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The Investigation of Oven and Vacuum Oven Drying Kinetics and Mathematical Modeling of Golden Berries[1]

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Abstract: Golden berry (*Physalis peruviana*) is a fruit that is natively cultivated in the Andean region. Due to its significant nutritional and functional properties, golden berry has been gradually attracting worldwide attention. In this study, oven and vacuum oven drying of golden berries were performed at 60, 70 and 80 °C. Throughout the experiments, the drying kinetic parameters of effective moisture diffusivity (D_{eff}) and activation energy (E_a) were investigated. Moreover, mathematical modeling of drying data was established with the most known modeling equations presented in literature. Experiments revealed that the drying times decreased with increasing temperature and with vacuum addition. The highest and lowest drying times were encountered as 480 minutes in oven drying at 60 °C, and 195 minutes in vacuum oven drying at 80 °C, respectively. D_{eff} values were calculated between 1.95×10^{-10}-3.80×10^{-10} m^2/s and 2.20×10^{-10}-5.45×10^{-10} m^2/s for oven and vacuum oven drying, respectively. E_a values, on the other hand, were found as 32.81 kJ/mol for oven drying and 44.30 kJ/mol for vacuum oven drying. Among the fourteen mathematical models applied to drying curve data, Midilli & Kucuk model provided the best fit for both oven and vacuum oven drying.

Keywords: Drying Kinetics, Golden Berry, Mathematical Modeling, Oven Drying, Vacuum Oven Drying.

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1. INTRODUCTION

Golden berry (*Physalis peruviana*), also called cape gooseberry, is an exotic fruit that is natively cultivated in the Andean region of the world (Etzbach et al., 2020; Junqueira et al., 2017). It is covered by a yellow peel and is protected through a surrounding dry parchment-like husk, named as calyx, which serves as a protective shield against adverse climatic conditions, birds, and insects (Bravo & Osorio, 2016; Lopez et al., 2013; Nawirska-Olszańska et al., 2017). It is a functional food that attracts particular attention due its nutritional composition and content of bioactive components. Golden berries contain substantial amount of vitamins (especially Vitamins A, C, K, and B complexes), minerals, fibers, ascorbic acid, polyphenols and carotenoids (Bravo & Osorio, 2016; Junqueira et al., 2017; Lopez et al., 2013; Nawirska-Olszańska et al., 2017; Puente et al., 2021). It is widely used in the field of medicine for the remedy of various diseases, due to its anti-parasitic, anti-infectious, and diuretic properties (Bravo & Osorio, 2016). It was reported that golden berries are used in the treatment of cancer, hypertension, asthma, ulcer, hepatitis, dermatitis, malaria, and rheumatism (Karacabey, 2016; Ramadan, 2011). The high levels of Vitamin K, which is responsible for protein synthesis in charge of blood clotting and bone metabolism, reduce the risk of cardiac diseases and occurrence of cancer (Ramadan, 2011). Due to its fructose content, golden berry is also recommended for diabetics (Nawirska-Olszańska et al., 2017; Ramadan, 2011).

Considering all of the aforementioned desirable nutritional and functional properties, golden berry is

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gradually becoming a fruit of particular interest to the food industry. Nevertheless, golden berry is a rapidly perishable fruit, a property of which hinders its desired commercialization. Consequently, this phenomenon necessitates the investigation of efficient methods for the extensive preservation of golden berries. One of these preservation methods is drying. The main objective of food drying is to preserve foods and to increase their shelf lives, by decreasing their moisture contents in order to inhibit the activities of microorganisms. Moreover, transport and storage costs are reduced, since the use of refrigeration systems is not necessary. There are many conventional methods employed for the drying of fruits; however among these methods, oven drying offers the easiest and simplest and application. Furthermore, it provides a more homogeneous, hygienic, and rapid drying than the other conventional methods. In some studies, oven drying is assisted with the use of vacuum. Vacuum assistance protects fruits against oxidation, while simultaneously preserving their nutritional values, texture, taste, and color (Calín-Sánchez et al., 2014; Guiné, 2018; Kaleta & Górnicki, 2010; Pan et al., 2008).

In this study, oven and vacuum oven drying of golden berries were investigated. Although there are numerous articles in the literature regarding the antioxidant properties of golden berries, investigation on their drying characteristics is still very scarce. This being the motivation of the present research, golden berry drying experiments were performed at 60, 70, and 80 °C. Moreover, drying kinetic parameters including the effective moisture diffusivities and activation energies were calculated. Fourteen mathematical models present in the literature were applied to the drying curve data. The results obtained for drying with and without the assistance of vacuum were comparatively evaluated.

2. MATERIALS AND METHODS

2.1. Sample Preparation

Golden berries used in the experiments, cultivated in Mersin province of Turkey, were bought from a local supermarket in İstanbul, on October 2021. Similar sized golden berries were selected for the experiments with approximate radii of 2 cm. Before the experiments, the golden berries were horizontally divided into two pieces for the investigation of thin layer diffusion process. In each experiment, 10 g of golden berry samples were used, which were equivalent to two or three golden berries for each run. Prior to drying, the initial moisture content of the golden berries was determined by AOAC method (AOAC International, 1975), using a KH-45 hot air drying oven (Kenton, Guangzhou, China) at 105 °C for 2 hours. In this regard, the initial moisture content of the golden berries was determined as 74.93% on wet basis, and 2.989 kg of water/kg dry matter.

2.2. Drying Methods

In this study, two different drying methods were used for the drying of golden berries, which were oven drying and vacuum oven drying. In oven drying, Nüve EV-018 model oven (Nüve, Ankara, Turkey) was used. In vacuum-oven drying, on the other hand, the same oven was used with KNF N022AN.18 model vacuum pump (KNF, Freiburg, Germany). The pressure inside the oven was measured as 0.3 atm during the experiments. In order to calculate the kinetic parameters, the experiments were performed at three different temperatures that were 60, 70, and 80 °C. During the drying process, the golden berries were weighed by a Radwag AS 220.R2 digital balance (Radwag, Radom, Poland) in every 15 minutes. When the weights of the golden berries were reduced to approximately 5% of the moisture content, the drying process was stopped.

2.3. Drying Kinetics

In order to calculate the kinetic parameters, the moisture content (M) as kg water/kg dry matter, the drying rate (DR) as kg water/(kg dry matter×min) and the moisture ratio (MR) as dimensionless were calculated by using Equations (1), (2) and (3), respectively (Başlar et al., 2014; Doymaz et al., 2016; Ismail & Kocabay, 2018):

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

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

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

In the aforementioned equations, m_w represents the water content of the golden berries in kg, m_d is their dry matter content in kg, t is the drying time in minutes and M_{t+dt} is the amount of moisture during the time t+dt in kg water/kg dry matter. M_0, M_t and M_e represent the amount of initial moisture, moisture at any time t and moisture at equilibrium, respectively. Since the moisture levels at equilibrium are very low compared to the initial and instantaneous moisture values, M_e is neglected in the calculations (Amiri Chayjan & Shadidi, 2014; Calín-Sánchez et al., 2014).

To describe moisture diffusion in food drying, which usually occurs during the falling rate period, Fick's second law of diffusion is used (Crank, 1975). In the present study, in order to perform the analytical solution of this equation, several assumptions were made, which are presented as follows:

- The shrinkage of the golden berries was neglected,
- The diffusion coefficient was accepted as constant,
- The mass transfer was assumed to occur symmetrically with respect to the center, only by diffusion.

Taking into account the foresaid assumptions, the analytical solution of Fick's second law for a thin layer with a thickness of 2 L is calculated with respect to Equation (4):

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

In Equation (4) n is a positive integer, D_{eff} is the effective moisture diffusivity in m^2/s, t is the time in seconds and L is the half of the sample thickness in meters. For elongated drying times, n is assumed as 1 (Doymaz et al., 2016; Ismail & Kocabay, 2018). Thus, Equation (4) can be simplified to Equation (5) as presented below:

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

By using Equation (5), D_{eff} can be calculated from the slope of ln(MR) versus t plot. Once D_{eff} is calculated, its relation with temperature can be expressed by Arrhenius equation, which is presented in Equation (6) (19):

$$D_{eff} = D_o\exp\left(\frac{-E_a}{R(T+273.15)}\right) \qquad \text{(Eq. 6)}$$

In the aforementioned equation D_0 is the pre-exponential factor in m^2/s, E_a is the activation energy in kJ/mol, R is the universal gas constant in kJ/(mol×K) and T is the drying temperature in °C. The activation energy, E_a, can be calculated from the slope of ln(D_{eff}) versus 1/T plot.

2.4. Mathematical Modeling of the Drying Process

For the mathematical modeling of the drying of golden berries, fourteen abundantly used mathematical models present in the literature were investigated. These mathematical drying 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 (Ismail & Kocabay, 2018; Kipcak et al., 2021; Ozyalcin & Kipcak, 2020, 2020).

Table 1: The mathematical drying models applied to the experimental data for oven drying and vacuum oven drying of golden berries.

Model Name	Parameter
Aghbashlo et al.	MR = exp($-k_1t/(1 + k_2t)$)
Alibas	MR = a·exp(($-kt^n$) + bt) + g
Henderson & Pabis	MR = a·exp(-kt)
Jena et al.	MR = a·exp(-kt + b⌧t) + c
Lewis	MR = exp(-kt)
Logarithmic	MR = a·exp(-kt) + c
Midilli & Kucuk	MR = a·exp($-kt^n$) + bt
Page	MR = exp($-kt^n$)
Parabolic	MR = a + bt + ct^2
Peleg	MR = a + t/($k_1 + k_2t$)
Two-Term Exponential	MR = a·exp(-kt) + (1 - a)·exp(-kat)
Verma et al.	MR = a·exp(-kt) + (1 - a)·exp(-gt)
Wang & Singh	MR = 1 + at + bt^2
Weibull	MR = a - b·exp(-(kt^n))

In the modelling process, Statistica 6.0 software (Statsoft Inc., Tulsa, OK) was used for the nonlinear regressions based on Levenberg-Marquardt procedure and parameters. While using the program, the experimental data is entered and nonlinear regression is selected. Once the selected mathematical model is defined, the program used iterative algorithms to find the best fits for the unknown constants through the reductions in the sum of the squared errors. During the testing of the mathematical models, the coefficient of determination (R^2), reduced chi-square (χ^2) and root mean square error (RMSE) were calculated for the experimental and predicted MR values, the formulas of which are given in various studies in literature (Alibas, 2014; Uribe et al., 2022; Vega-Gálvez et al., 2014; Zhu, 2018). The best model to describe the drying of golden berries was selected as the model giving the highest R^2, lowest χ^2 and lowest RMSE values (9).

3. RESULTS AND DISCUSSION

3.1. The Drying and Drying Rate Curves

Figure 1 and Figure 2 present the drying curves and the drying rate curves of oven drying and vacuum oven drying of golden berries, respectively. Considering Figure 1 first, it is seen that the drying times and the final moisture contents decreased with increasing temperature. Moreover, the drying times were observed to be shorter for vacuum oven drying. Similar results were obtained in literature studies (Ozyalcin & Kipcak, 2020). During the experiments made with oven drying, the drying times were found as 285, 300 and 480 minutes for drying temperatures of 80, 70, and 60 °C, respectively. On the other hand, these times reduced to 195, 285, and 435 minutes for the same drying temperatures during vacuum oven drying. From the moisture content point of view, vacuum oven drying yielded similar results. The initial moisture content of the golden berry samples, which was 2.989 kg water/kg dry matter, reduced to 0.156, 0.208, and 0.291 kg water/kg dry matter for oven drying at 80, 70, and 60 °C, respectively. For vacuum oven drying, the final moisture contents were calculated as 0.154, 0.204, and 0.269 kg water/kg dry matter for the same drying temperatures.

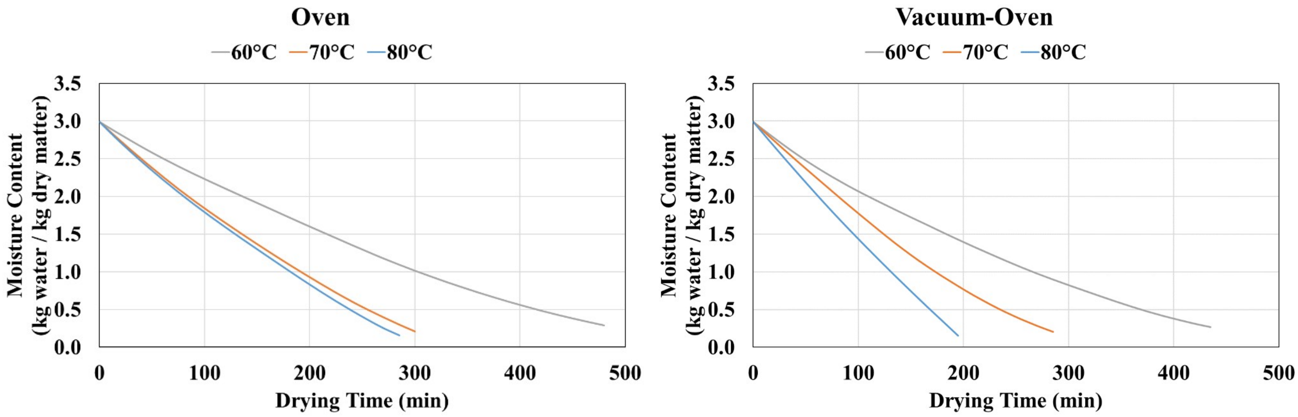


Figure 1: The oven and vacuum oven drying curves of golden berries.

For both of the drying methods, the rising-rate periods and falling-rate periods were observed as seen from Figure 2. In oven drying, the rising rate periods were obtained from the initial moisture content of 2.989 kg water/kg dry matter to 2.782, 2.798 and 2.861 kg water/kg dry matter for the drying temperatures of 80, 70,. and 60 °C, respectively. Then the falling-rate periods were encountered until the final moisture contents. For vacuum oven drying, the rising rate periods were obtained again from the initial moisture content of 2.989 kg water/kg dry matter to 2.744, 2.799, and 2.827 kg water/kg dry matter for the drying temperatures of 80, 70, and 60 °C, respectively.

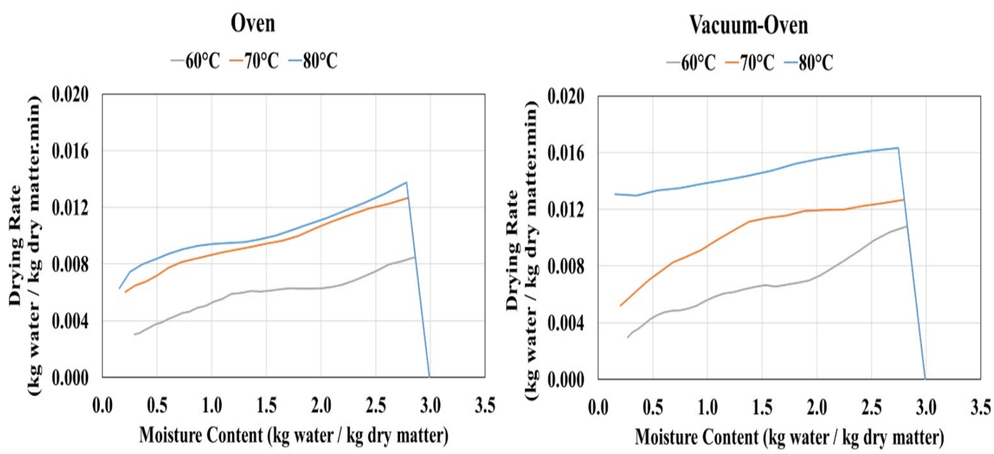


Figure 2: The oven and vacuum oven drying rate curves of golden berries.

3.2. Drying Kinetics: Effective Moisture Diffusivity and Activation Energy Results

For each drying temperature and drying method, D_{eff} values were calculated from the slope of the ln(MR) versus drying time plots, which are presented in Figure 3. The effective moisture diffusivities obtained for each method and for each drying temperature are presented in Figure 4a. As it can be seen from Figure 4a, D_{eff} values calculated for vacuum oven drying are greater than those for oven drying, due to the lower drying times obtained in the presence of vacuum. In oven drying, D_{eff} values were found as 1.95×10^{-10}, 3.37×10^{-10} and 3.80×10^{-10} m^2/s, for drying temperatures of 60, 70, and 80 °C, respectively. On the contrary, in vacuum oven drying, D_{eff} values were found as 2.20×10^{-10}, 3.72×10^{-10} and 5.45×10^{-10} m^2/s, during the experiments performed at 60, 70 and 80 °C, respectively.

Furthermore, in order to calculate the activation energy for the drying processes, D_{eff} values shown in Figure 4a were employed. The plots of ln(D_{eff}) versus 1/T are presented in Figure 4b. From the slopes of the foresaid ln(D_{eff}) versus 1/T plots, the values of E_a were calculated by multiplying the slope with the universal gas constant (R = 8.314×10^{-3} kJ/mol×K). Accordingly, the activation energies were found as 32.81 and 44.30 kJ/mol, for oven drying and vacuum oven drying, respectively. Since the assistance of vacuum increased the D_{eff} values, the activation energy was also observed to increase during vacuum oven drying.

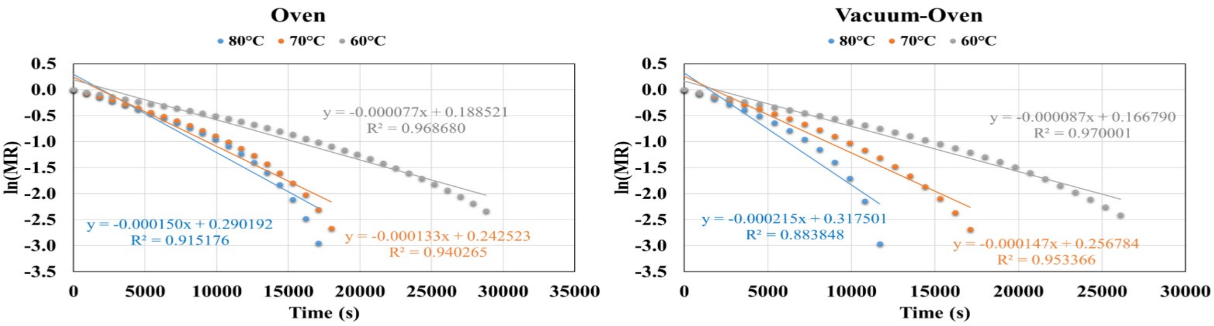
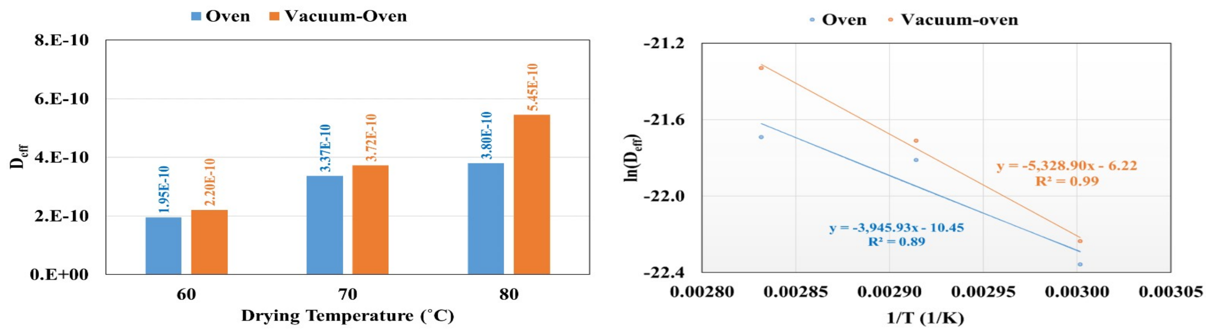


Figure 3: ln(MR) versus drying time plots for oven and vacuum oven drying.



(a) **(b)**

Figure 4: a) D_{eff} values calculated for each drying temperature and drying method. **b)** The plot of ln(D_{eff}) versus 1/T.

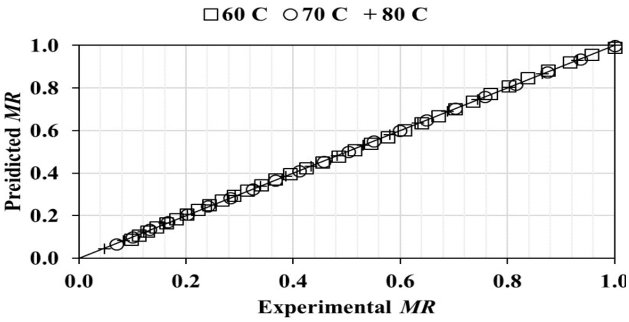
3.3. Mathematical Modeling Results

For the mathematical modeling of the drying of golden berries, fourteen mathematical models present in the literature were investigated. Regarding the model parameters and the statistical evaluation results (R^2 > 0.998), the models that provided the best fit for oven and vacuum oven drying are presented in Table 2. Among the fourteen mathematical models that were tested five models, namely Aghbashlo et al., Logarithmic, Midilli & Kucuk, Parabolic and Wang & Singh models, gave R^2 values higher than 0.998. For oven drying, the maximum R^2 (between 0.999799 and 0.999957), along with the minimum χ^2 (between 0.000004 and 0.000017) and RMSE (between 0.001879 and 0.003807) values were obtained from the model of Midilli & Kucuk. This model provided the best results for vacuum oven drying as well. Considering Midilli & Kucuk model, for vacuum oven drying of golden berries, R^2 values were between 0.999648 and 0.999998. χ^2 and RMSE values, on the other hand, were less than 0.000001-0.000029 and 0.000378-0.005089, respectively.

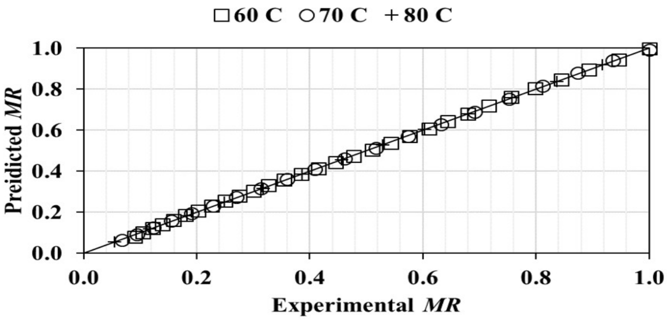
Table 2: Drying model constants and statistical parameters (R^2>0.998) for oven drying and vacuum oven drying of golden berries.

		Oven Drying			Vacuum Oven Drying		
Model	**Params**	**60 °C**	**70 °C**	**80 °C**	**60 °C**	**70 °C**	**80 °C**
Aghbashlo et al.	k_1	0.003198	0.003936	0.004039	0.002559	0.004231	0.005051
	k_2	-0.000897	-0.001724	-0.001959	-0.000965	-0.001907	-0.003148
	R^2	0.998865	0.999198	0.998328	0.999698	0.999977	0.998922
	χ^2	0.000088	0.000070	0.000153	0.000024	0.000002	0.000108
	RMSE	0.009057	0.007984	0.011738	0.004718	0.001380	0.009629
Logarithmic	a	1.434928	1.904526	2.205490	1.660257	1.735105	3.734810
	k	0.002295	0.002245	0.001970	0.001669	0.002824	0.001500
	c	-0.444364	-0.905562	-1.211370	-0.659638	-0.722035	-2.734230
	R^2	0.999770	0.999957	0.999908	0.999597	0.999322	0.999997
	χ^2	0.000019	0.000004	0.000009	0.000033	0.000067	<0.000001
	RMSE	0.004081	0.001843	0.002755	0.005446	0.007559	0.000465
Midilli & Kucuk	a	0.997277	0.999061	0.999956	0.990199	0.993081	1.000129
	k	0.003482	0.003167	0.003877	0.001446	0.001754	0.002966
	n	0.962940	1.013221	0.946609	1.099835	1.197080	1.019046
	b	-0.000499	-0.000980	-0.001396	-0.000386	-0.000540	-0.002428
	R^2	0.999799	0.999948	0.999957	0.999648	0.999852	0.999998
	χ^2	0.000017	0.000005	0.000004	0.000029	0.000016	<0.000001
	RMSE	0.003807	0.002036	0.001879	0.005089	0.003535	0.000378
Parabolic	a	0.983405	0.995936	0.991677	0.997178	1.010471	1.000051
	b	-0.003067	-0.004130	-0.004228	-0.002657	-0.004715	-0.005555
	c	0.000002	0.000003	0.000003	0.000002	0.000005	0.000004
	R^2	0.999617	0.999943	0.999856	0.999783	0.999665	0.999996
	χ^2	0.000031	0.000005	0.000014	0.000018	0.000033	<0.000001
	RMSE	0.005259	0.002122	0.003443	0.003999	0.005311	0.000555
Wang & Singh	a	-0.003217	-0.004183	-0.004342	-0.002680	-0.004572	-0.005554
	b	0.000003	0.000004	0.000004	0.000002	0.000004	0.000004
	R^2	0.999135	0.999916	0.999743	0.999769	0.999490	0.999996
	χ^2	0.000067	0.000007	0.000024	0.000018	0.000048	<0.000001
	RMSE	0.007907	0.002591	0.004604	0.004122	0.006557	0.000556

The comparison of the experimental and predicted MR results obtained from the mathematical model of Midilli & Kucuk is presented in Figure 5a for oven drying and in Figure 5b for vacuum oven drying. Regarding the figures, as all of the data lied on the 45° line, it can be concluded that the fitted Midilli & Kucuk model can be excellently used to represent the experimental drying data.



(a)



(b)

Figure 5: The plot of experimental MR versus predicted MR for Midilli & Kucuk model, in **a)** oven drying and **b)** vacuum oven drying.

4. CONCLUSION

In this study, oven and vacuum oven drying of golden berries were investigated, at drying temperatures of 60, 70, and 80 °C. It was observed that the increase in drying temperature and the assistance of vacuum caused shorter drying times. The duration of drying was between 285-480 minutes for oven drying and between 195-435 minutes for vacuum oven drying, respectively. Taking into account the drying rate curves, for both drying methods, a rapid rising-rate period followed by a falling-rate period was observed. Considering the drying kinetic parameters, the effective moisture diffusivities calculated for oven drying were between 1.95×10^{-10} and 3.80×10^{-10} m^2/s; and for vacuum oven drying were between 2.20×10^{-10} and 5.45×10^{-10} m^2/s. Calculations regarding the activation energy, on the other hand, unveiled 32.81 and 44.30 kJ/mol for oven and vacuum oven drying, respectively. Furthermore, fourteen mathematical models were fitted and tested to represent the drying curve data. Among the tested models Aghbashlo et al., Logarithmic, Parabolic and Wang & Singh models yielded very good fits, having R^2 greater than 0.998. For both oven and vacuum oven drying, Midilli & Kucuk model was found to yield the best fit among the employed models.

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