

Determination of Effective Diffusivity Coefficient and Activation Energy Of shelled pistachio by using fluidized bed dryer

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Abstract

Knowledge of desorption kinetics is essential to predict the behavior of the material during drying process and to design dryer equipment. The main objective of this study is to obtain the effective diffusivity coefficient and activation energy of shelled pistachio. Another goal is to find drying kinetics of shelled pistachio in fluidized bed dryer and so thin-layer characteristics of shelled pistachios were determined experimentally as a function of temperature and air velocity. Accordingly, 6 mathematical models (Two term model, Exponential model, Logarithmic model, Page model, Modified page model and Henderson & Pabis model) for describing the thin-layer drying behavior of shelled pistachios were investigated. Tests were conducted using four air temperature (25,30,45 and 60 C), and three air velocities (6, 8 & 10m/s). Out of the 6 models considered, the two term model were considered to be the most suitable for describing the drying behavior of the shelled pistachios. Also, for high air temperature and velocity, Henderson-Pabis model proved to be suitable. Results showed that air velocity and operating temperature enhanced the kinetics of drying of shelled pistachio and the drying air temperature had a great effect on the drying kinetics. By using of Fick's second Law the effective diffusivity coefficient and activation energy of pistachio was determined.

Keywords : Effective Diffusivity Coefficient, Activation Energy, Drying Kinetics, Fluidized Bed Dryer, Pistachio Drying

Nomenclature

A,B,a,b,c,g,n	Drying constants in drying models
k, b,d	Drying velocity constant in drying models (1/time Dimension)
L	Slice half thickness (mm)
M	Moisture content (% d.b)
M_0	Initial moisture content (% d.b)
MR	Moisture ratio (fraction)
M_{eq}	Equilibrium moisture content (d.b)
R	Universal gas constant
RH	Relative humidity
t	Time (min,h)
T	Temperature ($^{\circ}C$)

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V Air velocity (m/s)

Introduction

The pistachio tree is native to western Asia and Asia Minor, from Syria to the Caucasus and Afghanistan. Archaeological evidence in Turkey indicates that the nuts were being used for food as early as 7,000 B.C. The pistachio was introduced to Italy from Syria early in the first century A.D. Subsequently its cultivation spread to other Mediterranean countries. The tree was first introduced into the United States in 1854 by Charles Mason, who distributed seed for experimental plantings in California, Texas and some southern states. Due to high nutritional value and favorable taste, planting pistachio trees has become common in other parts of world. Iran is the largest pistachio producer and exporter in the world [1]. It has produced more than 250000 tones in 2003 and exported 115335 tones to different countries in 2002. Pistachios are served principally as salted nuts. A large percentage of pistachios are marketed in the shell for snack food. Non-split, filled nuts are used for processing. The food industry uses pistachios as an ingredient in cakes, biscuits, pies, candies, ice cream and pistachio butter. It is also used as the main ingredient of many Iranian desserts. They are also used as stuffing for both meat and snacks. Pistachio nuts contain 25% protein (mainly essential amino acids), 16% carbohydrate (mainly sucrose) and 55% oil (80% unsaturated fatty acids). Pistachios are also an excellent source of dietary fiber, containing 2.8 g of fiber per ounce. Good processing influences pistachio quality. Drying is an important operation in pistachio processing and the other food products. The main target of drying is removal of water from the material. In comparison with other food products, studies on drying of pistachio nuts are very limited. It is therefore necessary to design and simulate accurately drying systems for pistachio nuts. The objectives of this work were to determine experimentally the effect of different parameters (temperature & velocity of drying air) on drying time and rate of shelled pistachios and to fit the experimental data to mathematical models available from the literature. For this study, shelled pistachios were used as a process element for drying in the fluidized drying bed system. The main advantage of fluidized bed dryer is the high transfer rate for heat and mass between gases and

solid that ensures a rapid and uniform drying. Apart from this, heat transfer rate between the fluidized layer and immersed object is high. Therefore, only a small area is needed for heat transformation. In addition, the flow of fluidized particles that behave like fluids enables easily controlled continuous mechanical operation.

Kinetic modeling & drying process formulation

Numerous models have been proposed to describe the rate of moisture loss for food products and biological materials [2,3,5,11,27]. These studies are fundamental in developing mathematical and computer simulation drying models [12,13,15,17,22]. Some of Mathematical models that have been given by various authors for the drying curves are summarized in table 1. The few of them which might be adequate to describe drying data for the shelled pistachios are reviewed below.

Newton, Exponential or Lewis model

Lewis described that moisture transfer from the foods and agricultural materials can be seen as analogous to the flow of heat from a body immersed in cool fluid. This model assumes negligible internal resistance, which means no resistance to moisture movement from within the material to the surface of the material. By comparing these phenomena with Newton's law of cooling, the drying rate is proportional to the material being dried and equilibrium moisture content at the drying air condition as

$$MR = \exp(-kt) \quad (1)$$

Where MR is the moisture ratio defined as :

$$MR = (M - M_{eq}) / (M_0 - M_{eq}) \quad (2)$$

The equilibrium moisture content was calculated using the equation of Tia *et al.*

$$RH = \exp\left[\left(\frac{-21065}{RT}\right) \cdot M_{eq}^{-1.25}\right] \quad (3)$$

Where RH is the air relative humidity.

This model was used primarily because it is simple. The only drawback, however, was that it tended to over predict the early stages and under predict the later stages of drying curve.

Henderson and Pabis model

Various approximation and variations of the diffusion model have been used by researchers in modeling the drying characteristics of food and agricultural products. The simplest approximation from which only one term of the infinite series is used can be represented as

$$MR = \frac{M - M_e}{M_0 - M_e} = A \exp(-kt) \quad (4)$$

This model has been used to model thin-layer drying characteristics of various agricultural products. The slope of this model, Coefficient k, is related to effective diffusivity when drying process takes place only in the falling rate period and liquid diffusion controls the process.

Page model

Page suggested a two constant empirical modification of the exponential model to correct its shortcomings. This model has produced good fits to describe drying of many foods and agricultural products. This model can be shown as follows:

$$MR = \frac{M - M_e}{M_0 - M_e} = \exp(-kt^N) \quad (5)$$

Modified page model

Page model was modified to describe the drying of soybean and popcorn. It is written in the following form:

$$MR = \frac{M - M_e}{M_0 - M_e} = \exp(-kt)^N \quad (6)$$

Two term exponential model

Glenn developed a semi-empirical approach to thin-layer modeling by describing the kernel as discrete lumps. This model is a part of infinite series of negative exponentials derived from a general solution applies regardless of particle geometry and boundary conditions, but assumes that diffusivity is constant (i.e. requires constant product temperature during drying)

$$MR = \frac{M - M_e}{M_0 - M_e} = a \exp(bt) + c \exp(dt) \quad (7)$$

Two term exponential model has proved to be the most widely popular.

Thompson model

Thompson, Peartt, and Foster developed an empirical equation to describe the drying characteristics of shelled corn in the temperature range of 60-150°C. This model was also used to describe drying characteristics of sorghum.

$$t = A \ln(MR) + B(\ln(MR))^2 \quad (8)$$

Table 1: Mathematical models given by various authors for the drying curves

Model no.	Model name	Model equation	References
1	Newton or Lewis	$MR = \exp(-kt)$	[27, 19]
2	Page	$MR = \exp(-kt^n)$	[5,11]
3	Modified page	$MR = \exp(-(kt)^n)$	[20,30]
4	Henderson and Pabis	$MR = a \exp(-kt)$	[7,28]
5	Logarithmic	$MR = a \exp(-kt) + c$	[16]
6	Two term	$MR = a \exp(-bt) + c \exp(-dt)$	[10, 26]
7	Two term exponential	$MR = a \exp(-kt) + (1 - a) \exp(-kat)$	[23]
8	Wang and Singh	$MR = 1 + at + bt^2$	[20]
9	Thompson	$t = A \ln(MR) + B[\ln(MR)]^2$	[21, 24]
10	Diffusion approach	$MR = a \exp(-kt) + (1 - a) \exp(-kbt)$	[29]
11	Verma et al.	$MR = a \exp(-kt) + (1 - a) \exp(-gt)$	[25]
12	Modified Henderson and Pabis	$MR = a \exp(-kt) + b \exp(-gt) + c \exp(-ht)$	[14]
13	Simplified Fick's diffusion (SFFD) equation	$MR = a \exp[-c(t / L^2)]$	[8]

14	Modified Page equation-2	$MR = \exp[-k(t/L^2)^n]$	[9]
15	Midilli and Kucuk	$MR = a \exp(-kt^n) + bt$	[18]

Material and methods

Sample preparation

The pistachios used in this study are obtained fresh from the market. Only the split and uniform size pistachios were used in experiments. Initial moisture content of the samples is determined by drying it in an oven at $103 \pm 2^{\circ}C$ for about 15 hours. Firstly, the fluidized bed is switched on and hot air flow will circulate for about 30 min until an established condition is achieved in the bed before the experiment begins. This step aims to reduce the heat loss through the bed's wall that is still cold, at the moment the experiment starts. Next, the pistachio samples are put into the fluidized, and the experiment begins.

Drying equipment

Fluidized bed dryer, as shown in Fig.1, is designed, constructed and used for the experiments. It consists of a blower, two heaters and a drying chamber. The blower produce air flow (maximum $2.85 \text{ m}^3/\text{min}$ at $T=25^{\circ}C$ & $P=101.3 \text{ KPa}$) and the air temperature (range of $20 - 120^{\circ}C$) is supplied by using two electric heaters (their power are 2000 & 3000 watt) and controlled manually with temperature accuracy of $\pm 1^{\circ}C$. Dimension of drying chamber that is made of glass, is $60 \times 60 \times 500 \text{ mm}$. After uniform distribution, the heated air goes to the drying chamber and as

shown in Fig. 1, shelled pistachios are fluidized in dryer bed and dried.

Experimental procedure

Experiments were performed to determine the effect of process variables on the drying of shelled pistachios. The variables considered were the drying air temperature and air velocity. The experiments were conducted at four levels of air temperature ($25, 30, 45$ and $60^{\circ}C$), and three air velocities ($6, 8$ and 10 m/s). Before starting of each drying run, the pistachio sample was removed from refrigerator and placed in a plastic bag in the laboratory to bring the temperature of shelled pistachio to room temperature. Drying continued until the moisture content (w.b. %) of the sample reached about 5%. After each drying experiment, the sample was oven-dried at $103 \pm 2^{\circ}C$ to determine the moisture content.

Results and discussion:

Table 2 shows drying times for different drying conditions. The results showed that the drying air temperature had greater effect on the time of drying than the air velocity did. Results of the experiments were consistent with findings reported by other authors in which drying air temperature is considered as the main factor affecting drying rate.

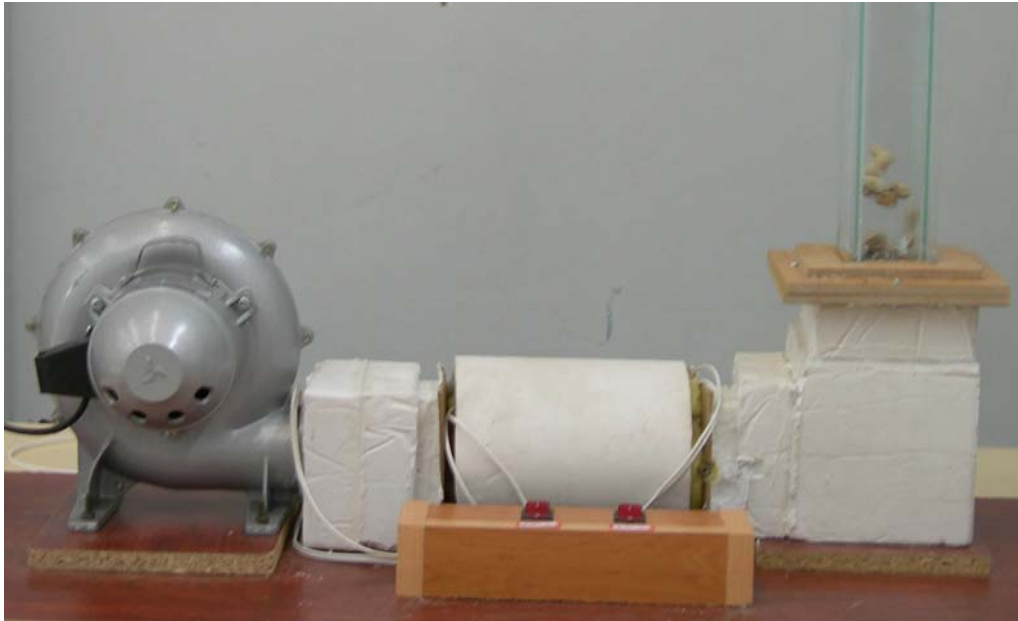


Fig.1. Lab scale fluidized bed dryer

Table 2: The effect of drying air condition on time of drying

Experiment number	Temperature ($^{\circ}C$)	Air velocity (m/s)	Drying Time (min)
1	25	6	450
2	25	8	400
3	25	10	380
4	30	6	380
5	30	8	340
6	30	10	320
7	45	6	280
8	45	8	260
9	45	10	240
10	60	6	220
11	60	8	190
12	60	10	170

Effect of temperature

Fig. 2.shows the profile of moisture content changes at various drying times in different temperatures for $V=6$ m/s. The time needed to achieve the required moisture content and moisture content equilibrium can be attained from moisture content versus time curve. For air velocity of 8m/s and 10m/s, moisture content curve and moisture content equilibrium obtained are almost the same. The overall findings show that at a fixed air velocity, the use of high air temperature can shorten the drying time.

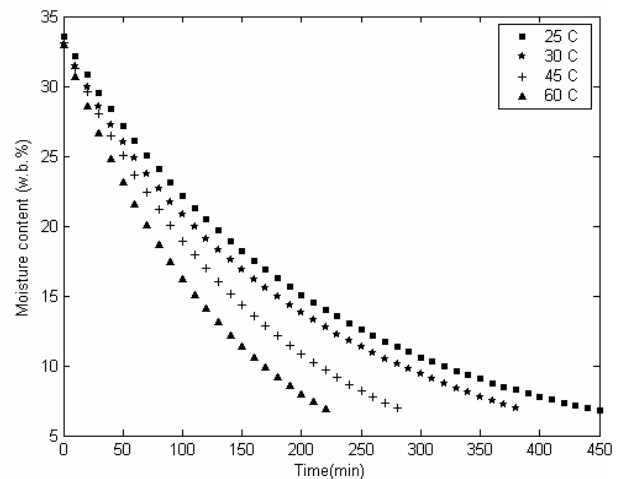


Fig.2. Effect of temperature on moisture content of shelled pistachios.($V=6$ m/s)

The drying kinetics were observed from the drying rate curve, (dX/dt) against drying time, (t) . Fig.3. shows the changes in drying rate with drying time at different temperature for air velocity of 6m/s.

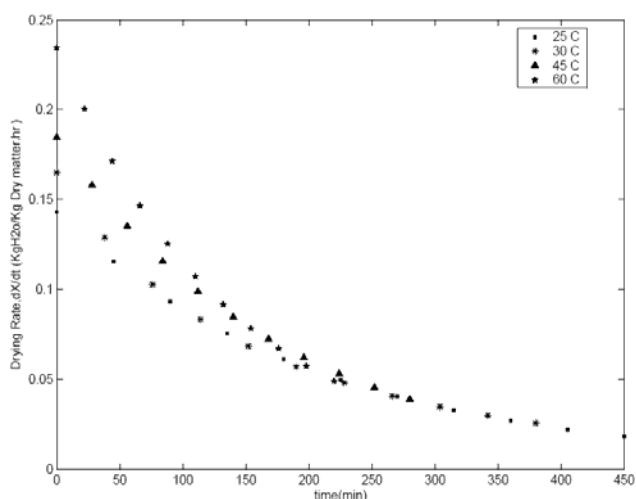


Fig. 3. Effect of temperature on drying rate of shelled pistachios. (V=6m/s)

It was found that the drying rate increases with the increase of temperature and consequently the drying time reduces.

Effect of air velocity

Fig.4. and Fig.5. demonstrate the effect of air velocity on moisture content and drying rate of shelled pistachio. The increase in the drying air velocity decreases moisture content and consequently increases drying rate and reduces drying time.

Modeling of the Fluidized bed drying

In the analysis of drying data, the moisture content is essential to describe different drying models [4,6]. It was fitted to the 6 drying models (exponential model, Henderson and Pabis model, Two term model, Page model, modified page model and Logarithmic model). The models were evaluated based on the sum of square error (SSE) and coefficient of determination (R-square). The

details of the statistical analysis for 6 models are presented in Tables 3.a , 3.b.

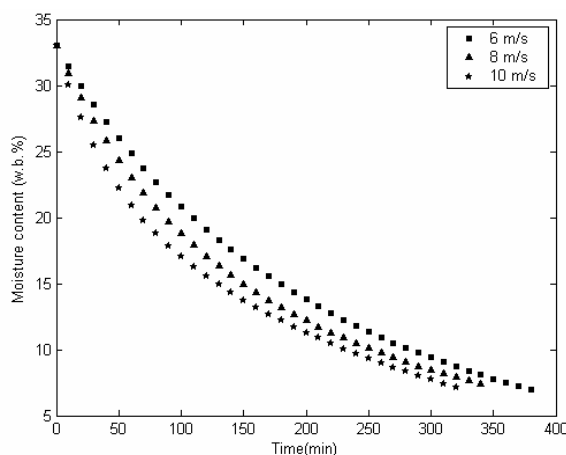


Fig.4. Effect of air velocity on moisture content of shelled pistachios (T=25)

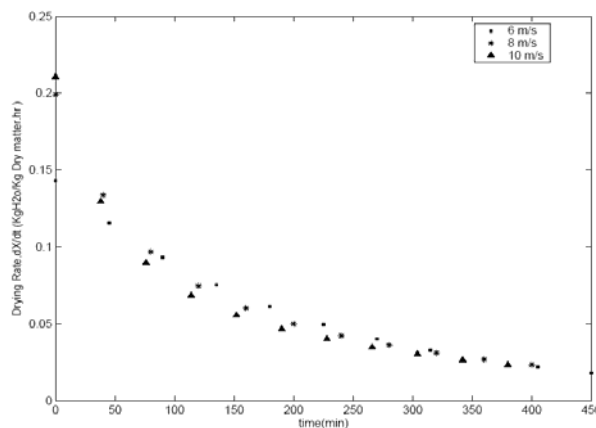


Fig.5. Effect of air velocity on drying rate of shelled pistachios. (T=25)

Table 3.a: Statistical results obtained for Two term, Henderson and Pabis & Logarithmic drying models

Run	Two term model		Henderson and Pabis model		Logarithmic model	
	R2	SSE	R2	SSE	R2	SSE
T=25 ⁰ C , V=6m/s	0.997	0.00218	0.990	0.00998	0.920	0.0999
T=25 ⁰ C , V=8m/s	0.998	0.00213	0.991	0.00498	0.911	0.0598
T=25 ⁰ C , V=10m/s	0.996	0.00301	0.900	0.00789	0.890	0.0889
T=30 ⁰ C , V=6m/s	1.000	0.00364	0.995	0.00458	0.895	0.0558
T=30 ⁰ C , V=8m/s	0.998	0.00065	0.995	0.00142	0.885	0.0442
T=30 ⁰ C , V=10m/s	0.997	0.00176	0.992	0.00598	0.872	0.0698
T=45 ⁰ C , V=6m/s	0.998	0.00008	0.992	0.00059	0.892	0.0592

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T=45 ⁰ C , V=8m/s	1.000	0.00009	1.000	0.00059	0.8880	0.0692
T=45 ⁰ C , V=10m/s	1.000	0.000009	0.999	0.000086	0.900	0.0866
T=60 ⁰ C , V=6m/s	0.999	0.00008	0.995	0.00076	0.886	0.0786
T=60 ⁰ C , V=8m/s	0.999	0.000005	0.998	0.000046	0.889	0.0496
T=60 ⁰ C , V=10m/s	0.998	0.000002	0.998	0.000035	0.901	0.0735

Table 3.b: Statistical results obtained for Page, Modified page & Exponential drying models

Run	Page model		Modified page model		Exponential model	
	R2	SSE	R2	SSE	R2	SSE
T=25 ⁰ C , V=6m/s	0.900	0.0198	0.910	0.00999	0.899	0.00991
T=25 ⁰ C , V=8m/s	0.911	0.0198	0.921	0.00998	0.901	0.00908
T=25 ⁰ C , V=10m/s	0.920	0.0189	0.900	0.00909	0.900	0.00983
T=30 ⁰ C , V=6m/s	0.915	0.0158	0.912	0.00978	0.912	0.00958
T=30 ⁰ C , V=8m/s	0.905	0.0142	0.935	0.00932	0.903	0.00942
T=30 ⁰ C , V=10m/s	0.902	0.0198	0.942	0.00958	0.912	0.00998
T=45 ⁰ C , V=6m/s	0.902	0.01059	0.912	0.00954	0.903	0.00959
T=45 ⁰ C , V=8m/s	0.913	0.01059	0.910	0.00955	0.902	0.00959
T=45 ⁰ C , V=10m/s	0.909	0.01086	0.904	0.00984	0.903	0.00986
T=60 ⁰ C , V=6m/s	0.901	0.00976	0.903	0.00975	0.905	0.00976
T=60 ⁰ C , V=8m/s	0.908	0.009046	0.906	0.009046	0.907	0.009146
T=60 ⁰ C , V=10m/s	0.904	0.009035	0.914	0.009038	0.908	0.009435

The coefficient of Two term model (a,b,c & d) and Henderson-Pabis model (a,b) for each drying run were calculated (Tables 4, 5).

Although for many runs, acceptable R-square were obtained, generally, for all conditions Two term model and for high air temperature and velocity, Henderson-Pabis model, presented higher values than other drying models (Tables 3.a,3.b.). SSE values indicate the sum of square errors of the observed data from predicted line. The nearest SSE value to zero is recommended for the selection of models and R-square was stated not to be only

good criteria for evaluation non-linear mathematical models. Two term model and Henderson-Pabis model showed lower SSE values than other models .Hence, the Two term model for all condition and Henderson-Pabis model for high air temperature and velocity gave better predictions than others, and satisfactorily described the fluidized bed drying of shelled pistachios. Fig.6. and Fig.7. present the variations of content moisture from 2 models (see table 1) versus drying time for shelled pistachios.

Table 4: Results of moisture ratio modeling(Two term model) according to drying time for shelled pistachios in fluidized bed dryer

Run	First coefficient (a)	2th coefficient (b)	3th coefficient (c)	4 th coefficient (d)
T=25 ⁰ C , V=6m/s	0.83	-0.00504	0.18	-0.0024
T=25 ⁰ C , V=8m/s	0.1035	-0.02598	0.8926	-0.004474
T=25 ⁰ C , V=10m/s	0.1179	-0.0312	0.8034	-0.004419
T=30 ⁰ C , V=6m/s	0.03524	-0.02363	0.9565	-0.004735
T=30 ⁰ C , V=8m/s	0.2252	-0.01639	0.7765	-0.0045
T=30 ⁰ C , V=10m/s	0.234	-0.03234	0.7701	-0.00483
T=45 ⁰ C , V=6m/s	-0.07322	-4.139e-005	1.076	-0.005573
T=45 ⁰ C , V=8m/s	-0.06493	0.000218	1.006	-0.006044

T=45 ⁰ C , V=10m/s	-0.06379	0.000292	0.9988	-0.006624
T=60 ⁰ C , V=6m/s	-0.03976	0.001475	1.038	-0.007328
T=60 ⁰ C , V=8m/s	-0.114	-0.001391	1.081	-0.008094
T=60 ⁰ C , V=10m/s	-0.06092	0.0004972	0.9954	-0.009893

Table 5: The results of moisture ratio modeling (Henderson-Pabis model) according to drying time for shelled pistachios in fluidized bed dryer

Run	First coefficient (a)	2th coefficient (b)
T=25 ⁰ C , V=6m/s	1.009	-0.00425
T=25 ⁰ C , V=8m/s	0.9569	-0.004807
T=25 ⁰ C , V=10m/s	0.8704	-0.004825
T=30 ⁰ C , V=6m/s	0.9889	-0.00485
T=30 ⁰ C , V=8m/s	0.9597	-0.005442
T=30 ⁰ C , V=10m/s	0.9143	-0.005836
T=45 ⁰ C , V=6m/s	1.016	-0.006405
T=45 ⁰ C , V=8m/s	0.9544	-0.006966
T=45 ⁰ C , V=10m/s	0.9483	-0.007644
T=60 ⁰ C , V=6m/s	1.011	-0.008177
T=60 ⁰ C , V=8m/s	0.9792	-0.009551
T=60 ⁰ C , V=10m/s	0.9478	-0.01141

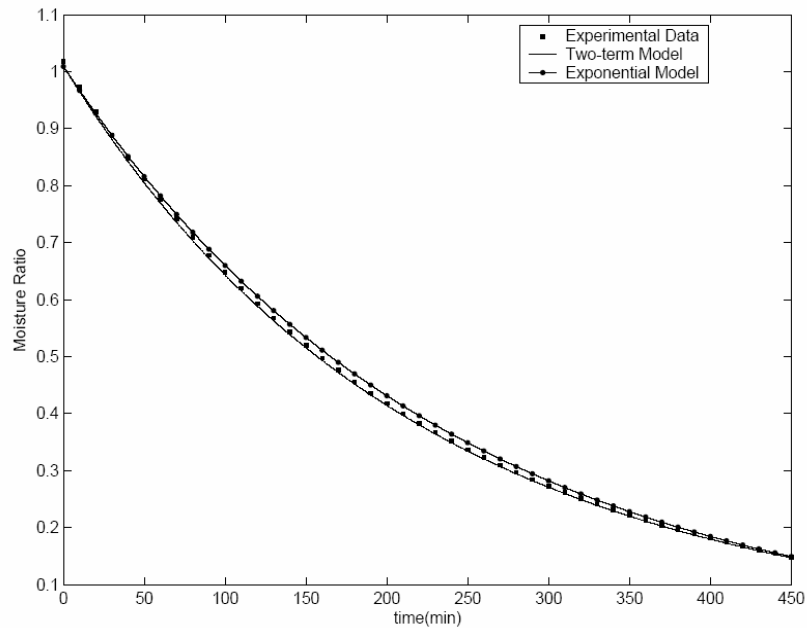


Fig.6. Variation of moisture ratios from 2 important dying models versus drying time for shelled pistachios in fluidized drying process (T=25,V=6m/s)

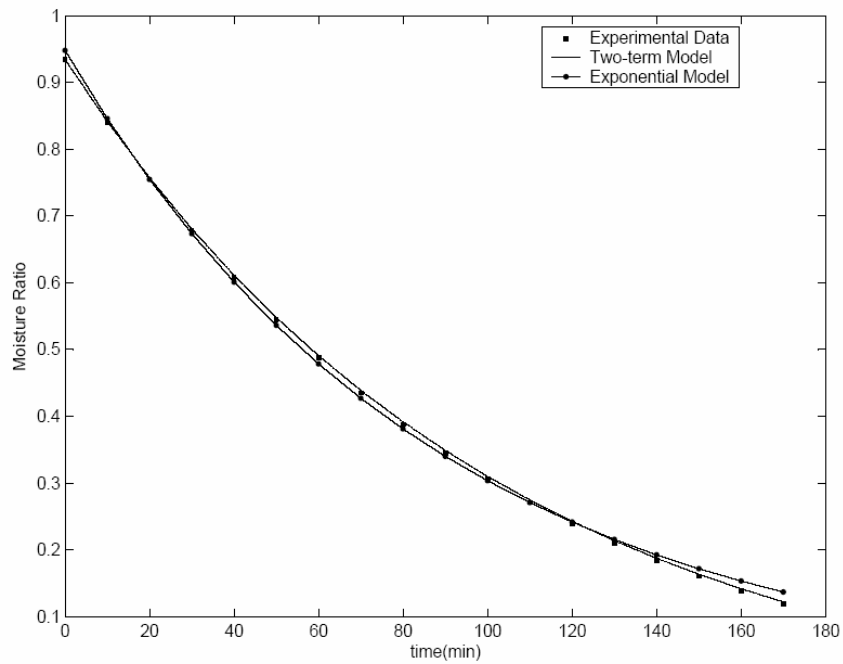


Fig.7. Variation of moisture ratios from 2 important drying models versus drying time for shelled pistachios in fluidized drying process ($T=60, V=6m/s$)

The comparison of results with the other works demonstrated that drying time of pistachio in fluidized bed drying is smaller than other drying methods. This comparison for fluidized bed and thin-layer dryer are showed in fig.8 and fig.9.

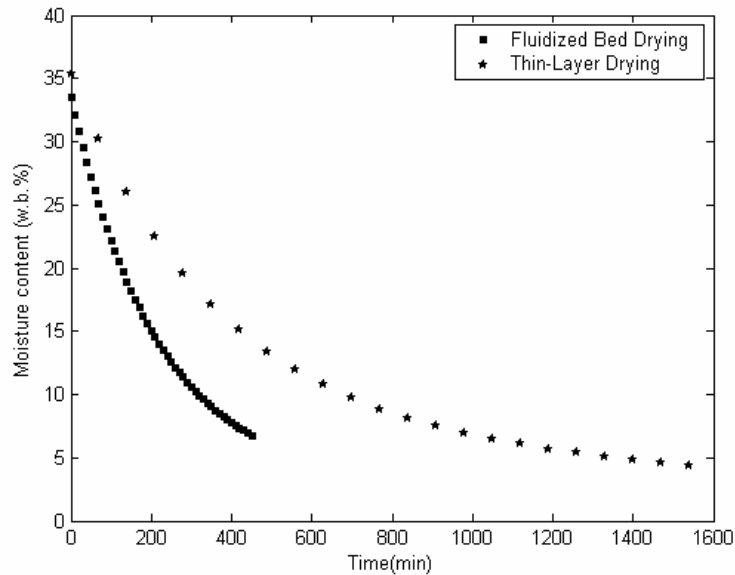


Fig. 8. Comparison of drying time of pistachio in Fluidized bed & Thin-Layer dryer ($T = 25^{\circ}C$)

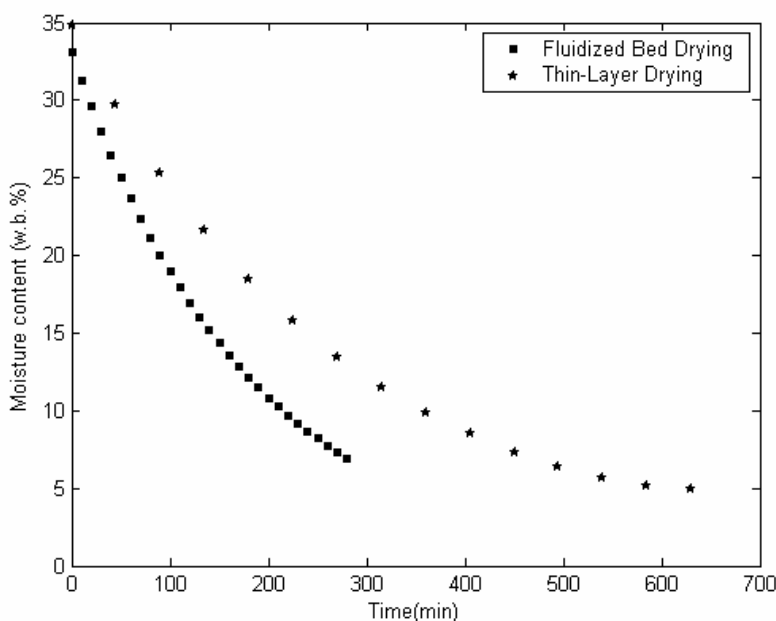


Fig. 9. Comparison of drying time of pistachio in Fluidized bed & Thin-Layer dryer ($T = 45^{\circ}C$)

Calculation of Effective Diffusivity Coefficient and Activation Energy

As explained, the results show that the drying of pistachio takes place in the falling rate period and therefore we can use Fick's law for calculation of effective diffusivity and activation energy of shelled pistachio. The second Fick's law is:

$$MR = \frac{M - M_{eq}}{M_0 - M_{eq}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 D_{eff} \pi^2 t}{R^2}\right) \quad (9)$$

Table 6 shows the diffusivity coefficient for all runs.

Table 6 - Diffusivity Coefficient of shelled pistachio

Run	Effective Diffusivity (m^2 / s)
T=25 ⁰ C , V=6m/s	7.02×10^{-10}
T=25 ⁰ C , V=8m/s	9.12×10^{-10}
T=25 ⁰ C , V=10m/s	1.32×10^{-9}
T=30 ⁰ C , V=6m/s	7.98×10^{-10}
T=30 ⁰ C , V=8m/s	9.95×10^{-10}
T=30 ⁰ C , V=10m/s	1.56×10^{-9}
T=45 ⁰ C , V=6m/s	8.87×10^{-10}
T=45 ⁰ C , V=8m/s	1.45×10^{-9}
T=45 ⁰ C , V=10m/s	2.49×10^{-9}

T=60 ⁰ C , V=6m/s	9.36×10^{-10}
T=60 ⁰ C , V=8m/s	2.03×10^{-9}
T=60 ⁰ C , V=10m/s	3.34×10^{-9}

Now, it can be used from the equation

$$D_{eff} = D_0 \exp\left(-\frac{E_a}{RT_a}\right)$$

and the results that obtained for effective diffusivity coefficient for determination of activation energy of shelled pistachio.

Conclusions

In order to explain the drying behavior and develop the mathematical modeling of shelled pistachios, 6 models in the literature were applied to the thin-layer fluidized bed drying process. The results can be concluded as follows:

1. Among these models, the two term model for all condition and Henderson-Pabis model for high air temperature and velocity gave the best results and showed good agreement with the experiment data obtained from the experiments including the thin-layer fluidized bed drying process of shelled pistachios.
2. The reduction of moisture content is highly dependent on temperature and air velocity.

3. Drying air temperature is more important than air velocity in drying of shelled pistachios.
4. The increase in the drying air temperature and air velocity increases drying rate. The curve of drying rate of shelled pistachio shows that the drying of pistachio takes place in the falling rate period
5. The effective diffusivity coefficient of shelled pistachio obtained between 3.34×10^{-9} and 7.02×10^{-10}

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تعیین ضریب نفوذ موثر و انرژی فعالیت پسته طی فرآیند خشک کردن بستر سیال

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چکیده

خشک کردن یکی از مراحل مهم فرآوری پسته است. در این پژوهش، جهت تعیین ضریب نفوذ موثر، انرژی فعالیت و سینتیک خشک شدن پسته، یک خشک کن بستر سیال ناپیوسته آزمایشگاهی طراحی و ساخته شد. مدل‌های تجربی مختلفی جهت انطباق با داده‌های آزمایشگاهی مورد بررسی قرار گرفت. بدین منظور مهمترین پارامترهای موثر در فرآیند خشک کردن یعنی دمای هوا (در چهار سطح مختلف $25^{\circ}C$, $30^{\circ}C$, $45^{\circ}C$, $60^{\circ}C$) و سرعت جریان هوا (در سه سطح 6 , 8 , 10 m/s) بررسی شد. دما و سرعت جریان هوا بر زمان خشک شدن پسته به طور قابل توجهی اثر گذار بوده، ضمن اینکه تاثیر دما به مراتب نسبت به سرعت جریان هوا بیشتر است. ضریب نفوذ موثر پسته همچون اغلب مواد غذایی بین 10^{-9} تا 10^{-11} تعیین شده است. همچنین بر اساس نتایج بدست آمده می‌توان گفت خشک شدن پسته در مرحله سرعت نزولی اتفاق می‌افتد و کنترل کننده فرآیند خشک کردن، نفوذ رطوبت می‌باشد. با تجزیه و تحلیل نتایج بدست آمده می‌توان دریافت که مدل دو پارامتری در تمام محدوده مورد آزمایش و مدل هندرسون - پیپیس در دماها و سرعت جریان‌های بالا بهترین انطباق را با داده‌های آزمایشی دارند.

کلمات کلیدی: ضریب نفوذ موثر، انرژی فعالیت، خشک کردن بستر سیال، پسته، مدل‌سازی سینتیکی

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