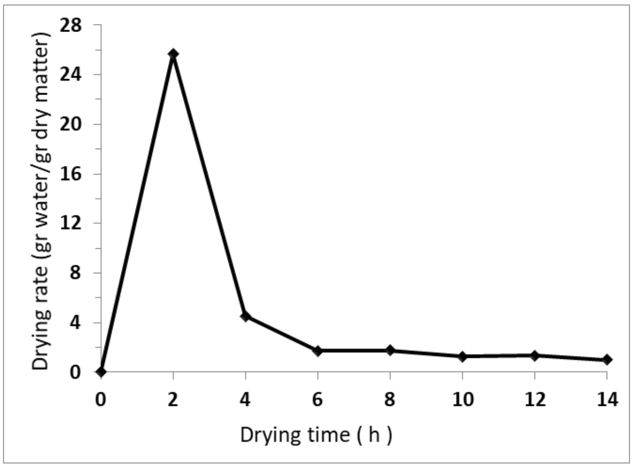

Figure 7. Drying rate curve as a function of drying time.

Figure 7 illustrates a variation that results from the varying plate temperatures in the freeze drier. In Figure 3 the freezer dryer temperature was -40°C before gradually raising it to 10°C to avoid scorching the hawthorn samples. If we examine Figure 7, it is evident that drying slowed down when the drying process prolonged and the moisture content of the samples decreased. It suggests that there is no steady rate period when hawthorn is freeze-dried. Diffusion predominates during the falling-rate stage for mass transfer. Water vapors present at the interface are transferred to the surfaces of the samples using a dried region capillary and extracted using a freeze-dryer's condenser. Mathematical model-dependent graphs were created for eight drying kinetic models based on evaluating a substance's moisture content and calculating time-dependent mass losses. Such processes were carried out using MATLAB simulation. The estimated moisture ratio (MR), used in MATLAB, has been demonstrated using eight different drying kinetic models, as shown in Table 1.

The coefficient of determination (R^2), root mean square error (RMSE), and the reduced chi-square (X^2) are the three main metrics for demonstrating agreement between the moisture ratios determined by the tests and the kinetic models. Equations 3, 4, and 5 can be solved to determine the following parameters:

$$X^2 = \frac{\sum_{i=1}^{n}\left(MR_{exp}-MR_{pre}\right)^2}{N-z} \tag{3}$$

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{n}\left(MR_{pre,i}-MR_{exp,i}\right)^2\right]^{1/2} \tag{4}$$

$$R^2 = 1-\left[\frac{\sum\left(MR_{exp}-MR_{pre}\right)^2}{\sum\left(MR_{pre}\right)^2}\right] \tag{5}$$

Equation 3 demonstrates a significant correlation between the kinetic and experimental values, which rises when the chi-square (X^2) reduces. The RMSE indicates the gap between the projected and experimental results (Equation 4). It evaluates the adequacy of the model equations. Equation 5 also contains high coefficients of determination (R^2) values, and the fact that they are close to 1 indicates that the applicability of the kinetic model. To determine the coefficients in the best-fitting model, a multi-regression model is applied [26, 38]. Based on the values of R^2, X^2, and RMSE, and using the results of experiments and eight kinetic drying models, most effective drying model is decided (shown in Table 2). R^2 value is 0.9987, which is closest to 1, so the Diffusion Approach Model is the most suitable and efficient drying model. The X^2 value is 1.959x10-4, which is close to 0. This model's RMSE is 0.011063, which is closest to 0, which also makes it appropriate." '

Table 1. Semi-empirical and empirical equations for drying kinetics models

Model No.	Model name	Model
1	Newton [25]	$MR = exp\ (-kt)$
2	Page [26]	$MR = exp\ (-kt^n)$
3	Modified Page I [16]	$MR = exp\ [-(kt)^n]$
4	Henderson and Pabis [24]	$MR = a.exp\ (-kt)$
5	Logarithmic [27]	$MR = a.exp\ (-kt) + c$
6	Two-term exponential [28]	$MR = a.exp\ (-kt) + (1-a)\ exp\ (-kat)$
7	Wang and Singh [29]	$MR = 1 + at + bt^2$
8	Diffusion approach [30]	$MR = a.exp\ (-kt) + (1-a)\ exp\ (-kbt)$

Table 2. Results of eight kinetic drying models

Model Name	Model Parameters	R^2	X^2	RMSE
Newton	k = 0.453	0.967	$3.45x10^{-3}$	0.05495
Page	k = 0.765	0.9973	$3.392x10^{-4}$	0.0159
	n = 0.560			
Modified Page I	k = 0.663	0.9970	$3.717x10^{-4}$	0.01669
	n = 0.527			
Henderson and Pabis	a = 0.975	0.968	$9.26x10^{-4}$	0.02635
	k = 0.442			
Logarithmic	a = 0.932	0.984	$2.315x10^{-3}$	0.03803
	c = 0.0598			
	k = 0.572			
Two-term Exponential	a = 0.2949	0.982	$2.178x10^{-3}$	0.04042
	k = 1.152			
Wang and Singh	a = -0.211	0.793	$2.561x10^{-2}$	0.13860
	b = 0.0106			
Diffusion approach	a = 0.5405	0.9987	$1.959x10^{-4}$	0.01106
	b = 0.0989			
	k = 2.08			

This congruence is shown in Figure 8, demonstrating that the Diffusion Approach Model has been used to determine the MR values. The experimental MR values and those predicted by theory agree very well. It also confirms that the model is appropriate to forecast the drying properties of hawthorn fruit by indicating that the data points are located close to the 45° straight line.

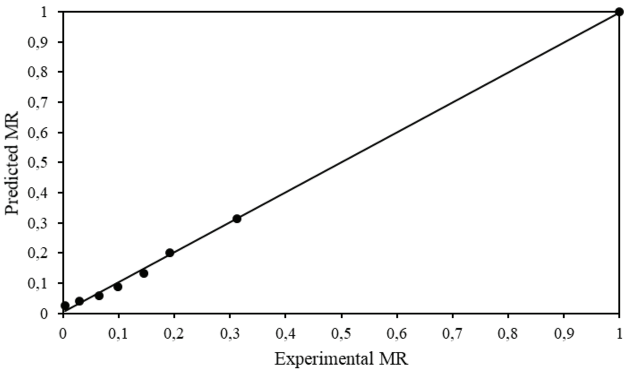

Figure 8. Comparison between the predicted and experimental moisture ratio values (Diffusion Approach).

Uncertainty analysis is a popular technique for determining the precision and accuracy of the results, particularly for experimental studies [21]. The uncertainty analysis was performed in accordance with the Guide on the Expression of Uncertainty in Measurement [22], as shown by Equation 6.

$$U_f = \sum_{n=1}^{N} \left(\frac{\partial_f}{\partial_{x_n}} u_n \right)^2 \tag{6}$$

The uncertainty is measured using Equation 6. Equation 9 uses Gaussian propagation of uncertainties to derive overall uncertainty U_f for the value of f (in our example, drying characteristics) where N is their number, u_n is the uncertainty of associated variable x_n, and x_n are the independent variables. To determine the uncertainty of the corresponding values for drying properties, Equation 6 can be modified with ± 0,1. Fick's diffusion equation has a second law that transforms it into a mass-diffusion equation. Effective diffusivity is a crucial transport property that is influenced by a material's moisture and temperature. The answer to this equation, which is depicted in the equation below, can be used to determine the theoretical model of the drying processes.'

$$\frac{\partial M}{\partial t} = D_{eff} \, \nabla^2 M \tag{7}$$

Crank was the first to employ the diffusion equation solution (Equation 7) for slab shape. He made the following assumptions: negligible constant diffusivity, external resistance, negligible shrinkage, and uniform initial moisture distribution [32]:

$$MR = \frac{8}{\pi^2} \left[\begin{array}{c} exp\left(-\frac{\pi^2 D_{eff}\, t}{4L^2}\right) + \frac{1}{9} exp\left(-9\frac{\pi^2 D_{eff}\, t}{4L^2}\right) \\ + \frac{1}{25} exp\left(-25\frac{\pi^2 D_{eff}\, t}{4L^2}\right) + \frac{1}{49} exp\left(-49\frac{\pi^2 D_{eff}\, t}{4L^2}\right) \ldots . \end{array} \right] \tag{8}$$

Here, L represents sample half-thickness (m), t represents drying time (s), and D_{eff} represents effective diffusivity (m^2/s). In order to account for prolonged drying times with a steady diffusion coefficient (Cartesian coordinate system), as demonstrated by Equation 9, we reduced Equation 8 to a limiting diffusion equation [17]:

$$MR = \frac{8}{\pi^2} exp\left(\frac{\pi^2 D_{eff} t}{4L^2}\right) \tag{9}$$

After determining the effective diffusivity (D_{eff}) values and visualizing ln (MR) vs. time (the experimental drying data), the results are shown in Figure 9.

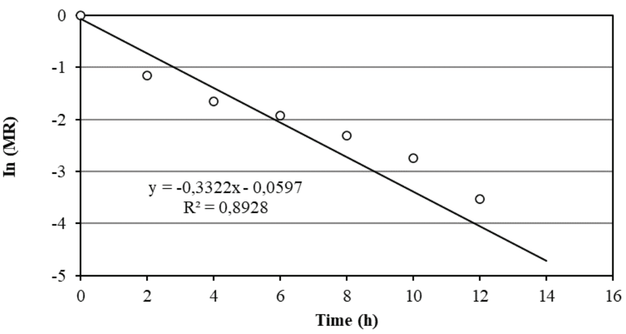

Figure 9. ln (MR) vs. freeze-drying time for Hawthorn samples.

Eq. 8 demonstrates that the drying time vs. ln (MR) is a straight line with slope K:

$$K = \frac{\pi^2 D_{eff}}{4L^2} \tag{10}$$

In Figure 9, we calculated the graph's slope (K). Effective diffusion value (D_{eff}) for 5mm thick hawthorn slices was calculated using Equation 9, and its value was $2.33742 x 10^{-10}$ m^2/s. According to this study, the effective diffusion value for drying food products falls between the reference range 10^{-12}–10^{-8} m^2/s [33]. The literature indicates that no studies have been conducted to date to establish the hawthorn kinetic model. It shows no effort to measure the moisture content during freeze-drying. We draw the conclusion that hawthorn's effective diffusivity is in good agreement with the range of effective diffusivity that is typically used to dry food products.

CONCLUSIONS

We analyzed the results of our trials and concluded that freeze-drying is the simplest and most effective technique to de-moisturize food products since it maintains food quality and flavor, which helps to maintain their market value. In contrast to conventional drying procedures, this approach has higher operational and investment expenses. In this experiment, hawthorn slices were freeze-dried with an average weight of 100g in order to preserve them. During the 14-hour process, a gadget (SCANVAC COOLSAFE) was used. It is worth mentioning here that the 5mm thick hawthorn fruit slices contained 74.67% water.

From eight options, we selected an appropriate kinetic drying model based on MR and DR values. We measured mass losses every two hours. Consequently, the Diffusion Approach Model is the most effective because its R^2 value (0.9987) is the closest to 1, and the X^2 and RMSE values were $1.959 x 10^{-4}$ and 0.011063, respectively, which are the closest to 0.

Additionally, we calculated the effective diffusivity, which was $2.33742 x 10^{-10} m^2/s$ for the aforementioned hawthorn slices. It was verified that the predicted effective diffusivity value fell within the reference range (10^{-12}–10^{-8} m^2/s) for food products.

NOMENCLATURE

a, b, c, n	Dimensionless drying constants in the models used.
DR	Drying rate (g water/g dry matter).
t	Time (min).
M_d	The final equilibrium moisture content (g water/g dry matter).
M_t	The moisture content at a time t (g water/g dry matter).
N	Number of observations.
L	Half-thickness of samples (m).
MR_{pre}	Predicted moisture ratio.
MR	The moisture ratio (dimensionless).
R^2	Coefficient of determination.
MC	Moisture content (g water/g dry matter).
D_{eff}	The effective diffusivity (m).
MR_{exp}	Experimental moisture ratio.
M0	The initial moisture content (g water/g dry matter).
RMSE	Root mean square error.
X^2	Reduced chi-square.

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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