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The effect of ultrasound pretreatment on oven and vacuum oven drying kinetics of blueberries

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Blueberries (*Vaccanium corymbosum*) are small, round fruits having vital nutritional and functional properties. However, they are seasonal fruits with short shelf lives, a feature which hinders their desired commercialization. This condition necessitates the investigation of efficient drying methods for their extensive preservation. In literature, although there are numerous articles focusing on the antioxidant capacities and nutritional contents of blueberries, studies investigating their drying kinetics and the effects of various pretreatments on the process are still scarce. Therefore, in this study, the effect of ultrasound pretreatment on the oven drying and vacuum oven drying of blueberries is investigated. During the experiments, drying temperatures were selected as 60, 70 and 80°C. For both methods, experiments were conducted with 30 s and 60 s ultrasound pretreatment and the results were compared with the untreated sample data. The kinetic parameters of effective moisture diffusivities (D_{eff}) and activation energies (E_a) were calculated. Moreover, the drying curves were modeled with 14 mathematical modeling equations given in the literature. The drying times were seen to decrease by increasing the drying temperature and with the effect of vacuum. The lowest drying time (150 min), highest D_{eff} (8.41×10^{-10} m^2/s) and highest E_a (48.23 kJ/mol) were obtained at the vacuum oven drying experiment conducted without any pretreatments. Ultrasound pretreatment was seen to have an adverse effect on the drying of blueberries. The highest drying time (960 min), lowest D_{eff} (1.57×10^{-10} m^2/s) and lowest E_a (29.47 kJ/mol) were obtained at the oven drying experiment performed after 60 s of ultrasound pretreatment.

Keywords: Blueberries, oven drying, vacuum oven drying, ultrasonic pretreatment, effective moisture diffusivity, activation energy.

INTRODUCTION

In the recent years, the significance of berries has substantially increased due to their taste, phytonutrients and health benefits. Among the most salient ones are blueberries, which are known as the second most consumed kind of berry after strawberries. Blueberries (*Vaccinium corymbosum*) are small, round fruits with dark purple color and a sweet-sour taste [1]. They are mostly cultivated in America, with the United States being the largest producer, and in Europe [2].

Blueberries are excellent sources of vitamins, minerals, phenolic acids, anthocyanins, proanthocyanidins, flavonoids and dietary fibers. They are considered as one of the richest fruits in vitamin C and antioxidants. Consequently, they have protective properties against many diseases like Alzheimer’s disease, muscular degeneration, cardiovascular and urinary diseases, vision problems, diabetes, cancer, as well as aging [1-3]. However, blueberries have a limited seasonal availability. They are prone to mechanical damage due to their tender structure, and they are easily perishable [1, 3, 4]. Therefore, various food processing technologies are employed to enhance their preservation and consequently, their shelf lives. Drying is extensively used to preserve food products, especially fruits. Drying is the reduction of the water content present in food products with the purpose to prevent harmful microbial and physicochemical reactions, while inhibiting enzymatic activities. It is of great importance in the field of food science, as it offers numerous advantages. For instance, drying provides longer shelf lives, while decreasing the costs of packaging, storage and transportation due to reduced weight and volume. Furthermore, dried fruits are excellent options for new alternative product patterns with maintained, or even enhanced nutritional values, and can be used as additives in various other food products [5-7].

Among the traditional methods employed for drying, oven drying offers the most simple and easy application. Oven drying provides a faster, more hygienic and homogeneous drying than sun or solar drying, methods of which can also be stated among the traditional drying procedures. It provides a more flexible process with a high throughput. Moreover, installation, maintenance and repair costs are lower for oven drying [8, 9]. Sometimes, oven drying is assisted with vacuum. Vacuum drying is a process suitable for the drying of food products which are

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sensitive to oxygen and heat [1]. The use of vacuum in drying protects the food products against oxidation and preserves their nutritional values, tastes, textures and colors. Moreover, it provides a shorted drying time and higher energy efficiency [1, 7, 10]. However, drying is a time and energy consuming process. Therefore, additional measures are investigated to optimize its use. The application of pretreatment processes can be stated among these measures. Pretreatments shorten the drying time, reduce the energy consumption and preserve the quality of food products [6, 11]. One of these trending pretreatment methods is the ultrasound pretreatment, which is reported to have a great potential in decreasing the processing time and increasing the quality of the dried fruits. In fact, ultrasonic energy applications have been a topic of interest for the last four decades. Ultrasound is defined as a sound frequency in the range above 16 KHz, which is greater than the range above the threshold of the human ear [5]. When ultrasound is applied in a liquid, the ultrasound waves cause alternating expansions and compressions. In the literature, this is usually explained by the repeated squeeze and release of a sponge (so called sponge effect) [5, 11-14]. During these rapid expansions and compressions, bubbles are formed and collapsed with varying intensities, which is considered as the main trigger for cellular disruption. Because of the resulting air pressure disturbances, cavitation is also responsible for the formation of some microscopic channels in the fruits that enhances moisture removal by reducing the diffusion boundary layer and increasing the convective mass transfer in the fruit [5-7, 13]. In short, the ultrasonic waves improve mass transfer through the cavitation effect, which provides easier moisture transport.

Ultrasonic pretreatment is considered as a safe and environmentally benign operation. Other advantages of ultrasound pretreatment are not having the necessity of using mechanical agitation and high temperatures, as the process can easily be carried out at ambient conditions [5, 7]. Studies in literature, in which ultrasound pretreatment is employed in agro-products have been extensively reviewed in some articles [6, 15]. Nevertheless, Mothibe *et al*. [5] stated that ultrasound pretreatment shows varying effects on different fruit materials. The authors explained that while some fruits gain water during their exposure to ultrasound, others show loss of water. This is also mentioned in the work of Fernandes *et al*. [16]. As stated by the foresaid authors, the application of the ultrasound technology is still troublesome, especially in dense and less porous fruit and vegetables. Therefore, with the aim of contributing to the obscurities in this field of investigation, in this study the effect of ultrasound pretreatment on the oven drying and vacuum oven drying of blueberries is investigated. During the experiments, the drying temperatures were selected as 60, 70 and 80°C. For both oven drying and vacuum oven drying, the experiments were conducted with 30 s and 60 s prior ultrasound pretreatment and the results were compared with the untreated dried sample data. The kinetic parameters of effective moisture diffusivities (D_{eff}) and activation energy (E_a) values were calculated. Moreover, the drying curves were modeled with the 14 most known mathematical modeling equations given in the literature.

EXPERIMENTAL

Sample preparation

The blueberries used in the experiments were imported from Peru and were retrieved from a local market in Istanbul, Turkey. Similar-sized blueberries, with approximately 1 cm radius were selected and horizontally cut into two parts in order to investigate the thin-layer diffusion. 5 g of blueberries were dried in each experiment. Prior to drying, the initial moisture contents (M_0) of the blueberries were determined through AOAC method [17], by drying the blueberries at a conventional hot air-drying oven (KH-45, Kenton, Guangzhou, China) at 105°C for 3 hours. Accordingly, the initial moisture content of the blueberries without any pretreatment was determined as 6.0388 kg water/kg dry matter and 85.79% on wet basis. On the other hand, for the blueberry samples that were subjected to 30 s and 60 s ultrasonic pretreatment, the initial moisture contents were determined as 6.1208 kg water/kg dry matter (85.96% on wet basis) and 6.1020 kg water/kg dry matter (85.92% on wet basis), respectively.

Experimental methods

The oven drying experiments were carried out at a Nüve EV-018 model oven (Nüve, Ankara, Turkey). The vacuum oven drying experiments were made on the same oven of Nüve EV-018, while vacuum assistance was supplied through a KNF N022AN.18 model vacuum pump (KNF, Freiburg, Germany). The pressure inside the oven was measured as 0.3 atm during the experiments. The ultrasonic pretreatments prior to drying experiments were performed by using an ultrasonic bath which had an accuracy of 1°C and 120 W ultrasonic power (Isolab, Escau, Germany).

In order to calculate the kinetic parameters, the drying experiments were performed at 60, 70 and

80°C. Blueberry samples were weighed to determine their moisture contents in every 15 minutes. Sample weights were measured by using a digital balance (AS 220.R2, Radwag, Radom, Poland), which had a weighing accuracy of 0.001 g. Two parallel experiments were conducted in each drying method and the drying process was stopped when the weights of the blueberry samples were reduced approximately to 5% of their initial moisture contents.

Drying curves

In order to obtain the drying curves, the moisture contents (M), drying rates (DR) and moisture ratios (MR) of the blueberries must be determined. These parameters were calculated by using Equations 1, 2 and 3 given below [18-20]:

$$M = \frac{m_w}{m_d} \quad (1)$$

In Equation 1, M is the moisture content (kg water/kg dry matter), m_w is the water content of the blueberries (kg), and m_d is the dry matter content of the blueberries (kg).

$$DR = \frac{M_{t+dt} - M_t}{dt} \quad (2)$$

In the abovementioned Equation 2, DR represents the drying rate (kg water/kg dry matter × min), t represents the drying time (min), M_t is the moisture content at any time t (kg water/kg dry matter) and M_{t+dt} is the moisture content at the time t+dt (kg water/kg dry matter).

$$MR = \frac{M_t - M_e}{M_0 - M_e} \quad (3)$$

In Equation 3, MR is the moisture ratio (dimensionless), M_0, M_t and M_e are the moisture contents initially, at any time and at balance, respectively (kg water/kg dry matter). Since the moisture content at balance is very low when compared to the initial and instantaneous moisture contents, M_e is neglected in the calculations [18, 19].

Effective moisture diffusivity and activation energy calculations

In order to describe the moisture diffusion in the drying of food products, Fick's second law of diffusion is used. In this study, several assumptions were made while solving this equation. Firstly, the shrinkage of the blueberries was neglected. Moreover, it was assumed that the mass transfer occurred symmetrically with respect to the center only by diffusion, and the diffusivity was accepted as constant. In regard to the aforementioned assumptions, Fick's second law for a thin layer with a thickness of 2L is transformed to Equation 4 [19, 21]:

$$MR = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D_{eff} \times t}{4L^2}\right) \quad (4)$$

In Equation 4, *n* is a positive integer, t is the time (s), D_{eff} is the effective moisture diffusivity (m^2/s) and L is half of the thickness of the sample (m). For elongated drying times, n is assumed as 1 [19, 21]. Hence, Equation 4 can be simplified into Equation 5:

$$\ln(MR) = \ln\left(\frac{8}{\pi^2}\right) - \left(\pi^2 \frac{D_{eff} \times t}{4L^2}\right) \quad (5)$$

By using Equation 5, D_{eff} can be calculated from the slope of the ln(MR) *versus* t plot. Once D_{eff} is calculated, its relation with temperature can be given through Arrhenius equation given below as Equation 6 [19, 22]:

$$D_{eff} = D_o \exp\left(-\frac{E_a}{R \times (T + 273.15)}\right) \quad (6)$$

Here, D_0 is is the pre-exponential factor (m^2/s), E_a is the activation energy (kJ/mol), R is the universal gas constant (kJ/mol × K) and T is the drying temperature (°C). Thus, E_a can be calculated from the slope of the plot of $\ln(D_{eff})$ *versus* 1/T graph. Activation energy is an important parameter in drying kinetics, as in regard to the energy provided by the drying devices to the product to be dried, higher activation energy will result in faster drying.

Mathematical modeling

For the mathematical modeling of the drying of blueberries, 14 abundantly used mathematical drying models present in the literature were considered. The models applied to the experimental data were Aghbaslo *et al.*, Alibas, Henderson & Pabis, Jena *et al.*, Lewis, Logarithmic, Midilli & Kucuk, Page, Parabolic, Peleg, Two-Term Exponential, Verma *et al.*, Wang & Singh and Weibull models, which are presented in Table 1.

For the models presented in Table 1, a, b, c and g are coefficients; n is the drying exponent specific to each equation; k, k_1 and k_2 are drying coefficients and t is the time in minutes. In the modeling process, Statistica software (Statsoft Inc., Tulsa, OK) was used for the nonlinear Levenberg-Marquardt procedure regressions. The suitability of the models to the drying data was determined with respect to the coefficient of determination (R^2), reduced chi-square (χ^2) and root mean square error (RMSE) values, which were obtained from Equations 7 to 9, given below [22, 23]. In these equations, N is the total number of experiments, z is the number of constants used in the model equations, MR_{exp} and MR_{pre} represent the experimental and predicted moisture ratios, respectively. The model that yielded the highest R^2, the lowest χ^2 and the lowest RMSE was selected as the most convenient model.

Table 1. Mathematical drying models applied to the experimental data [18, 19].

Model Name	Model Equation
Aghbaslo *et al.*	$MR = \exp(-k_1 t / (1 + k_2 t))$
Alibas	$MR = a \times \exp((-kt^n) + bt) + g$
Henderson & Pabis	$MR = a \times \exp(-kt)$
Jena *et al.*	$MR = a \times \exp(-kt + b\sqrt{t}) + c$
Lewis	$MR = \exp(-kt)$
Logarithmic	$MR = a \times \exp(-kt) + c$
Midilli & Kucuk	$MR = a \times \exp(-kt^n) + bt$
Page	$MR = \exp(-kt^n)$
Parabolic	$MR = a + bt + ct^2$
Peleg	$MR = a + t/(k_1 + k_2 t)$
Two-Term Exponential	$MR = a \times \exp(-kt) + (1-a) \times \exp(-kat)$
Verma *et al.*	$MR = a \times \exp(-kt) + (1 - a) \times \exp(-gt)$
Wang & Singh	$MR = 1 + at + bt^2$
Weibull	$MR = a - b \times \exp(-(kt)^n)$

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2}{\sum_{i=1}^{N}\left(MR_{exp,i} - \left(\frac{1}{n}\right)MR_{exp,i}\right)^2} \qquad (7)$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2}{N - z} \qquad (8)$$

$$RMSE = \left(\frac{1}{N}\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pre,i}\right)^2\right)^{\frac{1}{2}} \qquad (9)$$

RESULTS AND DISCUSSION

Drying curve results

Figure 1 presents the drying curves and the drying rate curves of blueberries for oven drying, without any pretreatment (Figure 1a), with 30 s ultrasound (US) pretreatment (Figure 1b) and 60 s US pretreatment (Figure 1c). Considering the moisture contents, for oven drying without any pretreatments, the initial moisture content of 6.0388 kg water/kg dry matter decreased to 0.4480, 0.3939 and 0.3858 kg water/kg dry matter for drying temperatures of 60°C, 70°C and 80°C, respectively. The drying times were obtained as 390, 270 and 195 min for the aforementioned temperatures. For oven drying with prior 30 s US pretreatment, the initial moisture content of 6.1208 kg water/kg dry matter decreased to 0.4522, 0.3640 and 0.3350 kg water/kg dry matter for drying temperatures of 60°C, 70°C and 80°C, respectively. For this set of experiments, a remarkable increase in the drying times was observed. The drying times increased from 390 min to 630 min at 60°C, from 270 min to 300 min at 70°C, and from 195 min to 255 min at 80°C, when 30 s US pretreatment was employed. When the duration of the US pretreatment was further increased to 60 s, even more prolonged drying times were encountered. The drying times were obtained as 960, 480 and 300 min for drying temperatures of 60°C, 70°C and 80°C, respectively.

Ultrasonic pretreatment on vacuum oven drying of blueberry samples gave similar results. Figure 2 presents the drying curves and the drying rate curves of blueberries for oven drying, without any pretreatment (Figure 2a), with 30 s US pretreatment (Figure 2b) and 60 s US pretreatment (Figure 2c). Nevertheless, the prominent impact of vacuum assistance on the drying durations is incontrovertible. During vacuum oven drying without any pretreatments, the drying times were 345 min, 210 min and 150 min at 60°C, 70°C and 80°C, respectively. Likewise, in the oven drying experiments, ultrasonic pretreatments resulted in an increase in drying times, though their effects were less distinct. The drying times increased from 345 min to 375 min at 60°C, from 210 min to 255 min at 70°C, and from 150 min to 180 min at 80°C, when 30 s US pretreatment was employed. For 60 s US pretreatment on the other hand, the drying times were obtained as 390, 270 and 180 min for drying temperatures of 60°C, 70°C and 80°C, respectively.

Drying kinetics results

As it was elaborately given in the Experimental section, D_{eff} values were calculated by using Equation 5 from the slope of ln(MR) *versus* drying time plots. The obtained equations from these plots are given in Equations 10 to 27 below. In these equations, oven drying is designated with the initials OD and vacuum oven drying is designated with the initials VOD, respectively.

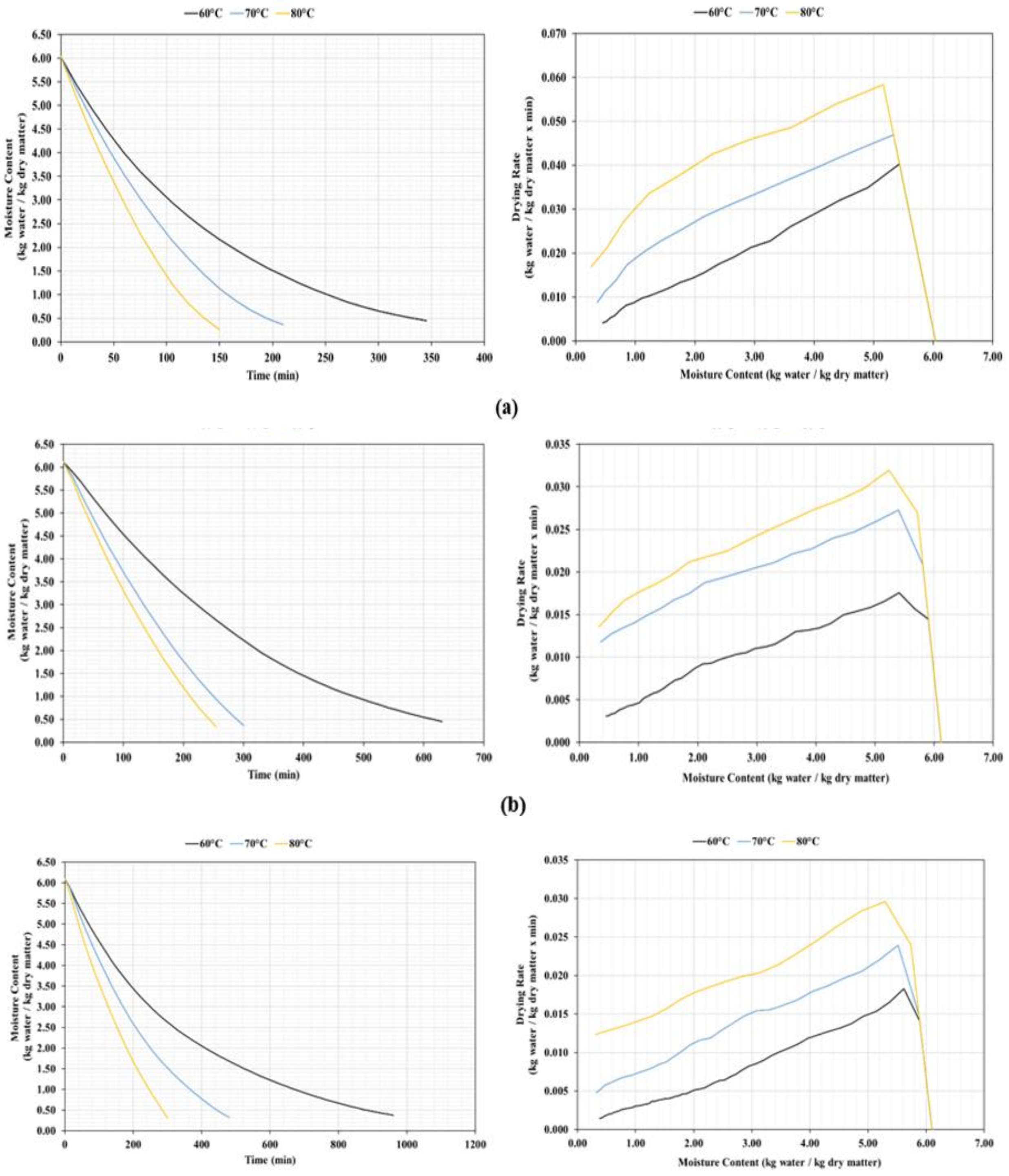

Figure 1. Drying curves (on the left) and drying rate curves (on the right) of blueberries for oven drying (a): without any pretreatment, (b): 30 s US pretreatment, (c): 60 s US pretreatment.

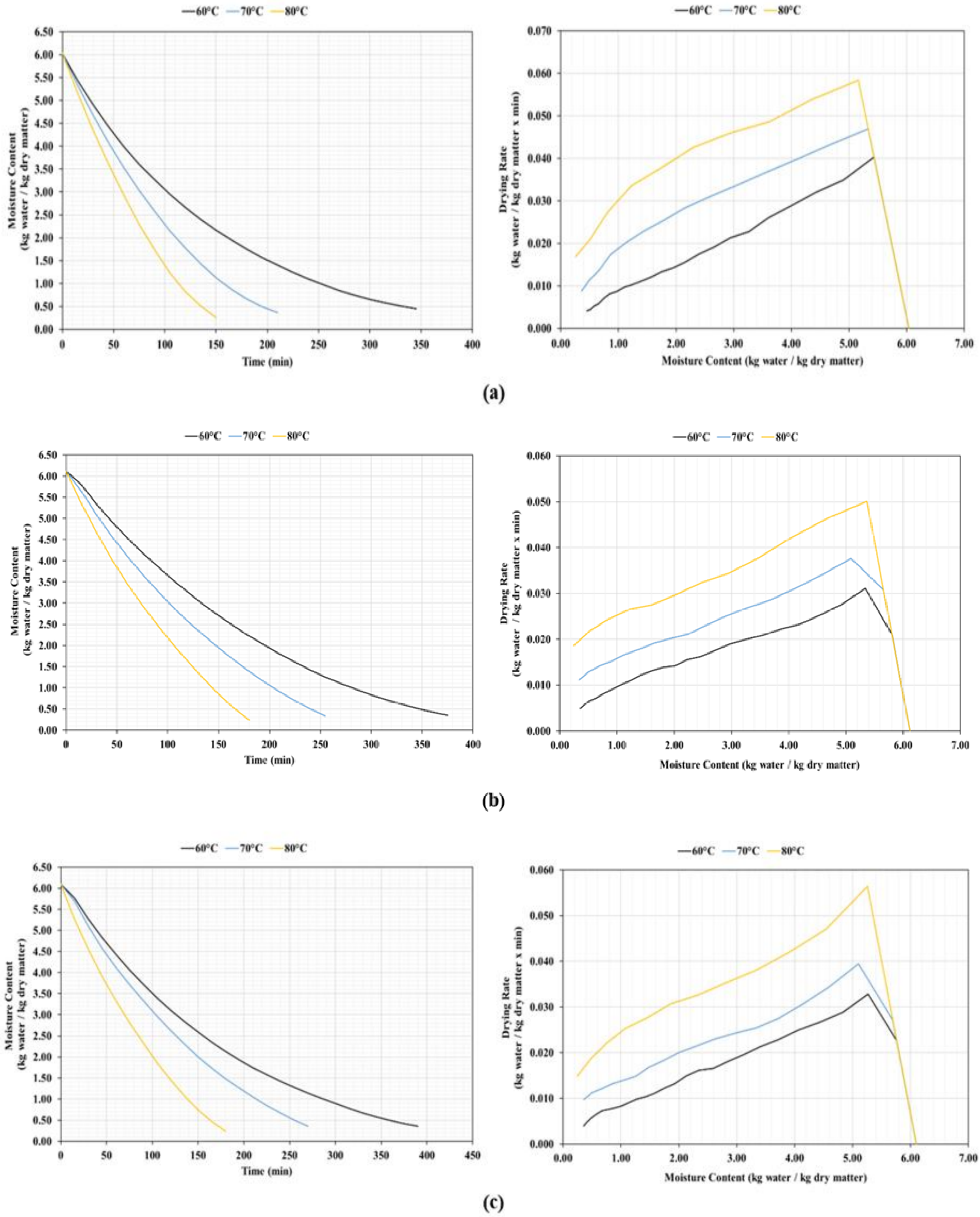

Figure 2. The drying curves (on the left) and the drying rate curves (on the right) of blueberries for vacuum oven drying (a): without any pretreatment, (b): 30 s US pretreatment, (c): 60 s US pretreatment

OD, no US (60°C) → $\ln(MR) = -0.000108t + 0.127915 \quad (R^2 = 0.989875)$ (10)

OD, no US (70°C) → $\ln(MR) = -0.000162t + 0.208640 \quad (R^2 = 0.973694)$ (11)

OD, no US (80°C) → $\ln(MR) = -0.000214t + 0.255830 \quad (R^2 = 0.936406)$ (12)

OD, 30 s US (60°C) → $\ln(MR) = -0.000068t + 0.138591 \quad (R^2 = 0.992120)$ (13)

OD, 30 s US (70°C) → $\ln(MR) = -0.000142t + 0.269506 \quad (R^2 = 0.941314)$ (14)

OD, 30 s US (80°C) → $\ln(MR) = -0.000171t + 0.280785 \quad (R^2 = 0.934234)$ (15)

OD, 60 s US (60°C) → $\ln(MR) = -0.000046t + 0.012590 \quad (R^2 = 0.997188)$ (16)

OD, 60 s US (70°C) → $\ln(MR) = -0.000096t + 0.201783 \quad (R^2 = 0.975189)$ (17)

OD, 60 s US (80°C) → $\ln(MR) = -0.000146t + 0.261697 \quad (R^2 = 0.937894)$ (18)

VOD, no US (60°C) → $\ln(MR) = -0.000124t + 0.053750 \quad (R^2 = 0.997411)$ (19)

VOD, no US (70°C) → $\ln(MR) = -0.000219t + 0.202322 \quad (R^2 = 0.977932)$ (20)

VOD, no US (80°C) → $\ln(MR) = -0.000322t + 0.295706 \quad (R^2 = 0.946609)$ (21)

VOD, 30 s US (60°C) → $\ln(MR) = -0.000123t + 0.197021 \quad (R^2 = 0.980831)$ (22)

VOD, 30 s US (70°C) → $\ln(MR) = -0.000175t + 0.238284 \quad (R^2 = 0.955666)$ (23)

VOD, 30 s US (80°C) → $\ln(MR) = -0.000265t + 0.295492 \quad (R^2 = 0.920488)$ (24)

VOD, 60 s US (60°C) → $\ln(MR) = -0.000118t + 0.146794 \quad (R^2 = 0.988373)$ (25)

VOD, 60 s US (70°C) → $\ln(MR) = -0.000165t + 0.215812 \quad (R^2 = 0.967004)$ (26)

VOD, 60 s US (80°C) → $\ln(MR) = -0.000273t + 0.281198 \quad (R^2 = 0.939041)$ (27)

Table 2. Calculated D_{eff} and E_a values for the drying of blueberries

Method	D_{eff} (m^2/s)	E_a (kJ/mol)
Oven Drying No US, 60°C	2.74×10^{-10}	33.50
Oven Drying No US, 70°C	4.10×10^{-10}	
Oven Drying No US, 80°C	5.42×10^{-10}	
Oven Drying 30 s US, 60°C	2.01×10^{-10}	31.56
Oven Drying 30 s US, 70°C	2.91×10^{-10}	
Oven Drying 30 s US, 80°C	3.83×10^{-10}	
Oven Drying 60 s US, 60°C	1.57×10^{-10}	29.47
Oven Drying 60 s US, 70°C	2.15×10^{-10}	
Oven Drying 60 s US, 80°C	2.86×10^{-10}	
Vacuum Oven Drying No US, 60°C	3.14×10^{-10}	48.23
Vacuum Oven Drying No US, 70°C	5.55×10^{-10}	
Vacuum Oven Drying No US, 80°C	8.41×10^{-10}	
Vacuum Oven Drying 30 s US, 60°C	3.12×10^{-10}	37.50
Vacuum Oven Drying 30 s US, 70°C	4.43×10^{-10}	
Vacuum Oven Drying 30 s US, 80°C	6.71×10^{-10}	
Vacuum Oven Drying 60 s US, 60°C	2.99×10^{-10}	36.98
Vacuum Oven Drying 60 s US, 70°C	4.18×10^{-10}	
Vacuum Oven Drying 60 s US, 80°C	6.37×10^{-10}	

With respect to the equations given above, the calculated D_{eff} and E_a values are presented in Table 2. As it can be seen from Table 2, the effective moisture diffusivity values increase with drying temperature and vacuum assistance. The application of ultrasonic pretreatment resulted in a decrease in both D_{eff} and E_a values. The longer ultrasonic pretreatment was employed, the greater decrease in the kinetic parameters was observed. In the literature, ultrasonic pretreatments on the drying of agro-products do not show a distinct influence in a certain way. As stated by Mothibe *et al.*, ultrasound pretreatment shows varying effects on different fruit materials [5]. Though ultrasonic pretreatment shows a positive impact on the drying behavior of some food products, it has an adverse effect on others, similar to the results obtained from this study. For instance, in a study on the drying of melon tissues [11], it was reported that the fruit gained water as a result of ultrasonic pretreatment. Nowacka and Wedzik [13] analyzed the effect of ultrasound pretreatment on fresh and dried carrot slices in a convective dryer operated at 70°C. The authors stated that there was no reduction in the drying time in the ultrasound-pretreated samples. Instead of expected shortening of the drying time, a small prolongation was observed for the time needed for achieving the desired moisture content. As for the effective moisture diffusivity, D_{eff}, the highest value was found for the untreated sample, just like the case in the present study. There was an 8-12% reduction observed for D_{eff} values calculated for ultrasound-pretreated samples. The authors observed structural changes and formation of microchannels during the pretreatment, which were reported not to cause an acceleration in the drying process.

Ozyalcin and Kipcak investigated the effect of ultrasonic pretreatment on the thin layer infrared drying characteristics of squid [14]. The authors found out that, without any pretreatment, the drying times were 277 min, 240 min and 150 min for drying temperatures of 60°C, 70°C and 80°C, respectively. When ultrasonic pretreatment was used, the aforementioned drying times were seen to increase to 315 min, 300 min and 190 min, respectively. Moreover, similar to the presented findings here, a reduction in the effective moisture diffusivities and activation energies were also observed when ultrasound pretreatment was employed. This was attributed to the swelling with water during the pretreatment. In another article, in which the oven and vacuum oven drying characteristics of *Loligo vulgaris* (European squid) was investigated, conformable findings were reached [10]. The drying times for oven drying without any pretreatment were found as 300, 210, and 180 minutes for the drying temperatures of 60°C, 70°C and 80°C, respectively. When ultrasound pretreatment was employed, these durations at the same drying temperatures increased to 315, 240, and 210 minutes, respectively. Also, when ultrasonic pretreatment was employed in oven drying, a decrease in the effective moisture diffusivities was also recorded. When vacuum was assisting the oven drying process, a significant decrease in drying times were observed. The authors stated that the vacuum effect on the drying process reduced the moisture content. After applying ultrasound pretreatment, the same drying times were recorded. There was a 26.4% increase in activation energy when vacuum oven drying process was employed, and a reduction in activation energies when there was a prior ultrasonic pretreatment [10].

Fernandes *et al.* observed a decrease in water diffusivity during the drying of mangoes, when ultrasonic pretreatment was used [16]. The decrease in the water diffusivity ranged from 9.3 to 29.4%. Moreover, mangoes without pretreatment required 168 min to dry, removing 90% of its initial moisture while 5 minutes of ultrasound pretreatment increased this duration to 221 min. The authors attributed this result to the fact that mangoes are dense and have more fibers than most fruits. This kind of tissue structure differs from that of other fruits and is less susceptible to the effects induced by ultrasound application.

Mathematical modeling results

The mathematical modeling results obtained for oven drying of blueberries, with and without pretreatments are presented in Table 3 and those for vacuum oven drying are presented in Table 4. The tables show the results for the three models having the highest average R^2, the lowest χ^2 and lowest RMSE values among the 14 models that have been considered.

In regard to Table 3, for oven drying, the model having the highest compatibility with the drying data was found to be Midilli & Kucuk model for all sets. Considering the oven drying experiments without any pretreatments, R^2 values of 0.999956, 0.999907 and 0.999974 were obtained for this model at 60, 70 and 80°C, respectively. For oven drying with 30 s ultrasonic pretreatment, R^2 values of 0.999962, 0.999982 and 0.999986 were obtained at the same temperatures. Oven drying with 60 s prior ultrasonic pretreatment yielded R^2 values of 0.999882, 0.999971 and 0.999969 at 60, 70 and 80°C, respectively.

For vacuum oven drying experiments without any pretreatment, as it can be seen from Table 4, the most compatible model was seen to be Aghbashlo *et al.*, with R^2 values of 0.999885, 0.999982 and 0.999953 at the selected drying temperatures. For vacuum oven drying experiments with 30 s and 60 s ultrasonic pretreatment, again Midilli & Kucuk model was the most suitable. This model showed R^2 values of 0.999947, 0.999970 and 0.999987 for 30 s ultrasound; and 0.999954, 0.999929 and 0.999899 for 60 s ultrasound at the drying temperatures of 60, 70 and 80°C, respectively.

Table 3. Statistical data for the best 3 mathematical models obtained for oven drying

Oven Drying, No Pretreatment

Model	Midilli & Kucuk			Aghbashlo *et al.*			Parabolic		
Coeff.	60°C	70°C	80°C	60°C	70°C	80°C	60°C	70°C	80°C
a	0.995396	0.993993	0.997970				0.986549	1.000218	0.999966
b	-0.000133	-0.000367	-0.001263				-0.004268	-0.005709	-0.006542
c							0.000005	0.000008	0.000009
k	0.003432	0.003320	0.004203						
n	1.073446	1.128176	1.068818						
k_1				0.004683	0.005588	0.006109			
k_2				-0.000726	-0.001632	-0.002726			
R^2	0.999956	0.999907	0.999974	0.999955	0.999989	0.999774	0.999692	0.999992	0.999994
χ^2	0.000008	0.000020	0.000006	0.000007	0.000002	0.000045	0.000053	0.000002	0.000001
RMSE	0.002584	0.003929	0.002116	0.002618	0.001340	0.006200	0.006852	0.001131	0.001006

Oven Drying, 30 s US Pretreatment

Model	Midilli & Kucuk			Parabolic			Wang & Singh		
Coeff.	60°C	70°C	80°C	60°C	70°C	80°C	60°C	70°C	80°C
a	0.997453	1.001313		0.996298	1.008536	1.005261	-0.002733	-0.004325	-0.005127
b	-0.000060	-0.000683		-0.002709	-0.004436	-0.005207	0.000002	0.000004	0.000006
c				0.000002	0.000004	0.000006			
k	0.001685	0.002335	1.000725						
n	1.113352	1.113716	-0.000871						
R^2	0.999962	0.999982	0.999986	0.999842	0.999964	0.999978	0.999831	0.999905	0.999956
χ^2	0.000076	0.000004	0.000003	0.000001	0.000007	0.000004	0.000001	0.000018	0.000008
RMSE	0.008378	0.001714	0.001572	0.001134	0.002469	0.001932	0.001007	0.003979	0.002747

Oven Drying, 60 s US Pretreatment

Model	Midilli & Kucuk			Logarithmic			Aghbashlo *et al.*		
Coeff.	60°C	70°C	80°C	60°C	70°C	80°C	60°C	70°C	80°C
a	1.015031	1.005315	1.003840	0.989660	1.209125	1.552454			
b	-0.000034	-0.000166	-0.000711						
c				-0.000033	-0.192161	-0.546640			
k_1							0.002827	0.003570	0.004431
k_2							0.000052	-0.000789	-0.001643
k	0.004685	0.002581	0.003686	0.002727	0.003343	0.003175			
n	0.905849	1.078765	1.032469						
R^2	0.999882	0.999971	0.999969	0.999621	0.999900	0.999961	0.999624	0.999837	0.999588
χ^2	0.000005	0.000005	0.000006	0.000004	0.000018	0.000008	0.001027	0.000028	0.000075
RMSE	0.002151	0.002165	0.002267	0.002310	0.003997	0.002543	0.030217	0.005115	0.008251

Table 4. Statistical data for the best 3 mathematical models obtained for vacuum oven drying

Vacuum Oven Drying, No Pretreatment

Model	Aghbashlo *et al.*			Midilli & Kucuk			Logarithmic		
Coeff.	60°C	70°C	80°C	60°C	70°C	80°C	60°C	70°C	80°C
a				0.999504	0.995406	0.995971	1.036386	1.251195	1.444275
b				-0.000106	-0.000395	-0.000876			
c							-0.041313	-0.242949	-0.435884
k				0.007207	0.005143	0.005727	0.006390	0.006984	0.007581
n				0.981632	1.115297	1.146942			
k_1	0.006618	0.007817	0.009502						
k_2	-0.000296	-0.001994	-0.003566						
R^2	0.999885	0.999982	0.999953	0.999980	0.999879	0.999835	0.999964	0.999740	0.999640
χ^2	0.000018	0.000003	0.000011	0.000004	0.000021	0.000050	0.000006	0.000037	0.000095
RMSE	0.004100	0.001761	0.003014	0.001733	0.004589	0.005622	0.002281	0.006721	0.008299

Vacuum Oven Drying, 30 s US Pretreatment

Model	Midilli & Kucuk			Logarithmic			Parabolic		
Coeff.	60°C	70°C	80°C	60°C	70°C	80°C	60°C	70°C	80°C
a	1.002306	1.002973	1.000091	1.208746	1.378660	1.527093	0.998850	0.999427	0.991238
b	-0.000196	-0.000585	-0.001314				-0.004495	-0.005852	-0.007828
c				-0.192686	-0.370053	-0.529397	0.000005	0.000009	0.000014
k	0.003135	0.004492	0.007462	0.004306	0.004647	0.005491			
n	1.095731	1.060502	0.993375						
R^2	0.999947	0.999970	0.999987	0.999845	0.999941	0.999978	0.999830	0.999873	0.999867
χ^2	0.000049	0.000006	0.000003	0.000143	0.000012	0.000005	0.000012	0.000026	0.000031
RMSE	0.006573	0.002246	0.001540	0.010984	0.003155	0.001971	0.003155	0.004624	0.004868

Vacuum Oven Drying, 60 s US Pretreatment

Model	Midilli & Kucuk			Logarithmic			Aghbashlo *et al.*		
Coeff.	60°C	70°C	80°C	60°C	70°C	80°C	60°C	70°C	80°C
a	1.006484	1.004591	0.997235	1.119371	1.296584	1.395313			
b	-0.000124	-0.000420	-0.001062						
c				-0.104556	-0.283812	-0.399041			
k_1							0.005068	0.005722	0.008379
k_2							-0.000726	-0.001564	-0.002648
k	0.004167	0.004323	0.007954	0.004992	0.004976	0.006507			
n	1.054670	1.074623	1.008721						
R^2	0.999954	0.999929	0.999899	0.999906	0.999872	0.999920	0.999845	0.999779	0.999451
χ^2	0.000009	0.000015	0.000026	0.000017	0.000025	0.000019	0.000026	0.000041	0.000116
RMSE	0.002712	0.003439	0.004250	0.003870	0.004631	0.003783	0.004950	0.006084	0.009902

CONCLUSION

In this study, the effect of ultrasound pretreatment on the oven drying and vacuum oven drying of blueberries was investigated. It was observed that an increase in drying temperature and assistance of vacuum caused shorter drying times. On the other hand, ultrasonic pretreatment was seen to have an adverse effect on the drying durations. The drying duration was between 195-390 min for oven drying without pretreatments. This duration increased to 255-630 min for 30 s ultrasound pretreatment, and to 300-960 min for 60 s ultrasound pretreatment, respectively. Even though the drying times were shorter, vacuum oven drying experiments showed similar results. The drying duration of 150-345 min increased to 180-375 min for 30 s ultrasound pretreatment, and to 180-390 min for 60 s ultrasound pretreatment, respectively. By the application of ultrasonic pretreatment, a decrease in effective moisture diffusivities and activation energies was also observed. D_{eff} values were found between 2.74×10^{-10} - 5.42×10^{-10} m^2/s for oven drying without pretreatments; 2.01×10^{-10} - 3.83×10^{-10} m^2/s for oven drying with 30 s ultrasound pretreatment; and 1.57×10^{-10} - 2.86×10^{-10} m^2/s for oven drying with 60 s ultrasound pretreatment. When vacuum assistance was employed, D_{eff} values increased to 3.14×10^{-10} - 8.41×10^{-10} m^2/s for vacuum oven drying without pretreatments; 3.12×10^{-10} - 6.71×10^{-10} m^2/s for vacuum oven drying with 30 s ultrasound pretreatment; and 2.99×10^{-10} - 6.37×10^{-10} m^2/s for vacuum oven drying with 60 s ultrasound pretreatment. For activation energies, on the other hand, E_a of 33.50 kJ/mol decreased to 31.56 kJ/mol and 29.47 kJ/mol when 30 and 60 s of ultrasonic pretreatments were applied in oven drying, respectively. A similar tendency was observed in vacuum oven drying experiments. E_a of 48.23 kJ/mol decreased to 37.50 kJ/mol and 36.98 kJ/mol for 30 and 60 s of ultrasonic pretreatment, respectively. When the experimental data was statistically analyzed, Midilli & Kucuk model was seen to be the most compatible one in oven drying of blueberries. For vacuum oven drying without any pretreatments, Aghbashlo et al. model was seen to yield the best fit with the experimental data. For ultrasonic pretreatment sets, again Midilli & Kucuk model yielded the highest R^2 values in vacuum oven drying. In consequence, it can be concluded that the application of ultrasound pretreatment on the oven drying of blueberries, with and without the assistance of vacuum, did not show a positive effect on the drying duration, effective moisture diffusivity and activation energy values.

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