Quality Assurance and Safety of Crops & Foods, 2019; 11 (3): 211-220

Wageningen Academic Publishers

Kinetics of allicin potential loss in garlic slices during convective drying

M. Doganturk[1], E. Demiray[2], O. Gursoy[3] and Y. Yilmaz[3*]

[1]Graduate School of Natural and Applied Sciences, Division of Food Engineering, Burdur Mehmet Akif Ersoy University, Istiklal Campus, 15030, Burdur, Turkey; [2]Department of Food Engineering, Faculty of Engineering, Pamukkale University, Kinikli, 20070, Denizli, Turkey; [3]Department of Food Engineering, Faculty of Engineering and Architecture, Burdur Mehmet Akif Ersoy University, Istiklal Campus, 15030, Burdur, Turkey; yilmaz4yusuf@yahoo.com

Received: 19 May 2018 / Accepted: 21 November 2018

RESEARCH ARTICLE

Abstract

Allicin is an organosulfur compound formed in garlics, and it is slightly yellow in colour and gives unique odour to garlic. Allicin has been known to have an antioxidant and antimicrobial activity, and it can react with thiol groups containing proteins. Allicin potential (AP) in Taskopru garlic slices and its loss were monitored during drying in a cabinet drier at three temperatures (50, 60 and 70 °C). Initial AP of fresh garlic samples was 10.91±0.15 mg/g on the basis of dry matter (dm), and it reduced significantly during drying ($P<0.05$). APs of garlic samples dried at 50, 60 and 70 °C for up to 480 minutes were 5.35±0.029, 4.32±0.13 and 3.95±0.26 mg/g dm, respectively ($P<0.05$). Loss of AP values determined during drying followed a second-order reaction. Drying temperature had a significant influence on the loss of AP in garlic slices. Activation energy for AP loss was 25.48 kJ/mol. Q_{10} value was 4.18 for the drying temperature increase from 50 to 60 °C, and it reduced to 3.07 for the temperature increase from 60 to 70 °C. Therefore, the effect of the first temperature rise on AP loss was bigger than the second temperature rise.

Keywords: garlic, drying, allicin potential, kinetic

1. Introduction

Garlic is an important plant of *Allium sativum* L., which has been used by people since ancient times for the treatment of certain diseases, to give flavour and aroma to foods and for the preservation of some foods (Rahman, 2007). It is an important source of phenolic compounds (Martins *et al.*, 2016) and exerts various biological effects such as lowering cholesterol levels, tumour growth, and antibacterial activity (Lanzotti, 2006; Lawson, 1998). The major bioactive components of garlic are organosulfur compounds formed from precursors when garlic is crushed, and the most widely known is allicin. Allicin is rapidly produced by the action of allinase on alliin (Santhosha *et al.*, 2013). Allinase is activated by crushing or cutting the garlic gloves (Rahman, 2007; Rahman *et al.*, 2009). Allicin (diallyl thiosulfate) is responsible for its pungent smell and a major bioactive component in garlic products (Santosha *et al.*, 2013). Therefore, minimising the loss of allicin degradation during drying of garlic products is crucial for a final product with superior quality. The Allicin Potential (AP) is defined as the sum of possible free allicin and allicin that can be formed from endogenous alliin by catalysis with remaining active allinase. Alliin is heat-stable, whereas allinase is denatured by heat (Khanum *et al.*, 2004). Allicin is unstable at room temperature and may be converted to diallyl disulphides and sulphur dioxides after 20 hours (Zixing *et al.*, 2017). It was assumed that alliinase would be significantly altered during the drying process of garlic although still capable of converting alliin to allicin (Krest and Keusgen, 1999).

Drying provides one of the oldest and most effective means of preserving foods from spoilage. Once dried, many foods can be stored successfully for years without refrigeration, if appropriately packaged. Drying can cause changes in the physical properties such as colour and structure, as well as the deterioration of aroma compounds or degradation of nutritional substance reducing the product quality (Cui *et al.*, 2003; Ratti, 2001). Dehydration has been used an efficient method for long-term preservation of garlic slices. A variety of drying processes are used for the dehydration of garlic slices but convective drying is one of the methods that have been studied extensively. Drying method and air drying temperature significantly influence the physical properties of garlic slices as well as their allicin content (Prati *et al.*, 2014; Zhou *et al.*, 2017).

Drying kinetics is often used to describe the combined macroscopic and microscopic mechanisms of heat and mass transfer during drying, and it is affected by drying conditions, types of dryer and characteristics of materials to be dried. Since on-line measurement of temperature and moisture is difficult and time-consuming for drying, the drying kinetics models are essential for equipment design, process optimisation and product quality improvement (Giri and Prasad, 2007).

Retention of AP in garlic slices during drying is technologically important. Data on the allicin degradation in fresh garlic (Arzanlou and Bohlooli, 2010; Prati *et al.*, 2014) or garlic after dehydration (Abano *et al.*, 2011; Mendez-Lagunas *et al.*, 2017; Rahman *et al.*, 2009; Ratti *et al.*, 2007) are available in the literature but, to the best of our knowledge, kinetic data during the full course of convective drying, reaction order and activation energy for allicin degradation in actual garlic slices are unavailable. Drying temperature and time are two major factors influencing the AP loss kinetics of garlic constituents. Current study was conducted to determine the kinetics of AP loss from garlic slices during drying at three different temperatures (50, 60 and 70 °C).

2. Materials and methods

Materials

Fresh garlics were obtained from a local farmer in a town of Taskopru, Kastamonu, Turkey. Garlic samples in polyethylene packages were kept refrigerated until drying. Garlic samples were subjected to mild pressure by hand to separate them into cloves. Cloves were peeled and cut into slices (with a thickness about 3 mm) by a mechanic slicer. Then, slices were kept at room temperature for 30 minutes for the formation of allicin. The initial moisture content of samples (63.8%) was determined by the AOAC method (AOAC, 1990). Allicin standard was purchased from Santa Cruz Biotechnology (Dallas, TX, USA) while chromatographic grade methanol was obtained from Sigma-Aldrich (St. Louis, MO, USA).

Methods

Drying procedure

Garlic slices were dried in a convective drier (56×40×72 cm, w×d×h) manufactured by the Memmert Corporation (UN-260, Schwabach, Germany). For each drying experiment, 5 kg of garlics in uniform ripeness, colour and size were used. Samples were allowed to equilibrate for 2 hours at room temperature. Then, the samples were peeled and sliced with garlic slicer to give an average thickness of 3 mm.

Dryer was turned on about 1 h before the drying experiments to achieve steady-state conditions before each drying run. After the dryer reached steady state conditions for the operation temperatures, all samples were uniformly placed onto trays as a single layer and dried. For the determination of drying kinetics, a group of samples were taken from trays at certain intervals and weighed, then returned to the dryer immediately. The weight loss of samples was recorded by an analytical balance (ITEM PA214C, Ohaus, Parsippany, NJ, USA) with a range of 0-210 g (±0.001 g) at 60 minute intervals. Samples withdrawn from trays were either used to determine the initial dm content of garlic slices or wrapped in aluminium foil in polyethylene packages that were kept at -24 °C for further analyses. Garlic slices were dried until their water content reached approximately 15 g/100 g. Drying of garlic slices was monitored for 8 h at 50 °C and for 6 h at 60 or 70 °C. All experiments were carried out in triplicates.

Mathematical modelling

The dimensionless moisture ratios (MR) and drying rates (DR) of garlic slices during drying were determined by the Equations 1 and 2, respectively.

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

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

In these equations, MR, DR, M_t, M_0, M_e, dt, and M_{t+dt} are the dimensionless moisture ratio, drying rate (g moisture/g dm × min), moisture content of garlic slices at any time t (g moisture/g dm), initial moisture content of garlic slices (g moisture/g dm), equilibrium moisture content of garlic slices (g moisture/g dm), time between consecutive measurements in minutes and moisture content of garlic slices at time t+dt, respectively. In order to describe the drying behaviour of garlic slices dried at different temperatures, five different thin layer drying models in Table 1 were used.

In these drying models, MR is a dimensionless moisture ratio; a, b and c are model constants; k is a kinetic constant, and t is drying time. The coefficient of determination (R^2) (Equation 3), reduced mean square of the deviation X^2 (Equation 4) and root mean square error (RMSE) (Equation 5) were used to determine the adequacy of models for describing the drying behaviour of garlic slices (Yogurtcu, 2014). Microsoft Excel (Microsoft Corporation, Redmond,

Table 1. Thin layer drying models used to describe drying behaviour of garlic slices.

Model	Equation	References
Henderson and Pabis	MR=aexp(-kt)	Alibas (2012)
Newton	MR=exp(-kt)	Menges *et al.* (2005)
Page	MR=exp(-kt^n)	Doymaz (2005)
Modified Page	MR=exp(-kt)^n	Polatci (2012)
Logarithmic	MR=aexp(-kt)+c	Toğrul and Pehlivan (2004)

WA, USA) was used in calculations. Higher values of R^2 and lower values of X^2 and RMSE for a mathematical model indicated better goodness of fit to experimental data (Menges *et al.*, 2005; Midilli and Kucuk, 2003).

$$R^2 = \frac{\sum_{i=1}^{N}\left(MR_{exp,i}-MR_{expmean,i}\right)^2-\left(MR_{pre,i}-MR_{exp,i}\right)^2}{\sum_{i=1}^{N}\left(MR_{exp,i}-MR_{expmean,i}\right)^2} \quad (3)$$

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

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(MR_{exp,i}-MR_{pre,i}\right)^2\right]^{1/2} \quad (5)$$

In these equations, $MR_{exp,i}$ is the i^{th} experimental dimensionless moisture ratio; $MR_{pre,i}$ is the i^{th} predicted dimensionless moisture ratio; $MR_{expmean,i}$ is the mean of the i^{th} experimental dimensionless moisture ratio; N is the number of observations, and n indicates the number of constants in a model.

Determination of allicin potential

Allicin potential is considered as the sum of possible free allicin and allicin that can be formed from endogenous alliin by catalysis with remaining active alliinase. It was determined in both fresh and dried garlic samples by the HPLC (LC-20AD, Shimadzu, Japan) analytical procedure outlined by Ratti *et al.* (2007). Fresh or dried samples were crushed by a garlic press. Then, crushed samples were mixed with 50 ml cold distilled water and subjected to ultrasonication for 10 min in an ultrasonic water bath. Samples were transferred into polypropylene centrifuge tubes and centrifuged at 12,320×*g* for 20 min at 4 °C. Supernatants were filtered using a 0.45 µm PVDF syringe filters (Minisart, Sartorious, Waldbronn, Germany). Allicin contents of samples were determined by an HPLC system equipped with a quaternary pump (LC-20A), a 20 µl loop injector, a photodiode array detector (SPD-M20A), a degasser (DGU-20A) and a column oven (CTO-20A). Allicin fraction was separated on an MZ-Analysentechnik C18 column (MZ-Analysentechnik GmbH, Mainz, Germany) (250×4.6 mm, ID, 5 µm) isocratically at 30 °C by using the mobile phase of methanol-water (50:50, v/v) and the flow rate of 1 ml/min. Eluents were monitored at 220 nm.

Kinetics models of allicin potential loss

The loss of AP in garlic slices during drying were calculated by means of the standard equations for zero (Equation 6), first (Equation 7), and second-order (Equation 8) reactions, and degradation rate constants were determined by fitting the equations to experimental data.

$$C = C_0 + K_0 t \quad (6)$$

$$C = C_0 \exp(k_1 t) \quad (7)$$

$$\frac{1}{C} = \frac{1}{C_0} + k_2 t \quad (8)$$

where *C* is the concentration of the studied parameter (i.e. allicin potential) at any given drying time, C_0 are initial values of untreated samples and k_0, k_1, k_2 are rate constants.

The Arrhenius equation (Equation 9) is the most widely accepted method of accounting for the temperature dependence of the rate constant in food systems. Activation energy for the loss of AP in garlic slices during convective drying was calculated by the Arrhenius equation.

$$k = k_a \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

where k is the rate constant at the absolute temperature T (K), k_a is the frequency factor, E_a is the activation energy (kJ/mol), and R is the universal gas constant (8.314 J/mol.K).

Statistical analysis

Data were analysed by the Statistical Analysis System software (SAS Institute Inc., Carry, NC, USA). The level of significant difference among means was determined using the Duncan's multiple comparison test at α=0.05 and the lettering was obtained using the PDGLM800 Macro developed by Saxton (2000).

3. Results and discussion

Effect of drying temperature on moisture content and drying rate

Garlic slices were dried as a single layer at 50, 60, and 70 °C in a cabinet dryer. The initial moisture content of garlic slices was around 1.76±0.04 kg water per kg dm, and they were dried to the final moisture content of about 0.15±0.04 kg water per kg dm. Figure 1A presents the variations in their moisture contents at different drying

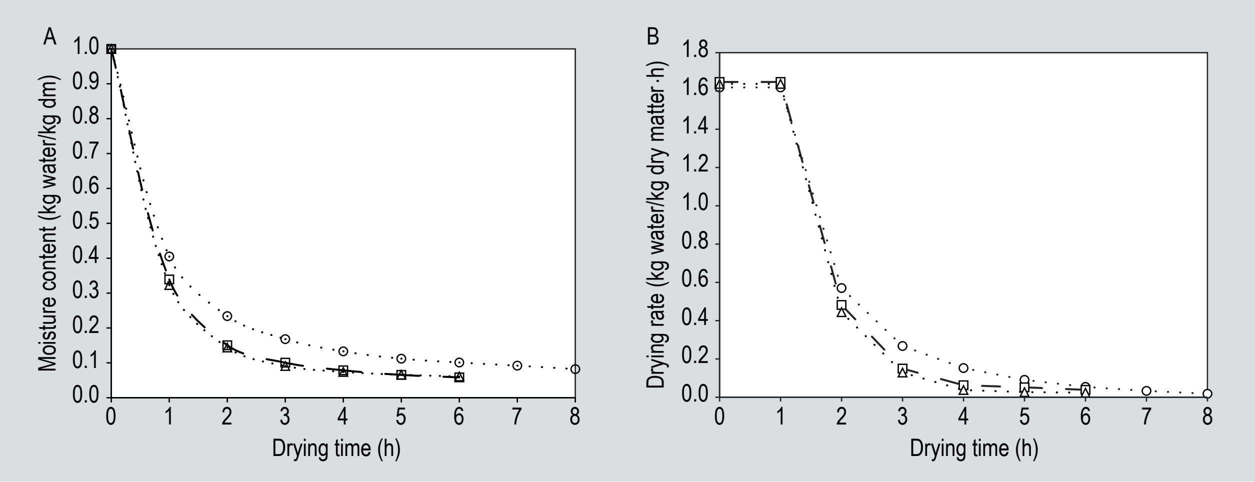

Figure 1. Moisture contents (A) and drying rates (B) of garlic slices dried at three different temperatures: ○ , 50 °C; □, 60 °C and △, 70 °C.

temperatures. Moisture content decreased by drying time at all temperatures, and drying temperature had a significant effect on the moisture content of the garlic slices as expected.

A falling-rate drying period was mostly found in garlic samples dried at different temperatures (Figure 1B) whereas a constant-rate drying period was rare. Rapid drying under high temperature creates a hardened outer layer in products to be dried, which may prevent the moisture removal from the central parts of a foodstuff. In current study, the rate of moisture transfer from garlic slices was steady as the drying temperature increased. The small thickness of garlic slices might have prevented the formation of a hardened outer layer of garlic slices.

Five thin layer drying models were used to describe drying characteristics of garlic sliced dried at three different temperatures in a cabinet type drier, and the coefficient of determination (R^2), reduced chi-square and RMSE values were determined for each model. Drying constants and coefficients for garlic slices dried at 50, 60 and 70 °C in a cabinet type dryer determined by Henderson and Pabis, Newton, Page, Modified Page and logarithmic models are shown in Table 2.

The mathematical modelling of the experimental data at 50 °C indicated that with the highest R^2 and the lowest RMSE values, the Page and Modified Page models represented the experimental values satisfactorily while logarithmic model was the best for garlic sliced dried at 60

Table 2. Constants, coefficients and adequacy of five thin layer drying models by nonlinear regression analysis for describing drying characteristics of garlic slices dried at three different temperatures.

Model	Temperature (°C)	Constants and coefficients			X^2	RMSE	R^2
Henderson and Pabis	50	k=0.0057	a=0.7765		0.0184	0.1196	0.9787
	60	k=0.0074	a=0.6669		0.0119	0.0963	0.9563
	70	k=0.0083	a=0.5698		0.0129	0.0983	0.8855
Newton	50	k=0.0057			0.0069	0.0730	0.9787
	60	k=0.0074			0.0012	0.0303	0.9563
	70	k=0.0083			0.0083	0.0788	0.8855
Page	50	k=0.0339	n=0.7137		0.0092	0.0845	0.9927
	60	k=0.0400	n=0.7415		0.0038	0.0547	0.9908
	70	k=0.0562	n=0.7079		0.0012	0.0230	0.9403
Modified Page	50	k=0.0087	n=0.7137		0.0063	0.0701	0.9927
	60	k=0.0130	n=0.7415		0.0019	0.0380	0.9908
	70	k=0.0171	n=0.7079		0.0015	0.0336	0.9403
Logarithmic	50	k=0.2736	a=2.6000	c=0.0610	0.0505	0.1983	0.9884
	60	k=0.0122	a=0.9463	c=0.0330	0.0383	0.1727	0.9975
	70	k=0.0177	a=1.0794	c=0.0330	0.0064	0.0693	0.9967

and 70 °C. However, decreases in experimental moisture contents indicated that the Page, Modified Page and logarithmic models were well compatible for all drying temperatures (Figure 2).

Thin layer drying models of the Page and Modified Page successfully described the experimental data of garlic sliced dried at 50 °C while the logarithmic model was the best fit for drying temperatures of 60 and 70 °C (Figure 3).

In a study on drying kinetics of garlic cloves, Sharma and Prasad (2001) dried garlic cloves in a microwave dryer at 40 W microwave power and 40, 50 and 70 °C at 1 or 2 m/s air velocity or in an hot air drier at 60 and 70 °C at 2.0 m/s air velocity. Authors reported that experimental data was described well with the Page model. In a study by Babetto *et al.* (2011), garlic slices with a thickness of 2 mm were dried in a laboratory type convective drier at 25, 30, 40, 45 and 50 °C, and Modified-Halsey model was in good conformance with the experimental data. Rahman *et al.* (2009) determined the drying kinetics and allicin potential in garlic slices with a 5 mm thickness dried in an air drier at 50, 60, 80, 90 and 105 °C, in a vacuum drier at 50, 60 and 90 °C and in the nitrogen environment at 60 and 80 °C. They reported that the Dinçer and Hüseyin model was the best for describing experimental data. Madamba *et al.* (1996) investigated the drying characteristics of garlic slices and found that the Page and Two-Compartment models were the best-fitted drying models for the garlic slices of 2-4 mm thickness exposed to drying temperatures at 50, 70 and 90 °C. In a study by Sacilik and Ünal (2005), dehydration properties of the Kastamonu garlic slices of 3-5 mm thickness were determined during convective drying at 40, 50 and 60 °C at a constant air velocity of 0.8 m/s. They reported that an increase in the thickness of garlic slices prolonged drying time and the most suitable drying model was the two-term thin film drying model. Calin-Sanchez *et al.* (2014) pre-dried garlic slices of 5 mm in a convective air drier followed by a vacuum microwave drier to determine kinetic energy consumption and quality characteristics. They found that the Velma model was the best suited to the experimental data at 60 °C by convective drying but the Page model was the best for vacuum microwave drying at 240, 260 and 480 W microwave power in a convective pre-drying at 60 °C. Rasouli (2011) studied the mathematical modelling and colour changes in garlic slices with 2, 3 and 4 mm thickness during drying in a convective dryer at 50, 60 and 70 °C, and found that the Weilbull model was the best fit for experimental data. Demiray and Tulek (2014) dried garlic slices with 2-3 mm thickness in a convective hot air at 55, 65

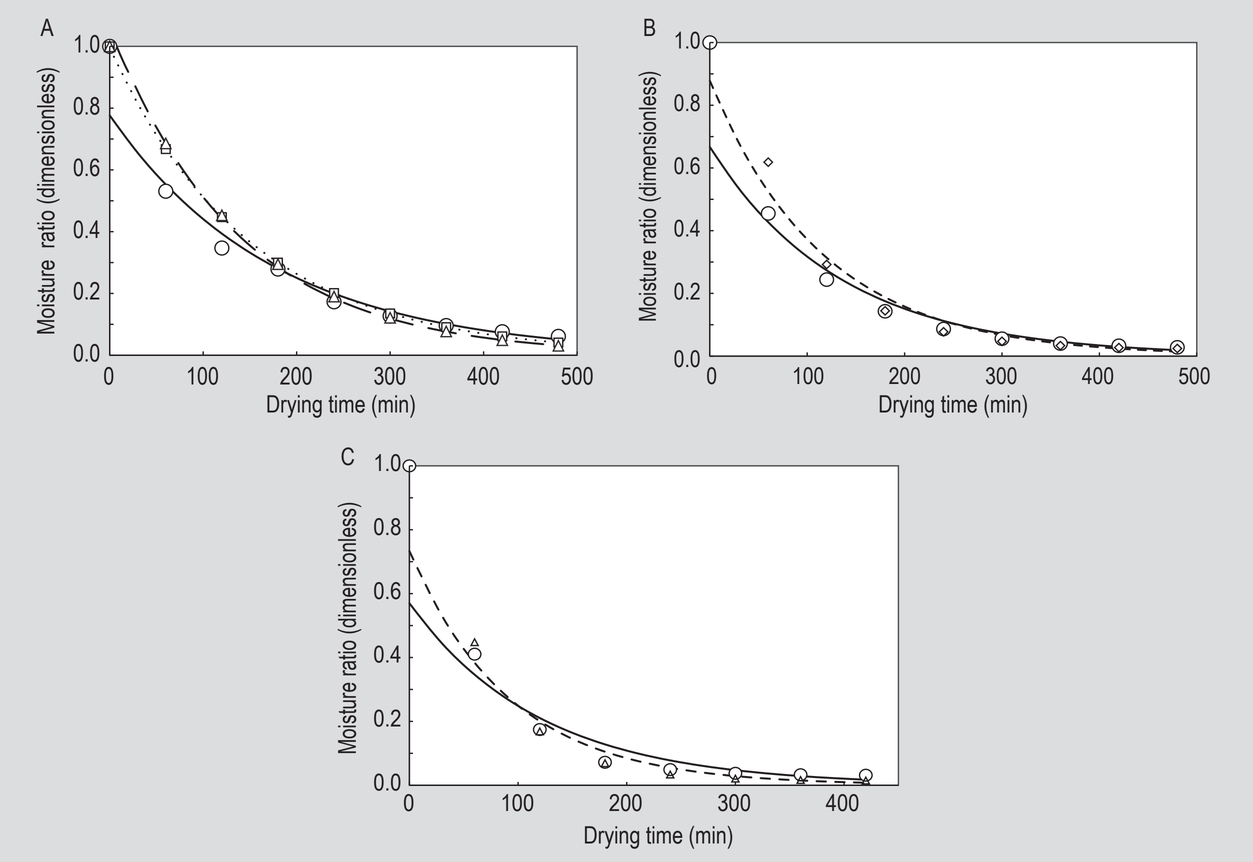

Figure 2. Comparison of experimental moisture ratio (○) and moisture ratios obtained by Page (□), Modified Page (△) or logarithmic (◇) models for garlic slices dried at 50 °C (A), 60 °C (B) or 70 °C (C) (lines indicate best fit to experimental data for a model).

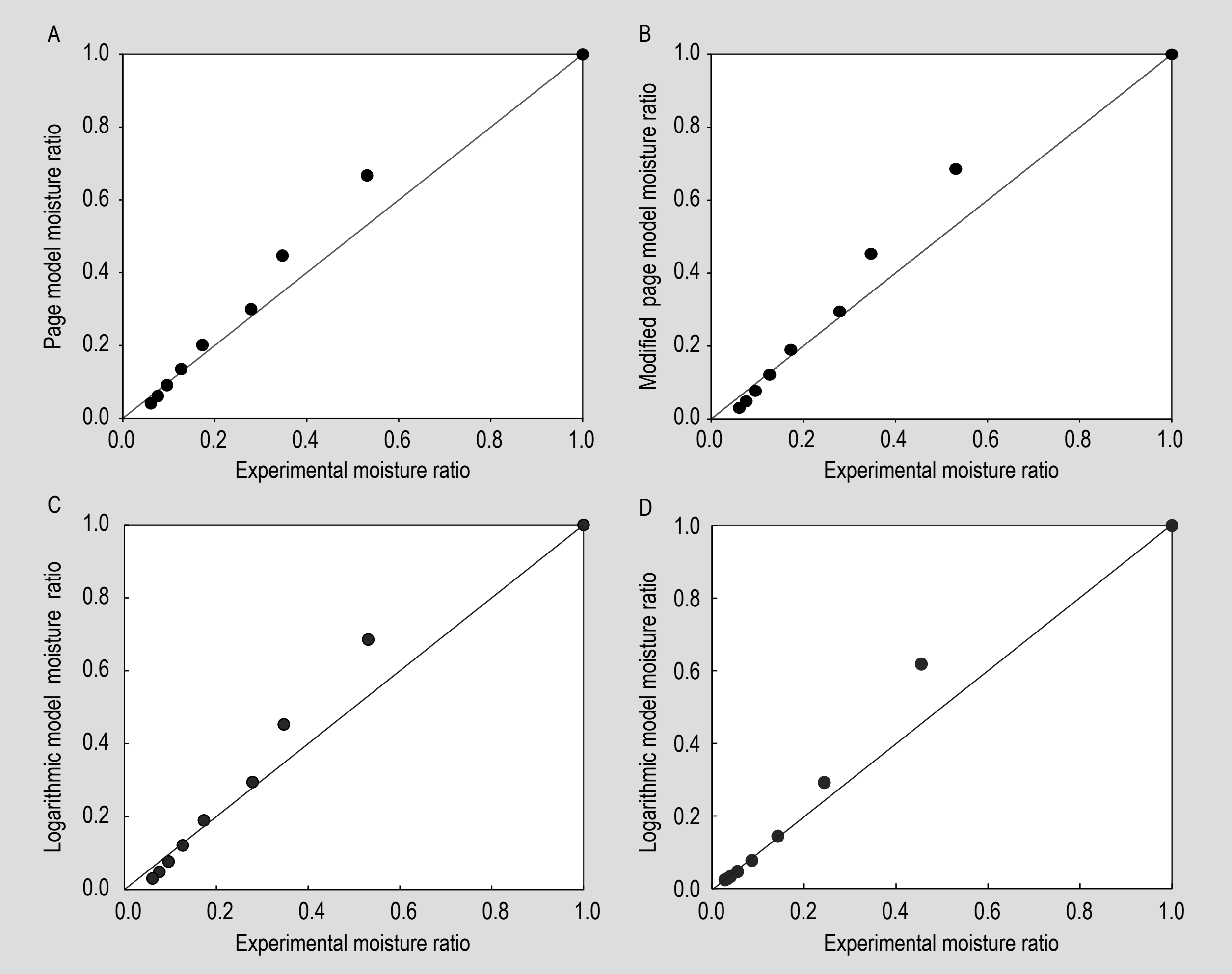

Figure 3. Conformity of experimental moisture ratios with predicted moisture ratios for garlic slices dried at 50 °C obtained by the Page (A) and Modified Page (B) models, at 60 °C obtained by the logarithmic (C) model and at 70 °C obtained by the logarithmic (D) model (diagonal lines indicated the best fit).

and 75 °C and reported that Page and Modified Page models described the experimental data the best. In current study, similar garlic variety was used but the logarithmic model was the best to describe experimental data at 60 and 70 °C since a hot air drier used in current study could result in the reduction in drying time significantly. Results indicated that various factors including drying temperature, type of drier used, slice thickness and hot air velocity could have a significantly influence on the conformity of a mathematical model for describing the experimental data obtained during drying of foods.

Allicin potential during convective drying

Allicin in garlic is formed after slicing by the transformation of alliin into allysin by allinase enzyme. Initial AP of Taskopru garlic slices stored at room temperature for about 30 min was 10.91±0.15 mg/g dm. In a study by Mendez-Lagunas *et al.* (2017), allicin content of fresh garlics was reported as 15.67±0.60 mg/g dm. Arzanlou and Bohlooli (2010) investigated the AP in Iranian green garlic parts such as leaves, shoots and fresh cloves, and reported that the AP values in the extracts of leaves, shoots and fresh cloves were 0.48, 0.44 and 0.26 mg/ml, respectively. Bocchini *et al.* (2001) determined the AP in purified and non-purified extracts of garlic samples, and found that depending on the detection methods, AP values in garlic extracts ranged from 1.7 to 4.6 mg/l, respectively. Abano *et al.* (2011) determined the effect of pretreatments such as citric acid, potassium metabisulphite and EDTA on allicin potential of garlic slices in a convective type of hot air drier at 45, 50 and 55 °C, and found that increase in AP was not linear. They reported that the Midilli and Kucuk model was the most suitable for untreated garlic slices while the Henderson and Pabis model was the best for pretreated counterparts. Canizares *et al.* (2004) investigated the effect of thermal decomposition of allicin on garlic extracts and inhibition of *in vitro* growth of *Helicobacter pylori* in two different methods of extracting garlic samples with ethanol and acetone. They reported the

AP values of 14.65 g/l in ethanol and 25.74 g/l in acetone garlic extracts.

In current study, the graphical method was used to determine the reaction order of AP loss in garlic slices during convective drying (Table 3). The plot of the inverse of AP against drying time indicated that the reaction order was second (Figure 4). Reactions occurring in foods are usually first-order reactions, while zero- and second-order reactions rarely occur. In some cases, however, reaction orders may have a fractional value. Although second-order reactions are less common in the decomposition of food constituents, thiamine decomposition in milk (Horak and Kessler, 1981) and ascorbic acid degradation in lemon juice (Robertsen and Samaniego, 1986) were reported to be a second-order reaction (Cemeroğlu, 2013). Studying the effect of thermal degradation of allicin in garlic extracts, Canizares *et al.* (2004) reported a first-order reaction for the loss of AP. Ilić *et al.* (2010) reported that the degradation of pure allicin and allicin entrapped in the gel by thermal treatment was of a first-order reaction. In current study, the reaction order of the loss of AP in garlic slices dried at 50, 60 and 70 °C was of a second-order.

The loss of AP in Taskopru garlic slices dried at 50, 60 and 70 °C is shown in Figure 5. The effect of both drying temperature and time on the AP of sliced garlic samples was statistically significant (P<0.05). Interaction of drying time with drying temperature was also found significant (P<0.05). The initial AP (10.91±0.15 mg/g dm) of Taskopru garlic slices decreased to 7.51±0.10 mg/g dm after 60 minutes of drying at 60 °C, and decreased to 7.38±0.32 mg/g dm after 120 minutes of drying at 50 °C. Similarly, AP at the end of 240 min drying period at 70 °C was 4.92±0.11 mg/g dm, while it decreased to 4.91±0.24 mg/g dm at the end of 300 min drying time at 60 °C, which were statistically insignificant (P>0.05). Rahman and co-workers (2009) found that the reduction in AP of garlic slices during hot air drying at 60 °C was greater than that at 50 °C. Similarly, they also reported that drying at 60 °C under nitrogen gas resulted in a greater reduction in AP than drying at 40 °C. Allicin was reported to be highly sensitive to thermal decomposition at high temperatures (Ilić *et al.*, 2010). The AP of garlic extracts could be influenced by the extraction solvent, and the loss in AP of garlic extracts with acetone was higher than the loss in AP of ethanolic garlic extracts at the same temperature (Canizares *et al.*, 2004).

Table 3. Statistical results for the determination of the reaction order for allicin loss potential in garlic sliced dried at three different temperatures.

Temperature (°C)	Reaction order	X^2	RMSE	R^2
50	0	6.76×10^{6}	2.60×10^{3}	0.86
	1	2.11×10^{-2}	1.30×10^{-1}	0.91
	2	4.76×10^{-8}	2.00×10^{-2}	0.96
60	0	1.46×10^{7}	3.83×10^{3}	0.79
	1	1.86×10^{-2}	1.24×10^{-1}	0.87
	2	1.61×10^{-7}	4.00×10^{-4}	0.93
70	0	1.87×10^{7}	4.32×10^{3}	0.77
	1	1.68×10^{-2}	1.18×10^{-1}	0.86
	2	1.81×10^{-7}	4.00×10^{-4}	0.93

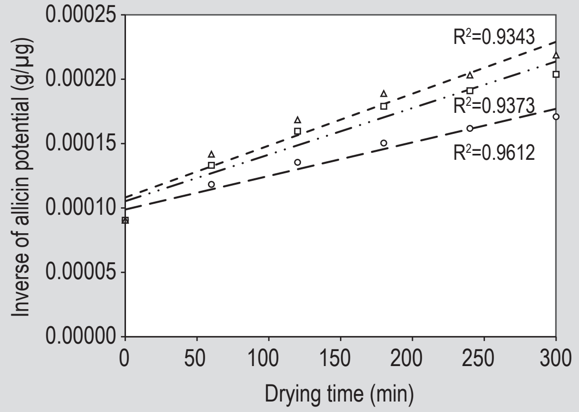

Figure 4. Second order loss of allicin potential in garlic slices dried at three different temperatures: ○ = 50 °C; □ = 60 °C and △ = 70 °C.

Activation energy is the energy that must be exceeded in order for a reaction to take place. Each reaction has its own activation energy. The high or low activation energy of a reaction indicates that the reaction will be easy or difficult (Acartürk, 2007). The activation energy of a reaction indicates the rate at which the rate of reaction changes depending on the temperature. The activation energy is calculated using Equation 9, and the slope of a line obtained by plotting the inverse of absolute temperatures against negative logarithm of the reaction rates gives the activation energy. Activation energy value for the AP loss in garlic slices dried at three different temperatures was calculated as 25.48 kJ/mol. The activation energy of each reaction is unique. The activation energy of reactions occurring in foods has a wide range of 8.4 kJ/mol to 628 kJ/mol; for example, for simple hydrolysis reactions E_a=4.2-84 kJ/mol, for the oxidation reactions of oils by free radicals E_a=62-105 kJ/mol, for non-enzymatic browning reactions E_a=209-628 kJ/mol and for enzymatic reactions E_a=16.6-62.6 kJ/mol (Cemeroğlu, 2013). Drying foods is related to both heat and mass transfer, and the mass transfer rate is directly related to the water vapor diffusion rate. There are different studies in the literature where activation energies are calculated for diffusions during drying in different foods. The activation energy for the thermal degradation of pure allicin and allicin entrapped in gel was determined as 46 kJ/mol (Ilić *et al.*, 2010). Canizares *et al.* (2004) reported the activation

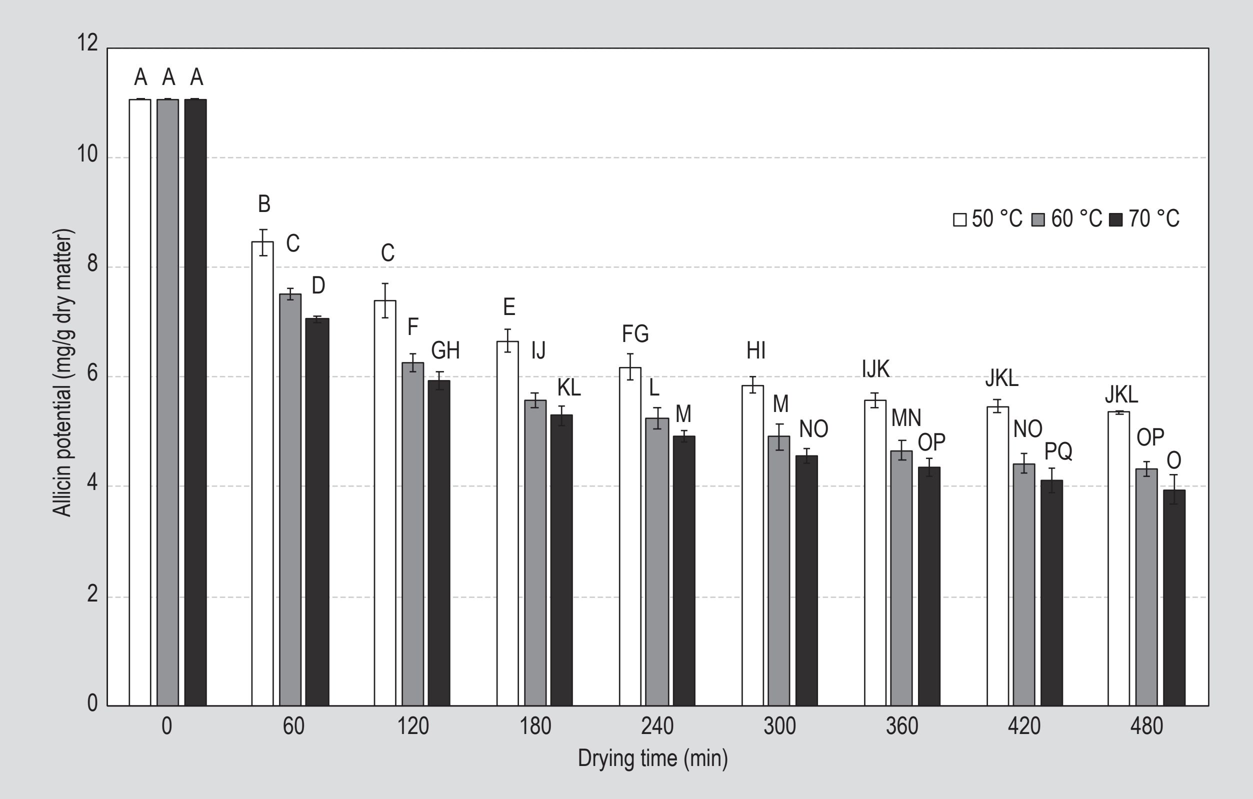

Figure 5. Changes in the loss of allicin potential of garlic slices dried at 50, 60 and 70 °C (Bars represent standard deviations while different letters across the figure indicate statistical significances at α=0.05 level).

energy for the thermal degradation of allicin as 97.4 kJ/mol in ethanol extracts and as 188.5 kJ/mol in acetone extracts of garlic samples.

In current study, activation energy required for the loss reaction of AP in Taskopru garlic slices during drying at 50, 60 and 70 °C was 25.48 kJ/mol. Demiray and Tulek (2014) studied the drying characteristics of Taskopru garlic slices and reported that the activation energy for drying was 30.58 kJ/mol. In a study on mango slices dried at 60, 70 and 80 °C (Akoy, 2014), the activation energy required for drying reaction was reported as 30.99 kJ/mol. Activation energy shows the degree of the dependency of a reaction rate on drying temperature, and the activation energy value of each system is unique and can change with the water activity level of a system (Cemeroglu, 2013).

The Q_{10} value indicates how a reaction is influenced by the level of drying temperature. For a temperature change from 50 to 60 °C, Q_{10} value for the loss of AP in garlic slices was calculated as 4.180. When the drying temperature increased from 50 to 70 °C, Q_{10} value changed to 2.858, and it was 3.065 for a temperature change from 60 to 70 °C. Based on Q_{10} values, increasing the drying temperature from 50 to 60 °C influenced the most the loss of AP in garlic slices.

4. Conclusions

Drying characteristics and mathematical modelling of Taskopru garlic slices dried at 50, 60 and 70 °C were determined in current study. The loss kinetics of AP was calculated for garlic slices during drying. Drying characteristics of Taskopru garlic slices indicated that the drying rate at 60 and 70 °C was higher than the rate at 50 °C as expected while there were similarities in drying rates for garlic slices dried at 60 and at 70 °C. Mathematical modelling of drying characteristics of Taskopru garlic slices revealed that the best conformance of the thin film drying models with the highest R^2 and the lowest RMSE and chi-square values at 50 °C was found for the Page and Modified Page models; however, at 60 and 70 °C drying process, the logarithmic model was the best. The loss reaction of AP in Taskopru garlic slices dried at different temperatures was of a second-order reaction, and an increase in drying temperature had a significant influence on the loss of AP in garlic slices. When initial APs of garlic slices were considered the highest, after 8 hours of drying of the garlic slices at 50 °C, allicin retention rates was 48.5%; however, 39.1 and 35.8% of initial allicin contents in garlic slices were retained at drying temperatures of 60 and 70 °C, respectively. Results showed that in order to maintain the highest content of allicin in dried garlic products, garlic slices should be dried at low temperatures. Moreover, drying time is another factor to be considered for the production of garlic derivatives with a high economic value, and results could be used as a guideline for the best combination of drying time and temperature for a product with high allicin potential. Slicing Taskopru garlic slices and storing them for 30 minutes at room temperature resulted in the formation of allicin potential with about 11 mg/g dm. It is recommended that garlic slices should be allowed to stand for a period of time for allicin formation in order to obtain a dried product with high AP. Current study on the loss kinetics of AP in garlic slices dried at different temperatures could be used for dried garlic derivatives with an optimum allicin retention rates.

Acknowledgements

This research was financially supported by the Coordinatorship of Scientific Research Projects of Burdur Mehmet Akif University under the Project Number of 0256-YL-15. Authors would like to thank Dr Hale SECILMIS CANBAY for her valuable help on the chromatographic analysis of current study.

References

Abano, E.E., Ma, H., Qu, W. and Teye, E., 2011. Modeling pre-treatments effect on drying kinetics of garlic (*Allium sativum* L.) slices in a convective hot air dryer. African Journal of Food Science 5(7): 425-435.

Acartürk, F., 2007. Modern pharmaceutical technologies. Fersa Matbaacılık, Ankara, Turkey, 142 pp. (in Turkish)

Akoy, E.O.M., 2014. Experimental characterization and modeling of thin-layer drying of mango slices. Sudan International Food Research Journal 21(5): 1911-1917.

Alibas, I., 2012. Development of a new model for the identification of drying curves of hot air-dried artichoke (*Cynara cardunculus* L. var. *Scolymus*) slices and comparison with existing models. Journal of Agricultural Faculty of Uludag University 26(1): 49-61.

Arzanlou, M. and Bohlooli, S., 2010. Introducing of green garlic plant as a new source of allicin. Food Chemistry 120: 179-183.

Association of Official Analytical Chemists (AOAC), 1990. Official methods of analysis, No. 934.06. AOAC, Arlington, VA, USA.

Babetto, A.C., Freire, F.B., Barrozo, M.A.S. and Freire, J.T., 2011. Drying of garlic slices: kinetics and nonlinearity measures for selecting the best equilibrium moisture content equation. Journal of Food Engineering 107: 347-352.

Bocchini, P., Andalò, C., Pozzi, R., Galletti, G.C. and Antonelli, A., 2001. Determination of diallyl thiosulfinate (allicin) in garlic (*Allium sativum* L.) by high-performance liquid chromatography with a post-column photochemical reactor. Analytica Chimica Acta 441: 37-43.

Calín-Sánchez, Á., Figiel, A., Wojdyło, A., Szarycz, M. and Carbonell-Barrachina, Á.A., 2014. Drying of garlic slices using convective pre-drying and vacuum-microwave finishing drying: kinetics, energy consumption, and quality studies. Food and Bioprocess Technology 7: 398-408.

Canizares, P., Gracia, I., Gomez, L.A., Garcia, A., Martin de Argila, C., Boixeda, D. and Rafael, L., 2004. Thermal degradation of allicin in garlic extracts and its implication on the inhibition of the *in-vitro* growth of *Helicobacter pylori*. Biotechnology Progress 20: 32-37.

Cemeroğlu, B., 2013. Unit operations in food engineering. Bizim Grup Basımevi, Ankara, Turkey, 769 pp. (in Turkish)

Cui, Z.W., Xu, S.Y. and Sun, D.W., 2003. Dehydration of garlic slices by combined microwave-vacuum and air drying. Drying Technology 21(7): 1173-1184.

Demiray, E. and Tulek, Y., 2014. Drying characteristics of garlic (*Allium sativum* L) slices in a convective hot air dryer. Heat and Mass Transfer 50: 779-786.

Doymaz, I., 2005. Drying characteristics and kinetics of okra. Journal of Food Engineering 69: 275-279.

Giri, S.K. and Prasad, S., 2007. Drying kinetics and rehydration characteristics of microwave-vacuum and convective hot-air dried mushrooms. Journal of Food Engineering 78: 512-521.

Horak, F.P. and Kessler, H.G., 1981. Influence of UHT heating and sterilization on lysine in milk. Milk Science International 36(6): 543-547.

Ilić, D.P., Nikolić, V.D., Nikolić, L.B., Stanković, M.Z. and Stanojević, L.P., 2010. Thermal degradation, antioxidant and antimicrobial activity of the synthesized allicin and allicin incorporated in gel. Hemijska Industrija 64(2): 85-91.

Khanum, F., Anilakumar, K.R. and Viswanathan, K.R., 2004. Anticarcinogenic properties of garlic: a review. Critical Reviews in Food Science and Nutrition 44: 479-488.

Krest, I. and Keusgen, M., 1999. Quality of herbal remedies from *Allium sativum*: differences between alliinase from garlic powder and fresh garlic. Planta Medica 65: 139-143.

Lanzotti, V., 2006. The analysis of onion and garlic. Journal of Chromatography A 1112: 3-22.

Lawson, L.D., 1998. Garlic: a review of its medicinal effects and indicate active compounds. In: Lawson, L.D. and Bauer, R. (eds.) Phytomedicines of Europe: their chemistry and biological activity. American Chemical Society, Washington, DC, USA, pp. 176-209.

Madamba, P.S, Driscoll, R.H. and Buckle, K.A., 1996. The thin-layer drying characteristics of garlic slices. Journal of Food Engineering 29: 15-97.

Martins, N., Petropoulos, S. and Ferreira, I.C.F.R., 2016. Chemical composition and bioactive compounds of garlic (*Allium sativum* L.) as affected by pre- and post-harvest conditions: a review. Food Chemistry 211: 41-50.

Mendez-Lagunas, L., Rodriguez-Ramirez, J. and Reyes-Vasques, D., 2017. Changes in physical properties and relations with allicin degradation during convective drying of garlic. Food Measure 11: 1227-1232.

Menges, O.H., Ertekin, C. and Aydin, C., 2005. Determination of a drying model suitable for convection drying of apple slices. Tarım Makinaları Bilim Dergisi 13: 229-236.

Midilli, A. and Kucuk, H., 2003. Mathematical modelling of thin layer drying of pistachio by using solar energy. Energy Conversation and Management 44: 1111-1122.

Polatci, H., 2012. The effect of different drying methods on drying time and quality of AVG (aminoethoxyvinylglycine) treated black beauty (*Prunus salicina* L) plum variety. Tarım Makinaları Bilimi Dergisi 8(2): 171-178.

Prati, P., Henrique, C.M, Souza, A.S.D., Silva, V.S.N.D. and Pacheco, M.T.B., 2014. Evaluation of allicin stability in processed garlic of different cultivars. Food Science Technology Campinas 34(3): 623-628.

Rahman, M.S., 2007. Allicin and other functional active components in garlic: health benefits and bioavailability. International Journal of Food Properties 10(2): 245-268.

Rahman, M.S., Al-Shamsi, Q.H., Bengtsson, G.B., Sablani, S.S. and Al-Alawi, A., 2009. Drying kinetics and allicin potential in garlic slices during different methods of drying. Drying Technology 27: 467-477.

Rasouli, M., 2011. Convective drying of garlic (*Allium sativum* L.). Part I: drying kinetics, mathematical modeling and change in color. Australian Journal of Crop Science 5(13): 1707-1714.

Ratti, C., 2001. Hot air and freeze-drying of high-value foods: a review. Journal of Food Engineering 49(4): 311-319.

Ratti, C., Araya-Farias, M., Mendez-Lagunas, L. and Makhlouf, J., 2007. Drying of garlic (*Allium sativum*) and its effect on allicin retention. Drying Technology 25: 349-356.

Robertson, G.L. and Sanaiego, C.M.L., 1986. Effect of initial dissolved oxygen levels on the degradation of ascorbic acid and the browning of lemon juice during storage. Journal of Food Science 51: 184-187.

Sacilik, K. and Unal, G., 2005. Dehydration characteristics of Kastamonu garlic slices. Biosystems Engineering 92(2): 207-215.

Santhosha, S.G., Jamuna, P. and Prabhavathi, S.N., 2013. Bioactive components of garlic and their physiological role in health maintenance: a review. Food Bioscience 3: 59-74.

Saxton, A.M., 2000. PDGLM800 macro for the SAS System (version 8 or higher). University of Tennessee, Knoxville, TN, USA.

Sharma, G.P. and Prasad, S., 2001. Drying of garlic (*Allium sativum*) cloves by microwave-hot air combination. Journal of Food Engineering 50: 99-105.

Togrul, I.T. and Pehlivan, D., 2004. Modelling of thin layer drying kinetics of some fruits under open-air sun drying process. Journal of Food Engineering 65: 413-425.

Yogurtcu, H., 2014. Lemon drying in microwave oven: kinetics and modelling. Firat University Journal of Engineering 26(1): 27-33. (in Turkish)

Zhou, L., Guo, X., Bi, J., Yi, J., Chen, Q., Wu, X. and Zhou, M., 2017. Drying of garlic slices (*Allium sativum* L.) and its effect on thiosulfinates, total phenolic compounds, and antioxidant activity during infrared drying. Journal of Food Processing and Preservation 41: e12734.

Zixing, C., Mingjiao, X., Chao, W., Hua, Z., Lokyee, F. and Xuesong, H., 2017. Thermolysis kinetics and thermal degradation compounds of alliin. Food Chemistry 223: 25-30.