Investigation of the freeze-drying characteristics of scrambled eggs

Çırpılmış yumurtaların dondurarak kurutma karakteristiğinin incelenmesi

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ERKEN GÖRÜNÜM

Investigation of the Freeze-Drying Characteristics of Scrambled Eggs

Highlights

❖ *Investigation of the freeze-drying process of scrambled eggs.*
❖ *Application of theoretical kinetic drying model using MATLAB software.*
❖ *Determination of best kinetic drying model in terms of statistical approach.*

Graphical Abstract

The theoretical kinetic drying model was determined by means of measurement of moisture content from experiments and drying ratio of moisture calculations. In addition, the effective diffusivity (D_{eff}) was calculated regarding the results of the freeze-drying process. As a result, it was observed that the best appropriate drying kinetic model was the Logarithmic model, whereas the effective diffusivity coefficient has good agreement with the literature by placing the range between 10^{-12} and 10^{-8} $m^2 s^{-1}$ for food products.

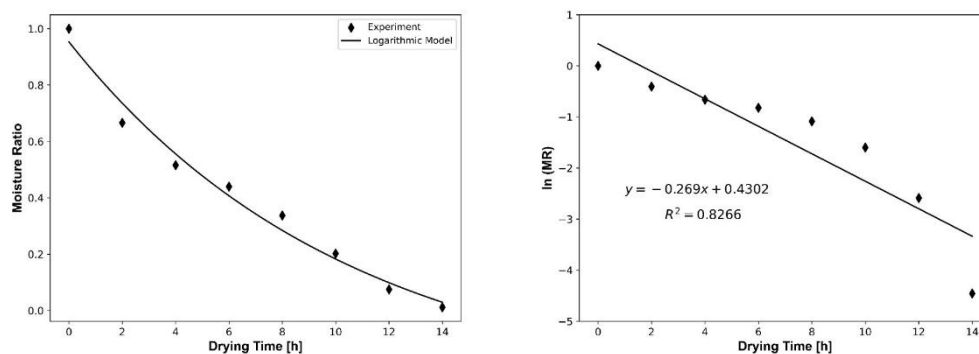**Figure.** Plot of Logarithmic drying model and ln(MR) vs. drying time

Aim

The present study aims to identify suitable freeze-drying characteristics of the product regarding calculating drying rate and moisture ratio in order to implement them into various theoretical drying models.

Design & Methodology

Scrambled egg specimens were prepared with a weight of 100 gr, and prepared specimens were placed into the freeze-drying instrument. Specimens' weight losses were measured at periodic intervals of 2 hours, and experimental results were implemented into 8 various kinetic drying models.

Originality

Process of freeze-drying using scrambled egg and determination of kinetic drying characteristics of the process.

Findings

It was determined that the coefficient of effective diffusivity was 4.8454×10^{-10} $m^2 s^{-1}$, which was within the limits between 10^{-12} and 10^{-8} $m^2 s^{-1}$ mentioned in the previous studies. The Logarithmic drying model was expressed as the superior model in terms of statistical parameters.

Conclusion

The best kinetic drying model was described by means of the calculation of MR and DR values. The Logarithmic model was chosen because R^2 was 0.9816, χ^2 was 2.74×10^{-3}, and RMSE 0.05241.

Declaration of Ethical Standards

The authors declare that the materials and methods used in this manuscript do not require ethical committee permission and/or legal-special permission.

Investigation of the Freeze-Drying Characteristics of Scrambled Eggs

Araştırma Makalesi / Research Article

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ABSTRACT

Eggs are one of the wealthiest protein products and have been widely used in industrial food preparation and daily cooking. One of the main objectives in the food industry is to have a long shelf life without losing the nutritional properties of protein-rich foods. Freeze-drying is a novel and promising method for dehydrating products containing temperature-sensitive ingredients to achieve extended shelf life, high quality, and excellent texture. The ice form of water is extracted from the material under low pressure by sublimation, and the lower temperature permits the highest control of the nutrient and bioactive compound as well. This study presents experimentally the determination of the freeze-drying process with scrambled eggs. Prepared 100 grams of specimens were freeze-dried, and the weight losses were measured to determine moisture reduction and ratio and drying rate as well. The kinetic results of the drying process were adapted to the total of eight various empirical drying models in order to define the suitable model representing weight loss through the freeze-drying process. Among the drying models, it has been determined that the Logarithmic drying model was the most proper drying model with a determination coefficient (R^2) of 0.9816, a reduced chi-square (χ^2) of 2.74×10^{-3}, and a root mean square error *(RMSE)* of 0.05241. The effective diffusivity was found to be 4.8454×10^{-10} m^{2}s^{-1}.

Keywords: Freeze-drying, scrambled egg, drying models, drying rate, effective diffusivity.

Çırpılmış Yumurtaların Dondurarak Kurutma Karakteristiğinin İncelenmesi

ÖZ

Yumurtalar hem endüstriyel yemekler hem de günlük pişirme işlemlerinde kullanılan, zengin protein kaynağı olan gıdalardan biridir. Gıda endüstrisindeki temel amaçlardan biri protein açısından zengin gıdaların besleyici özelliklerini kaybetmeden uzun raf ömrüne sahip olmasıdır. Dondurarak kurutma, uzun raf ömrü, yüksek nihai kalite ve mükemmel doku elde etmek amacıyla, sıcaklık hassasiyetli bileşenler içeren ürünlerin kurutulmasına yönelik yeni ve umut vaat eden bir kurutma yöntemidir. Dondurarak kurutma işleminde, buz formundaki su muhteviyatı, ürün içerisinden düşük basınç altından süblimasyon yoluyla çıkarılmakta ve işlemin düşük sıcaklıklarda yapılması besin maddesinin içeriğinin ve biyoaktif bileşiklerinin en yüksek düzeyde kontrol edilmesine olanak tanımaktadır. Bu çalışmada, çırpılmış yumurta ürününün dondurarak kurutulması işlemi ve kurutma performansı deneysel olarak incelenmiştir. 100 gram ağırlığında hazırlanan kurutma numuneler dondurarak kurutma işlemine tabi tutulmuş, ağırlık kayıplarının ölçülerek nem miktarı ve oranı, kurutma hızı parametreleri belirlenmiştir. Deneysel kurutma sonuçları, sekiz farklı kinetik kurutma modeline uygulanmış ve dondurarak kurutma işlemini uygun teorik model belirlenmeye çalışılmıştır. Karşılaştırılan kinetik kurutma modelleri arasında, determinasyon katsayısı (R^2) 0,9816, indirgenmiş ki-kare değeri (χ^2) $2,74 \times 10^{-3}$ ve kök ortalama kare hatası değeri (*RMSE*) 0,05241 olması sebebiyle Logaritmik Modelin en uygun model olduğu belirlenmiştir. Ayrıca, elde edilen deneysel sonuçlar neticesinde efektif yayılım değeri $4,8454 \times 10^{-10}$ m^{2}s^{-1} olarak bulunmuştur.

Anahtar Kelimeler: Dondurarak kurutma, çırpılmış yumurta, kurutma modelleri, kuruma hızı, efektif yayılım.

1. INTRODUCTION

Agricultural goods such as various kinds of fruits and vegetables are essential products for humans in terms of containing vitamins, nutrition, and health benefits. On the other hand, it isn't easy to find fresh products outside of their seasons and keep them in good condition for a long period due to their high moisture content and sensitive surface textures. Thus, drying processes are required to extend the lifespan of food products by decreasing the amount of water in products, and the freeze-drying technique has been one of the common drying methods that can be used for various types of food and raw materials [1, 2].

Dehydration is the well-known and primary method for food products by lowering the moisture content of foods, which aims to avoid the reproduction and increase of microorganisms that cause the decay and decomposition of the products [3]. There are several drying methods to perform the dehydration process in the food industry, and the most well-known can be classified as sun drying, spray drying, freeze-drying, conventional dryers, fluidized bed dryers, ultrasound drying, dielectric drying, osmotic drying, vacuum and microwave drying, microwave-freeze-drying, infrared radiation drying [4–6]. Among these drying methods, it is reported that freeze-drying is the most suitable method for food

dehydration because it preserves flavor and structural integrity, occurring minimal shrinkage, serving adequate nutrient retention, and allows long shelf life [7–9]. In addition, the product's excellent final quality is achieved by discontinuing microbiological reactions and most of the deterioration because the liquid water content is transferred and the process is performed under low temperatures [10]. The freeze-drying (FD) process, also known as lyophilization, is a simple and effective method for producing high-quality products with long shelf life. The FD process is a proper technique for products that are affected by oxidation and contain thermally sensitive compounds [11]. Recently, the FD process can be applied to various types of foods, fruits, vegetables, and products such as apples [12, 13], apricot [14], plums, prickly pears, tomatoes, mushrooms [15], jackfruit and snake fruit [16], various tropical fruits [17, 18], strawberry [19], cranberrybush [20], banana [21], orange [22], grapefruit [23], hawthorn [24], kiwi [25], blueberry [26], raspberry [27], melon, and pear [28]. In addition to food products, there is the possibility of applying the FD process to non-food products and materials such as flowers, ceramic powders, microorganisms, cosmetic products, chemical solvents, and pigments [29].

The fundamentals of the FD process are based on taking out the content of water from the frozen material by the sublimation of ice crystals through high pressure and low temperature. The FD process is divided into three stages. The initial stage is freezing the product at very low temperatures. The next stage is the primary drying phase, in which the water content is transferred from the product by sublimation. The final stage is secondary drying, where the non-freezing water content is removed from the product by desorption [30, 31]. The FD process has several advantages, such as stability, homogeneous drying, lightweight product, easy to apply, high product quality, products with long shelf life, long-term storage, ease of transport for products, retaining sensory quality, and preserving physical and chemical properties [30, 32, 33]. Despite these advantages, high installation and operating costs and slow process duration are the most significant disadvantages of freeze-drying [34]. Microwave-assisted freeze-drying systems can also serve high efficiency in terms of lower energy consumption and a shorter drying process [35–37].

The performance and behavior of functional properties of proteins have been directly affected by preparation, processing, storage, and consumption processes. Converting food proteins into suitable food products without changing functional properties is the primary goal of the food industry [38]. The egg is one of the essential protein sources for humans in terms of containing highly nutritional and functional components and has been utilized in various food products over the long term. The manufacture and stabilization of the emulsions, foaming stability, and thermal gelation are the main functional properties of food products that contain egg yolk [39, 40]. Low-density protein is the effective component of the egg, and after a long period of storage

of the egg mélange, no significant alterations in the sensory and functional characteristics have been observed up to 48 months [40, 41]. In addition, protein nanoparticles can be obtained using pasteurized liquid form egg white by diluting egg white solution, and nanoparticle protein powders can be produced by freeze-drying of the solution. Therefore, it is reported that the emulsifying properties of the nanoparticles were better than the native egg white protein [42]. Another use of egg white is a foam form, which is essential for bakery products, and the stability of the foam form of the egg is acquired with stabilizers. To achieve better stability, xanthan gum, and propylene glycol alginate stabilizers provide good structural stability with the foam-mat freeze-drying process. Regarding drying models for foam form, the accuracy of diffusion models is higher than that of other models for mass transfer rate and diffusion coefficient calculations [43, 44].

Although studies have investigated the freeze-drying process of eggs, researchers focus on either pure egg yolk, pure egg white, or a food product containing eggs. Besides, no previous studies focused on the freezing of scrambled eggs and performing various kinetic drying models to experimental results on the freeze-drying of eggs as well. This study aimed to experimentally study scrambled eggs' freeze-drying behavior in terms of calculating the drying rate, moisture ratio, and content. Furthermore, drying kinetics data were adapted to a total of eight various models to identify the theoretical model's applicability to the freeze-drying kinetics of scrambled eggs.

2. MATERIAL AND METHOD

2.1. Material

An example of the scrambled egg for experiments is shown in Figure 1. A total of seven specimens were whisked and placed in the test container. The weight of each scrambled egg was 100 grams. After the preparation procedure, the specimens were stabilized, and the drying process was performed on each specimen.

Figure 1. Scrambled egg specimen.

2.2. Process of Freeze-Drying

The process of the freeze-drying process was performed using a Labogene brand Scanvac Coolsafe type drying instrument. The freezing process of the specimens was achieved by reducing the temperature of the evaporator up to -55 °C inside the instrument. Throughout the experiments, the freeze-drying instrument was mounted to a vacuum pump, which had a vacuum power value of 4×10^{-4} mbar, and the pressure of the chamber was also reduced to 0.01 kPa. Figure 2 presents the visual illustration of the freeze-drying instrument.
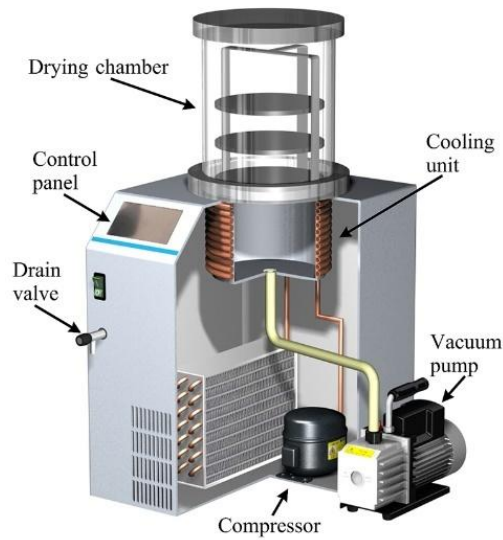

Figure 2. The schematic view of freeze-drying instrument.

The fundamental principle of freeze-drying is based on the sublimation of water. Figure 3 shows the sublimation process of water. The endothermic process, which is called sublimation, occurs at particular temperature and pressure levels which are below the triple point of the water, where the value of temperature is 0.0098 °C and the value of pressure is 4.579 mmHg. Subsequently, under the triple point of the product, the material phase directly changes from the solid state to the gas state without passing through the liquid phase. During the freeze-drying process, the content of moisture in the product is also frozen when it is frozen. If the process pressure is maintained below the crucial level of pressure and the temperature level increases, the content of moisture passes immediately into the vapor phase and leaves the product inside [45].

The ScanVac Coolsafe instrument operates under a low-pressure level to perform the freeze-drying operation of a specimen. While the inner condition is low pressure, the temperature of the specimen increases until the sublimation phenomenon occurs. The operating procedure of the freeze-drying instrument is that the vacuum pump adjusts drying chamber pressure to achieve desired physical properties, while the compressor regulates temperature for in-cabin drying processes. In the experiments, the specimens were positioned in the drying chamber of the instrument while the pressure and temperature were adjusted to the appropriate level by the control panel prior to the operation of the instrument.
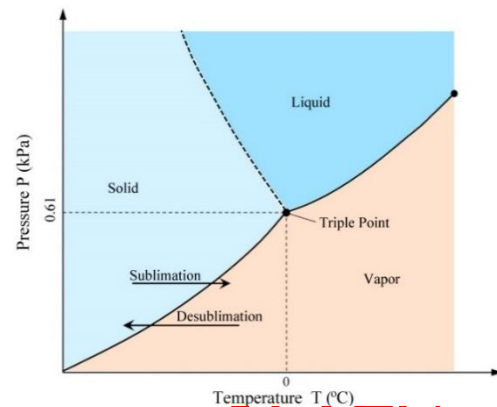

Figure 3. Fundamentals of a sublimation process [46].

The freeze-drying process involves three essential phases: freezing, primary drying, and secondary drying. The freezing stage is the first step of the drying process. The specimen is cooled to a temperature level that is below the freezing point by allowing the freezing of all contained solvents in the material. The primary drying stage is the first step of the drying process, and the frozen solvent is transferred from the specimen through sublimation. In this stage, the pressure of the drying chamber is kept close to or less than the vapor pressure level of the frozen solvent. The second drying phase begins when all the frozen water in the dried material is exhausted. The second drying period removes the water from the specimen by desorption under high vacuum. This phase operates at temperatures ranging from 10 to 50 °C depending on the thermal sensitivity of the material [47, 48]. In order to achieve freezing, primary and secondary drying stages, temperature profile, shown in Figure 4, as a function of drying time was used. The temperature level of -40 °C shows the freezing stage; temperature from -30 °C to 10 °C reflects the primary drying stage; and temperature above 10 °C exhibits the secondary drying stage. Initially, the required temperature, pressure, and drying time values were set on the freezing drying equipment setting panel with respect to Figure 4. The freeze-drying process was completed in a total of 14 hours in the experiments. The freeze-drying experiment was started at the -40 °C temperature level below 0.01 kPa pressure, which was kept constant throughout the whole experiment. The first freeze-drying phase is known as a process with limited mass transfer, and the second is also known as a heat transfer process. Thus, due to the sublimation during the first drying stage, the pressure of the drying chamber is reduced to a minimum level as the amount of water vapor passing through the drying material pores increases [36]. Then, the temperature level was increased to -30 °C. During the experiments, the specimen was exposed to a sequence temperature of 3 hours of -30 °C, 3 hours of -20 °C, 2 hours of -10 °C, 2 hours of 0 °C, 2 hours of 5 °C, and 1 hour of 10 °C, respectively.
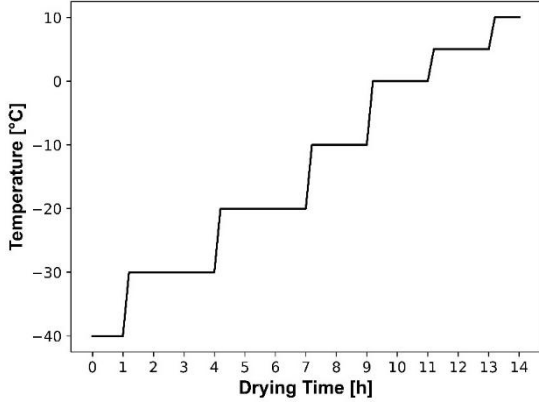
Figure 4. The temperature vs. drying time curve.

To determine the weight loss of the specimens at periodic intervals of 2 hours, a total of 7 specimens were prepared. This approach was used because of keeping the pressure of the inner chamber as stable as possible and preventing the transfer of moisture from the environment to the specimen. Weight reductions of specimens were measured using balance device with a 0.001 g precision. The freeze-drying experiments were performed taking into account the Figure 4 graph. The first specimen at a temperature of -40 °C was placed into the drying instrument and dried for 1 hour. The weight reduction of the dried specimen was measured and recorded. The second specimen at -40 °C temperature was then dried for 4 hours, and weight loss was also measured. Therefore, weight loss between specimens at the same temperature level as -30 °C could be compared. These periodic drying and measurement steps are applied to other samples with the same drying settings at the end of the 6, 8, 10, 12, and 14 hours. For the 6th and 7th specimens, after the process of freeze-drying, on account of continuing the drying process, the oven was used to obtain temperature levels of 5 °C and 10 °C, and the weight losses were measured. The desiccator device was used to dry the 7th specimen after 14 hours to ensure that all moisture was removed from the specimens. The dried specimen was taken out of the oven and placed into the desiccator, which had a curved glass filled with silica gel. The specimen in the desiccator was heated for about 15 minutes, and its weight was also measured.

The Moisture Ratio (MR) shows the changes in the scrambled egg specimens with respect to drying time, and Equation (1) expresses the calculation of MR. The Drying Rate (DR) of the specimens is also calculated using Equation (2).

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

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

MR changes over drying time (t) are calculated by Equation 1 and Equation 2. In Equation 1, M_0, M_t, and M_d identify the content of the initial moisture, the content of the moisture at a particular t time, and the content of the equilibrium moisture, respectively. Equation 1 represents the MR values of the freeze-drying process at particular t moments. MR is a dimensionless parameter, and it expresses the alteration of the scrambled egg with respect to the drying time for the process. Thus, the MR value was effectively computed by the declared equation. In Equation 2, DR expresses the rate of drying, and M_{t+dt} indicates the content of moisture at the t+dt moment [36].

Several mathematical theoretical models were developed in the national and international literature to depict the freeze-drying characteristics of products. Among those models, eight different models were used to perform fitting the experimental kinetic drying results for scrambled eggs (as seen in Table 1). An analysis of non-linear regression was conducted to determine the kinetic model parameters using MATLAB software, and as a result of performing mathematical models, the most suitable model was selected. In addition, on the basis of the following assumptions, experimental drying results were fitted into the drying kinetic models [49]:

- 1D heat and mass transfer are considered normal to the surface.
- The sublimation takes place at the interface parallel to the top surface of the specimen.
- The sublimation interface thickness is regarded as infinitesimal, and the water vapor concentration is in equilibrium with the content of ice.
- The homogeneous frozen region has uniform heat conductivity, density, and specific heat.
- The dried pressure is considered constant during the drying experiments.
- Water vapor is transferred from the dried layer of the specimen.

To perform a comparison between kinetic models, the statistical coefficients are widely used in literature. Theoretical freeze-drying models were evaluated using statistical approaches such as the root mean squared error (RMSE), the reduced chi-square (χ^2), and the determination coefficient (R^2). The higher R^2, lower RMSE, and χ^2 give the goodness of fit. RMSE, R^2, and χ^2 are calculated by Equation 3, Equation 4, and Equation 5, respectively [54–56].

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(MR_{pre,i} - MR_{exp,i}\right)^2} \tag{3}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp} - MR_{pre}\right)^2}{N - z} \tag{4}$$

Table 1. Equations of kinetic drying models of the process [36, 50–53].

Order	Name of Model	Equation of Model
1	Page Model	$MR = \exp\left(-\varepsilon t^{n}\right)$
2	Modified Page I Model	$MR = \exp\left[-\left(\varepsilon t\right)^{n}\right]$
3	Newton Model	$MR = \exp\left(-\varepsilon t\right)$
4	Wang and Singh Model	$MR = 1 + pt + qt^{2}$
5	Hend. and Pab. Model	$MR = p \times \exp\left(-\varepsilon t\right)$
6	Logarithmic Model	$MR = p \times \exp\left(-\varepsilon t\right) + w$
7	Two-term Exp. Model	$MR = p \times \exp\left(-\varepsilon t\right) + \left(1 - p\right)\exp\left(-\varepsilon p t\right)$
8	Diffusion Appr. Model	$MR = p \times \exp\left(-\varepsilon t\right) + \left(1 - p\right)\exp\left(-\varepsilon q t\right)$

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

The RMSE defines the mean differences between the prediction and experimental kinetic model values. Furthermore, decreasing the value of reduced chi-square (χ^{2}) describes the increase in agreement. In addition, the determination coefficient (R^{2}) defines the usability of the kinetic drying models when it is close to 1. The coefficients of the suitable kinetic drying models were achieved among the eight various kinetic models by means of performing the statistical calculations.

A diffusion phenomenon can represent the mechanism of moisture movements in a solid during a declining period according to the second law of Fick. Effective diffusivity is an essential transport function in the modeling of drying processes for food and other materials. The second law of Fick for unsteady state diffusion of moisture in food is shown as follows [57]:

$$\frac{\partial M}{\partial t} = D_{eff}\nabla^{2}M \qquad (6)$$

Analytical solutions representing mass transfer according to Fick's law were reported for various geometries, and the solution of Equation 6 is performed by Crank in terms of infinite series for a slab geometry and constant diffusivity as well [58]. The dimensionless amount of diffusing water in terms of the initial uniform distribution of moisture, constant diffusivity, inert shrinkage, and insignificant external resistance can be expressed as;

$$MR = \frac{8}{\pi^{2}}\sum_{m=0}^{\infty}\frac{1}{\left(2m+1\right)^{2}}\exp\left(-\frac{\left(2m+1\right)^{2}\pi^{2}D_{eff}t}{4L^{2}}\right) \qquad (7)$$

In Equation 7, the effective diffusivity is expressed by D_{eff} ($m^{2}s^{-1}$), the half-thickness of the specimens is defined by L (m), the drying time is presented by t (s), and m is a positive integer. For long drying periods, Equation 7 is clarified as logarithmically and defined as;

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

Plotting of ln(MR) with respect to drying time using results of the experimental process allows the calculation of effective diffusivity (D_{eff}) values. The angle of the straight line in the diagram is defined as K and can be calculated as [59];

$$K = \frac{\pi^{2}D_{eff}}{4L^{2}} \qquad (9)$$

3. RESULTS AND DISCUSSION

3.1. Freeze-Drying Experiments

Figure 5 and Figure 6 show the experimental variation of the content of moisture and the ratio with respect to drying time, respectively. In Figure 5, the content of moisture was calculated on a dry basis specimen. The moisture content was almost a value of 2 g water·g^{-1} dry matter at the beginning of the experiment because of the great moisture content on the surface of the specimens, and it dropped dramatically off within the first two-hour period. Then, the decreasing slope of the curve was considerably slow, and the moisture content reduced broadly with increasing freeze-drying time. Upon completion of the freeze-drying process, the content of moisture was almost constant at the 14th hour. In Figure 6, the moisture ratio gradually decreased from 1 to 0.7 in the first two hours, parallel to Figure 5, and this decreasing behavior continued until the 14th hour. When Figure 5 and Figure 6 are evaluated in terms of the mass transfer mechanism, the moisture reduction was rapid through the initial two-hour period of the drying process because a large amount of moisture was transferred from the outer surface of the specimen. This also leads to the considerable reduction in terms of the content of moisture and moisture ratio of the specimen [60].
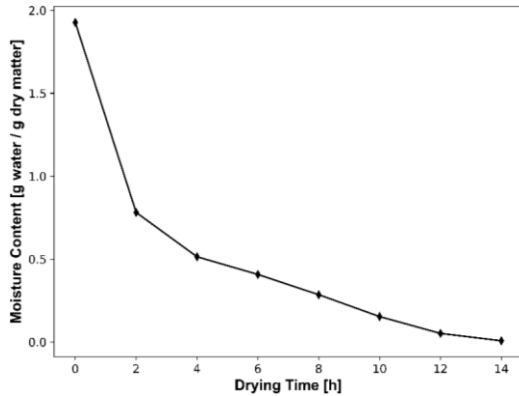
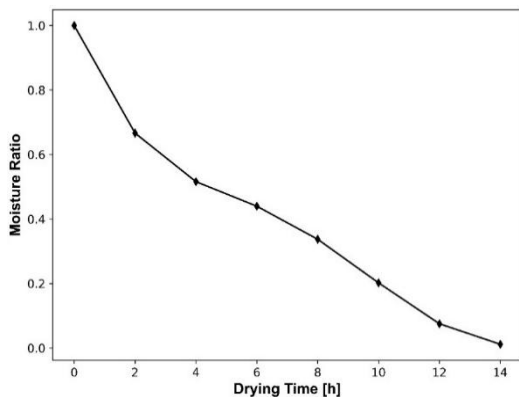**Figure 5.** Content of moisture versus drying time curve.

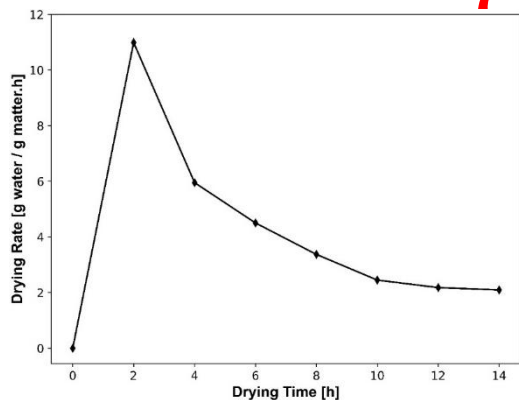**Figure 6.** Moisture ratio versus drying time curve.

Figure 7. Drying rate vs. drying time curve.

The changes in drying rate value in the freeze-drying process using scrambled eggs are shown in Figure 7. As seen from the figure, the drying rate was considerably high within the first two-hour period because of the high moisture concentration on the upper surface of the specimen. Thereafter, the rate of drying exhibited rapid decline due to the plate temperature of the device being noticeably low. Then, the drying rate showed decreasing behavior, and this rate of decline slowly reduced as a result of increasing the plate temperature until the 12th hour, and from this point the drying rate was almost constant until the end of the experiment. Since Figure 7 combines with the result values of Figure 5 and Figure 6,

it could be concluded that the moisture content and ratio gradually reduced within the first two-hour period due to the fact that the temperature of the freeze-drying instrument plate was -30 °C and moisture content on the outer surface of the specimen was removed rapidly. From that period, the decrease in curves became considerably slower due to the high amount of moisture evaporated from the specimen owing to the sublimation in the earlier stage of the freeze-drying process. Additionally, Figure 7 clearly illustrates that as the reduction of drying rate value, the content of moisture in the sample decreases as well [61–63].

3.2. Freeze-Drying Models

The experimental results of the freeze-drying process of scrambled eggs were fitted with eight various empirical, and Table 1 shows the semi-empirical kinetic drying models. The model parameters of the kinetic drying models in order to identify the drying attributes, and Table 2 demonstrates the statistical evaluation of the models using the R^2, χ^2, and RMSE criteria.

In the literature, kinetic drying models with the highest score of R^2 value and the lowest score of RMSE and χ^2 values are considered acceptable as the most suitable models [64, 65]. R^2 values in the drying models varied from 0.9627 to 0.9816. The highest and lowest values of R^2 were obtained using the Logarithmic Model and the Page Model, respectively. In addition, the χ^2 values changed between 2.74×10^{-3} and 4.73×10^{-3}. The highest and lowest of χ^2 were calculated using the Diffusion Approach Model and the Logarithmic Model, respectively. Besides, the highest RMSE of 0.06875 was achieved by the Diffusion Approach Model, and the lowest RMSE of 0.05241 was acquired by the Logarithmic Model. Figure 8 presents the comparison curves of the experiment and the freeze-drying kinetic models in terms of the moisture ratio with respect to drying time.
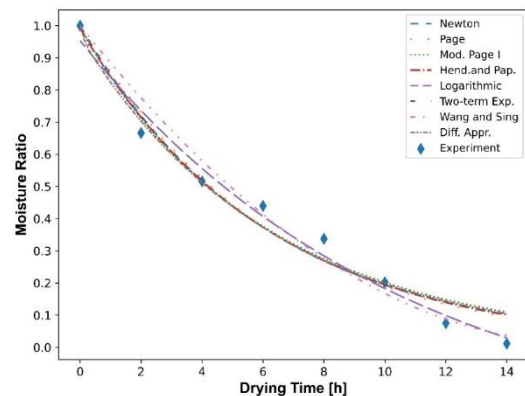

Figure 8. Comparison of moisture ratios of kinetic drying models and experimental results.

In the evaluation of the drying model results, the Logarithmic Model was chosen to depict the freeze-drying process of scrambled eggs with great accuracy

Table 2. Statistical results of drying models of the process.

Order	Name of Model	Parameters of Model		R²	χ²	RMSE
1	Page Model	ε:	0.153	0.9627	3.97×10⁻³	0.06303
		m:	1.036			
2	Mod. Page I Model	ε:	0.1629	0.9664	4.17×10⁻³	0.06459
		m:	0.9621			
3	Newton Model	ε:	0.1643	0.9677	3.44×10⁻³	0.05865
4	Wang and Sing Model	p:	-0.1193	0.9697	3.758×10⁻³	0.06131
		q:	0.003607			
5	Hend. and Pab. Model	p:	0.9906	0.9678	3.99×10⁻³	0.06319
		ε:	0.1627			
6	**Logarithmic Model**	**p:**	**1.255**	**0.9816**	**2.74×10⁻³**	**0.05241**
		w:	**-0.3016**			
		ε:	**0.09516**			
7	Two-term Exp. Model	p:	1.456	0.9638	3.852×10⁻³	0.06207
		ε:	0.1906			
8	Diffusion Appr. Model	p:	0.03792	0.9683	4.726×10⁻³	0.06875

Note: Bold terms present the best result.

because of presenting a high level of concordance with the experimental results. Although empirical models are applied to various materials under different conditions, they are generally not preferred because of their complex structures and several parameters to solve. Nevertheless, semi-empirical models have less complicated structures; however, the usage of those is restricted due to the equation parameters having valid only relevant products. The calculation of the drying rate can be performed using not only complex structure equations but also the results of experimental methods. However, the created equations from the experimental methods are also acceptable for the experimental specimens and conditions. The Logarithmic Model equation has been one of the most known equations, which is a suitable and widely used equation in semi-empirical models [66]. Table 3 shows the comparison of percentage error values between experimental and kinetic drying models, and Figure 9 illustrates the evaluation of the experimental and Logarithmic Model of moisture ratio with respect to drying time. In terms of average error percentage values of kinetic drying models, it can be seen that the average error rate of the Logarithmic Model is lower than other models at 17.93%. In addition, the Logarithmic Model performs better average percentage error performance than the other kinetic drying models for the long-term drying process at 60.76% for the 14th hour.

The agreement between the results of the predicted moisture ratio values using the Logarithmic Model and experimental values is shown in Figure 10. It is clearly seen that the data points are generally connected to the 45° straight lines on the plots. This supports that the Logarithmic Model is appropriate to predict the characteristics of the drying process of scrambled eggs. The Logarithmic Model is also suggested in other studies that have been performed this model to determine precisely the drying characteristics of persimmon puree [52], watermelon [67], cannabis [68], mushroom [69], date fruit powders and syrup [70], orange [71], turkey meat [72], sweet cherries [73], red pepper [74], and kiwi [75].
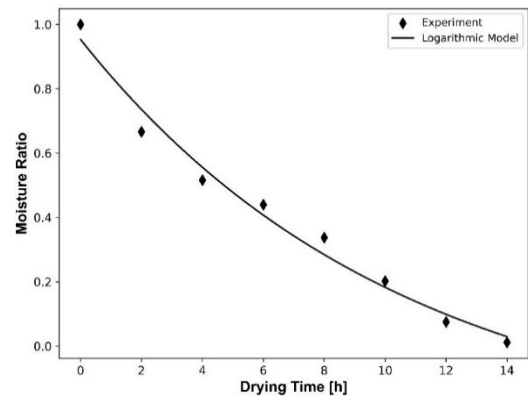
Figure 9. Evaluation of experimental results with Logarithmic model curve.

The plot of ln (MR) of the results of the experimental drying process versus the drying time is shown in Figure 11. The effective diffusivity (D_{eff}) values are obtained by applying the straight-line slope (K) given in Equation 9. The effective diffusivity value was found as 4.8454×10⁻¹⁰ m²s⁻¹, which was within the generally accepted range between 10⁻¹² and 10⁻⁸ m²s⁻¹ for the drying of food materials [76-78].

Table 3. Comparison of percentage error between experimental and kinetic drying models.

Drying Time [h]	Exper.	Page Model	Mod. Page I Model	Newton Model	Wang and Sing Model	Hend. and Pab. Model	Logarit. Model	Two-term Exp. Model	Diffusion Appr. Model
0	1.000	0.00%	0.00%	0.00%	0.00%	0.95%	4.91%	0.00%	0.00%
2	0.666	8.82%	6.41%	7.46%	14.13%	6.87%	9.45%	9.09%	5.30%
4	0.516	1.83%	0.00%	0.48%	11.16%	0.17%	7.22%	2.52%	0.69%
6	0.440	17.14%	16.93%	17.86%	6.20%	17.85%	7.97%	16.40%	17.90%
8	0.337	26.28%	22.52%	25.57%	21.99%	25.17%	18.59%	26.13%	24.20%
10	0.202	6.69%	0.00%	4.54%	20.50%	3.87%	10.54%	7.50%	2.22%
12	0.075	43.90%	49.45%	45.98%	14.43%	46.49%	23.98%	42.82%	47.77%
14	0.012	87.76%	89.44%	88.44%	68.56%	88.58%	60.76%	87.35%	88.95%
Average		24.05%	23.09%	23.79%	19.62%	23.75%	17.93%	23.98%	23.38%
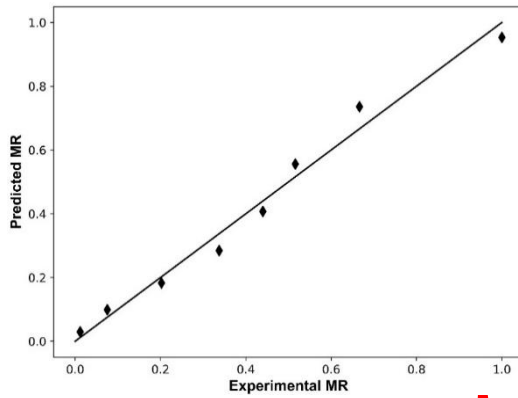
Figure 10. Comparison of the moisture ratios of experimental and Logarithmic model.

$$y = -0.269x + 0.4302$$
$$R^2 = 0.8266$$

Figure 11. Logarithmic MR versus drying time.

4. CONCLUSIONS

Freeze-drying is a process to dehydrate fruits, vegetables, spices, and even some non-traditional foods. In this study, the freeze-drying process of the scrambled egg product was investigated in terms of both experimentally and statistically. It was seen that the process can be adequately applied to the drying of the scrambled egg product with great accuracy. The variation in the MR rate of the drying process was experimentally measured to

determine the freeze-drying properties of scrambled eggs. The experiment results were implemented to a total of eight various empirical drying models to identify the best proper model to estimate the weight reduction through the freeze-drying process. Among the drying kinetic models, it was found that the Logarithmic Model represented the superior model to present the drying properties of scrambled eggs during the freezing drying process. The statistical values of R^2, χ^2, and RMSE for the Logarithmic Model were 0.9816, 2.74×10^{-3}, and 0.05241, respectively. The effective moisture diffusivity (D_{eff}) was calculated as the score of 4.8454×10^{-10} m^{2}s^{-1} which is on the same scale as many of the food materials (10^{-12} and 10^{-8} m^{2}s^{-1}).

Nomenclature

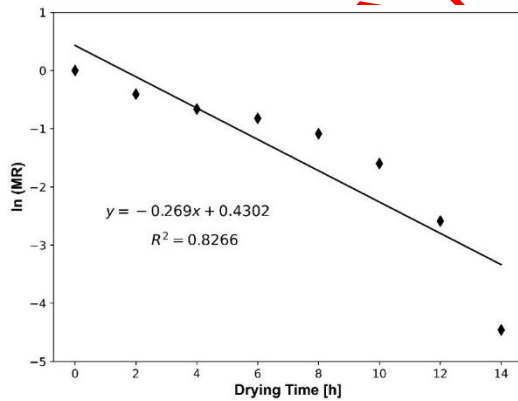|	
p, q, w, m	Constants of the models
z	The total number of model parameters
ε	Constant of Drying rate
t	Time
MC	Content of moisture
MR	The moisture ratio
DR	Drying rate
M_d	Content of final moisture
M_t	Content of moisture at a particular time t
M_0	Content of initial moisture
D_{eff}	Value of effective diffusivity
L	Half-thickness of samples
N	Observations number
RMSE	Root mean squared error
χ^2	Reduced chi-square
R^2	Determination coefficient

DECLARATION OF ETHICAL STANDARDS

The authors declare that the materials and methods used in this manuscript do not require ethical committee permission and/or legal-special permission.

AUTHOR CONTRIBUTIONS

Bahadır ACAR: Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, Validation, Writing Original Draft, Visualization.

Murat AYDIN: Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, Validation, Writing Original Draft, Visualization.

CONFLICT OF INTEREST

The authors have no relevant financial or non-financial interests to disclose. The authors have no conflict of interests to declare that are relevant to the content of this manuscript.

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