PAPER

# THE EFFECT OF TEMPERATURE AND METHOD OF DRYING ON ISOT (URFA PEPPER) AND ITS VITAMIN C DEGRADATION KINETICS

**Ş. DAĞHAN[1], A. YILDIRIM*[1], F. MEHMET YILMAZ[2], H. VARDIN[1]**
**and M. KARAASLAN[1]**
[1]Harran University, Faculty of Engineering, Food Engineering Department, Sanliurfa, Turkey
[2]Adnan Menderes University, Engineering Faculty, Food Engineering Department, Aydın Turkey
*Corresponding author: Tel. +90 5068430765
E-mail address: ayildirim10@gmail.com

## ABSTRACT

This study investigated drying and vitamin C degradation kinetics in isot (red peppers) at different temperatures (55, 65 and 75°C) and conditions (vacuum and hot air drying). The drying temperature and method had a significant effect on the loss of vitamin C. Vacuum dried samples at 55°C retained the highest quantity of vitamin C, while the samples dried at 75°C in a cabinet dryer lost the highest amount of vitamin C. The results showed that vitamin C is especially sensitive to the presence of oxygen and higher temperatures. The Weibull model was found to provide the mathematical equation best describing the ascorbic acid degradation kinetics in red peppers, while the Page model best reflected the drying kinetics.

*Keywords*: drying, ascorbic acid, isot, degradation kinetics, mathematical modeling

## 1. INTRODUCTION

Red pepper (*Capsicum annuum* L.) is native to American tropical zones and largely grown in relatively moderate regions as well. Red pepper is widely consumed as a fresh vegetable crop or is processed into various food products like roasted, dehydrated, flaked or powdered pepper. One of the oldest and most common processing methods is drying, and it is utilized to enhance the shelf life of food crops. Lowering water activity during drying prevents microbial and biochemical decay of food (KAMILOGLU *et al*., 2014). Dried red peppers are used in the production of ready to eat soups, ketchup, snacks, potato chips, dressings and sauces.

Peppers are not just used as a colorant, or flavoring, and/or as a source of pungency, but pepper is a good source of vitamin C, antioxidants and bioactive compounds. Among the antioxidant phytochemicals, polyphenols deserve a special mention due to their free radical scavenging properties. The red pepper, especially, has a significantly higher total phenolic content than green pepper. Red pepper contains a higher level of β-carotene (5.4 μg/g), capsanthin (8.0 μg/g), quercetin (34.0 μg/g) and luteolin (11.0 μg/g) (NADEEM *et al*., 2011).

However, the drying process may negatively affect food quality parameters such as nutritional value, bioactive-compound content, color and texture (FAZAELI *et al*., 2011) Non-enzymatic browning reactions, loss of pungency and degradation of bioactive compounds are the major changes occurring in red peppers during drying.

Red peppers are also a good source of lycopene, β-cryptoxanthin, fiber and an array of vitamins such as A, K and C. Vitamin C is one of the numerous bio-functional compounds found in red peppers. Several studies reported on the ascorbic acid content of red peppers (LEE *et al*., 1995; KUMAR and SAPE, 2009). Even though there are large differences in varieties KUMAR and SAPE, 2009), red peppers are generally recognized as a good source of vitamin C, and its vitamin content can be as high as 186 mg/100 g of fresh weight. Vitamin C has been shown to be associated with alleviation of cardiovascular disease and high blood pressure, with increased immune function, increased iron absorption and the promotion of high iron stores. Retention of vitamin C in dried foods indicates that processing conditions were not harsh and thus the other micro-nutrients present in the food matrix were most likely retained (HIWILEPO-VAN HAL *et al*., 2012). As vitamin C is a hydrophilic, heat-sensitive vitamin that is especially prone to both chemical and enzymatic oxidation, its concentration in food systems can be considered as a quality factor in plant-based foods. The use of dried food crops is mainly to enhance the quality, flavor and acceptability of the prepared dishes. To minimize the loss or destruction of a food component such as vitamin C or its color during processing, kinetic models that describe destruction rates and their dependence on such factors as temperature, moisture content and water activity must be determined.

The study of drying behaviour of different materials has been a subject of interest for various researchers on both theoretical and application grounds for the past 16 years. Recently, there have been many studies on the drying behaviour of various vegetables and fruits, such as mushrooms and pollen (MIDILLI *et al*., 1999), potato (GOGUS and MASKAN, 1998), onion (SARSAVADIA *et al*., 1999), green beans and pumpkin (YALDIZ and ERTEKIN, 2001), grapes (YALDIZ *et al*., 2001), pistachios (MIDILLI, 2001) and peppers (DI SCALA and CRAPISTE, 2008; VERAS *et al*., 2012; DARVISHI *et al*., 2014).

Mathematical equations and kinetic models are required for the design of optimal procedures for food-processing steps such as drying and storage (KAYMAK-ERTEKIN and GEDIK, 2005). This study was carried out to report on the degradation kinetics of ascorbic acid and the drying kinetics of red peppers processed under different drying conditions at various temperatures. The loss of nutritional quality during food processing has drawn more and more attention in recent years as nutrient deterioration can be the limiting factor determining the consumer demand, especially for vegetable-fruit-based foodstuffs. A review of the degradation kinetics of vitamins in fruits, vegetables and cereals during thermal processing was published by VILLOTA and HAWKES (1986). Thus, food processors are concerned in protecting nutrient quality and developing the technological capability to predict nutrient losses during handling and processing. This requires the identification and understanding of the processing parameters responsible for nutrient degradation.

Considering the rare reports available on ascorbic acid degradation kinetics in dried fruit or vegetables, and the growing interest in many bio-functional compounds including ascorbic acid in recent years, it is important to study the degradation kinetics of these compounds. The degradation kinetics of vitamin C gives a better insight into corresponding food processing conditions, and thus, helps to adapt the best processing methods to preserve the nutritional content of the products. This study was designed to determine the optimum drying conditions for preserving the micro-nutrients of Urfa pepper (İsot) that has a large trading potential in Urfa province. Therefore, we studied the drying of red peppers using different drying techniques at different temperatures and established the vitamin C degradation equations.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Red pepper (*Capsicum annuum* L.) cultivated in Şanlıurfa Province was purchased from local markets and used for dried red pepper production. Peppers were sliced by hand before the drying processes. The samples obtained either during or at the end of the drying process were stored in a freezer (-20°C) until the analyses were carried out.

### 2.2. Chemicals

Meta-phosphoric acid ($HPO_3$) was obtained from Merck (Germany), ascorbic acid standard with 99% purity and methanol of HPLC grade were both obtained from Sigma-Aldrich Company (Germany).

### 2.3. Drying equipment

The drying processes were carried out in vacuum and cabinet (hot air) dryers. A vacuum dryer (WiseVen, WOV-70, Witeg, Germany) was used to dehydrate red peppers under vacuum conditions. The dryer has three metal shelves. Split red peppers were laid on each shelf in a density of 1600 $g/m^2$. Red peppers were dried under the conditions of -0.1 MPa atmospheric pressure and at temperature levels of 55, 65 and 75°C.

A cabinet dryer (elektro-mag, M7040-R, Turkey) was used for drying red pepper using hot air with a velocity of (1.2 m/s). The dryer has three grill shelves, a fan and ventilation hole. Split red peppers were laid on each shelf in density of 1600 $g/m^2$ and dried at three different temperatures (55, 65 and 75°C). The temperature values were determined according to the results of preliminary experiments. All drying processes were carried out in triplicate.

## 2.4. Calculations

The drying rate (DR) of peppers was calculated using Eq. 1, where $M_t$ and $M_{t+dt}$ are the moisture content (kg of water per kg of dry solid) at t and t +dt, where t is the drying time in minutes.

$$DR = \frac{M_{t+dt} - M_t}{dt} \quad (1)$$

For drying model selection, drying curves were fitted to 5 well known drying models, which are given in Table. 1. The moisture ratio (MR) of pepper during the drying experiments was calculated using the following equation:

$$MR = \frac{M_t - M_e}{M_o - M_e} \quad (2)$$

where $M_t$, $M_o$, and $M_e$ are the moisture content at any drying time (in minutes), and the initial and equilibrium moisture content (%, d.b.), respectively. The values of $M_e$ are relatively small compared to those of $M_t$ or $M_o$, hence the error involved in the following simplification is negligible (AGHBASHLO *et al.*, 2008) and accordingly we can write:

$$MR = \frac{M_t}{M_o} \quad (3)$$

**Table 1**. Models used to fit the drying data.

| Model | Equation | Reference | Eq. No. |
|---|---|---|---|
| Page | $MR = \exp(-kt^N)$ | Diamonte and Munro (1993) | (4) |
| Modified Page | $MR = \exp[(-(kt)^N)]$ | White *et al.* (1981) | (5) |
| Newton | $MR = \exp(-kt)$ | Henderson (1974) | (6) |
| Henderson and Pabis | $MR = a\exp(-kt)$ | Zhang and Litchfield (1991) | (7) |
| Wang and Singh | $MR = 1 + at + bt^2$ | Wang and Singh (1978) | (8) |

For the effect of drying temperature on the rate constant (*k*) for Eq. 4, Page's model was used with Arrhenius's equation (Eq. 9):

$$\ln(\mathrm{k}) = \ln(\mathrm{k_o}) - \frac{\mathrm{E_a}}{\mathrm{RT}} \quad (4)$$

Where, $T$, $E_a$, $R$ and $k_o$ are the drying temperature in K, the activation energy in kJ mol$^{-1}$, the ideal gas constant of $8.314\times10^{-3}$ mol$^{-1}$ K$^{-1}$ and the pre-exponential factor, respectively. All calculations were done in triplicate.

## 2.5. Sample Preparation for HPLC analysis

Firstly, dried and frozen red pepper samples were blended (Yazıcılar, G1, Turkey) to make fine powder. Approximately 2 g of dried red pepper was weighed into a centrifuge tube

(50 mL) and it was combined with 50 ml of 3% metaphosphoric acid and shaken for 5 minutes and then centrifuged at 4000 rpm for 10 minutes. The supernatant was then transferred to a 100 mL volumetric flask with 3% metaphosphoric acid. Each sample was filtered into vials before injection into an HPLC Column.

### 2.6. Ascorbic Acid Analysis by HPLC

The detection and quantifying of L-ascorbic acid levels in the samples was carried out using HPLC equipped with a UV-DAD detector (Shimadzu), according to PUWASTEIN *et al.* (2011) and STEFANELLI *et al.* (2014). The HPLC equipped with an LC-20AD pump, autosampler, and an ODS C18 column (250 mm×4.6 mm×5 $\mu$m) was used, and the UV-DAD detector was set to a wavelength of 254 nm. The isocratic mobile phase was methanol: water (5:95, v/v) at a pH of 3 fixed by $H_3PO_4$, and the flow rate was 1ml/min with an injection volume of 20 $\mu$l. Various concentrations of standard ascorbic acid was used to obtain a calibration curve, and the peak areas were used to calculate the ascorbic acid content. Results were expressed as mg/100g of dry matter. All HPLC measurements were carried out in triplicate.

### 2.7. Statistical analyses

One-way analysis of variance (ANOVA) was carried out with SPSS 16.0 to determine the main influence of vacuum and hot air drying techniques on the drying and ascorbic acid degradation parameters. The Duncan multiple range test was employed to compare the differences among groups. The non-linear regression analysis was done using a Sigma plot (version 10) software package. The correlation coefficient ($R^2$) was one of the main criteria for selecting the best model. In addition to the coefficient of correlation, the goodness of fit was determined by root mean square error (RMSE) values, residual-predicted plot and experimental-predicted plot. For a quality fit, the $R^2$ values should be close to 1 and the RMSE values should be lower.

## 3. RESULTS AND DISCUSSION

### 3.1. Change of moisture ratio and drying rate during hot air and vacuum drying

Drying of the red peppers by both hot air and vacuum dryers started with an initial moisture content of around 91.26% (w.b.) and continued until a final moisture content of 12.50% (w.b.) was reached. The variations of moisture ratio with time at 55, 65 and 75°C for both hot air and vacuum dryers are given in Fig. 1. As expected, an increase in drying temperature resulted in a decrease in the drying time for both hot air and vacuum drying of red peppers at different temperatures (55, 65 and 75°C). The times to reach 12.50% (w.b.) moisture content from the initial moisture content of red peppers at 55, 65 and 75°C were found to be 960, 742 and 594 minutes for hot air drying, and 247, 231 and 195 minutes for vacuum drying, respectively.

Based on the final moisture content (12.50% w.b.), drying time decreased from 960 minutes to 247 minutes at 55°C when comparing hot air drying to vacuum drying. Similarly at 65°C, drying time decreased from 742 minutes to 231 minutes, and at 75°C drying time decreased from 594 minutes to 195 minutes. The vacuum drying was able to reduce the drying time of peppers by 74.1% at 55°C, 69.3% at 65°C and 67.0% at 75°C, compared with hot air drying (Fig. 1). These results are in good agreement with previous observations for mint leaves (GIRI and PRASAD, 2007) and for mushrooms (THERDTHAI and ZHOU, 2009).

The changes in the drying rates (DR, % d.b min$^{-1}$) versus both drying time (minimum) and moisture content (%, d.b) for both hot air and vacuum dryers are shown in Fig. 2. It is apparent that the drying rate decreased with drying time for both hot air and vacuum drying. The drying rate also decreased continuously with decreasing moisture content or for increasing drying times. These findings are in the agreement with previous studies (TOGRUL and PEHLIVAN, 2002; YALDIZ and ERTEKIN, 2001; YALDIZ *et al.*, 2001). There is no constant-rate drying period in these drying rate curves, and all the drying operations are seen to occur over the falling rate period.

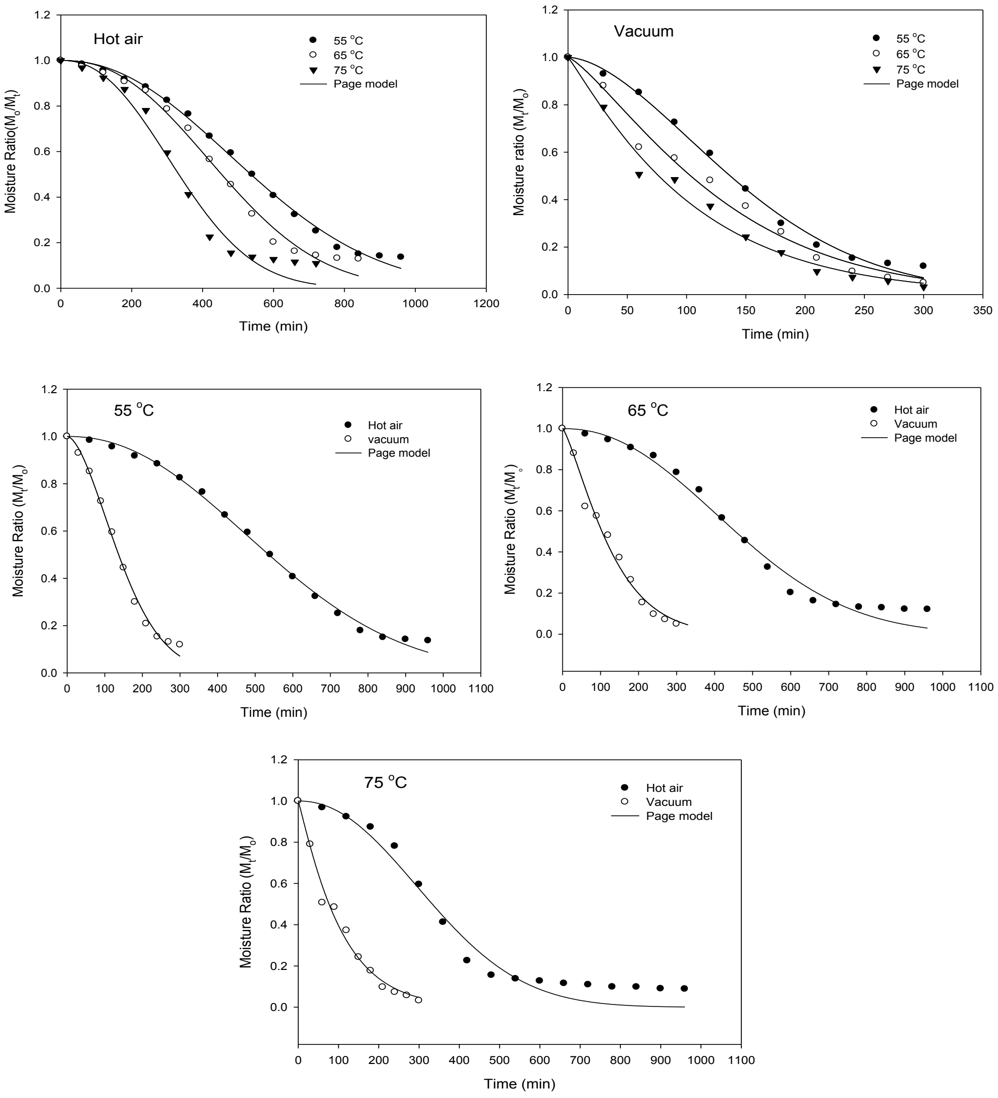
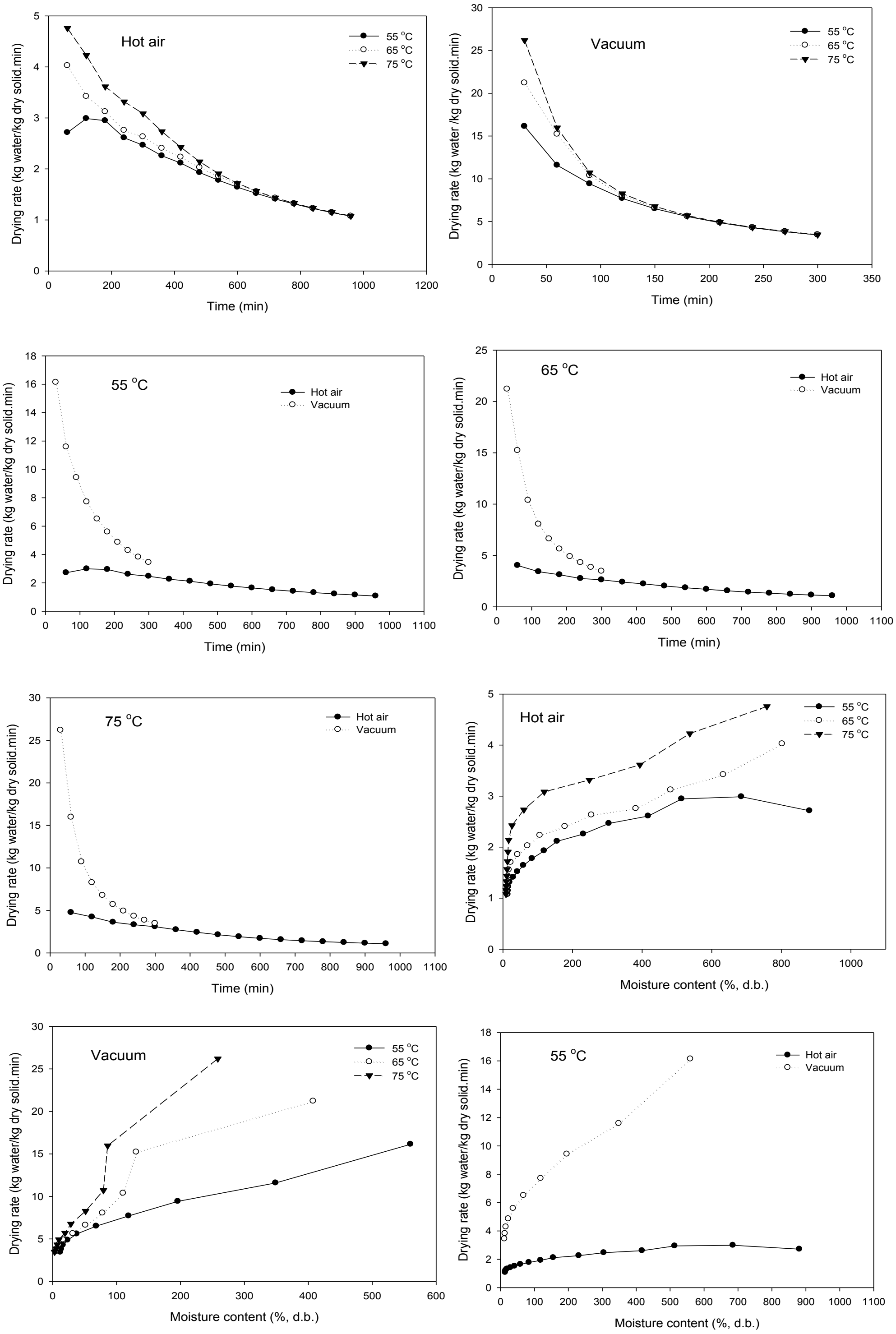


**Figure 1**. Fitting of the average experimental and simulated data of hot air and vacuum drying to the Page model at 55, 65 and 75°C temperatures.


Hot air
55 °C
65 °C
75 °C
Drying rate (kg water/kg dry solid.min)
Time (min)
Vacuum
Drying rate (kg water /kg dry solid.min)
55 °C
Hot air
Vacuum
65 °C
75 °C
Moisture content (%, d.b.)

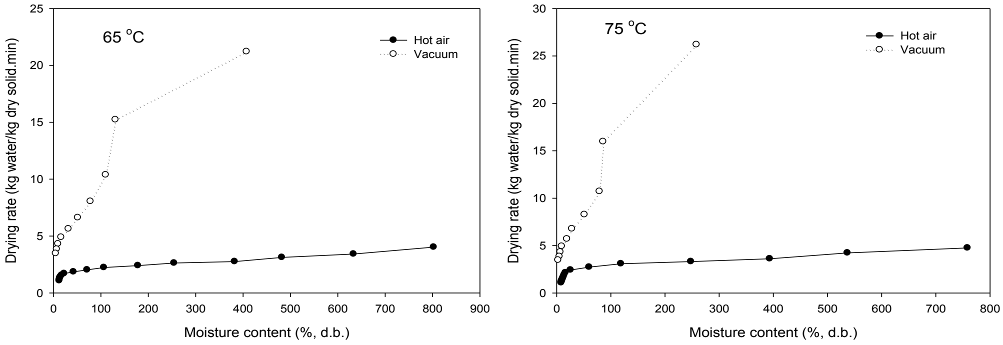


**Figure 2**. Drying rate versus time and moisture content at different temperatures for hot air and vacuum drying of peppers.

Increases in the drying temperature of red peppers also increased the drying rate and decreased the drying time (Fig. 2). The drying time is shorter when the temperature is higher, such as 75°C, and can be explained by the increase in the drying rate due to the increased heat transfer potential between the air and the peppers, therefore favoring the evaporation of water from the peppers. The effect of temperature on the drying rate has been also studied and reported on by some researchers (HENDERSON and PABIS, 1961; AKPINAR *et al*., 2003).

The vacuum drying was able to increase the drying rate of peppers by 76.6% at 55°C, 73.6% at 65°C and 70.2% at 75°C, compared to hot air drying (Fig. 2), respectively. Increases in the drying rates confirmed the decrease in drying times when the peppers were dried with a vacuum dryer. These results are in good agreement with the study by GIRI and PRASAD (2007) for mushroom vacuum drying with a drying time reduction range of 70 to 90%, and earlier observations (KAYMAK-ERTEKIN, 2002; AKPINAR *et al*., 2003).

## 3.2. The drying kinetics of peppers

### 3.2.1 Modeling of pepper moisture ratio as a function of drying time

Fig. 1 shows the change in moisture ratio of pepper samples with time at 55, 65 and 75°C for hot air and vacuum drying. It can be seen that the moisture ratio decreases continuously with drying time for both hot air and vacuum drying. The mass transfer within the samples was more rapid during higher temperatures because more heat generation within the sample created a large vapor pressure difference. The advantage of vacuum drying is to accelerate the drying process, to increase the mass transfer through an increased pressure gradient between the inner and outer layers, and to maintain the drying process at lower temperatures (PERE and RODIER, 2002).

The statistical and regression results from the 5 different models are given in Table 2. The $R^2$ and RMSE values for models were found to be in the range of 0.8596 to 0.9966 and 0.13 to 0.02, respectively.

Based on the criteria of the highest $R^2$ (0.9996 to 0.9697) and the lowest RMSE (0.02 to 0.06), Page's model was selected as the most suitable model to represent the hot air and vacuum drying behavior for red peppers. The model parameters were significant with a 95% confidence interval, and the predictive curves arising from the Page model (Fig. 1) adequately described the experimental data. The residual-predicted plot for the Page model regressed on the data is displayed in Fig. 3 and the residual points seem to be randomly distributed, with most residuals lying within two standard deviations.

**Table 2**. Statistical parameters of the drying models for different conditions.

| Process | Temp. (°C ) | Model | a | b | k (min$^{-1}$) | N | $R^2$ | RMSE |
|---|---|---|---|---|---|---|---|---|
| Hot air | 55 | Page | | | $8.73\times10^{-7}(\pm0.03)^{a,x}$ | $2.16(\pm0.01)^{a,x}$ | 0.9966 | 0.02 |
| | | Modified Page | | | $1.57\times10^{-3}$ | 2.16 | 0.9966 | 0.02 |
| | | Newton | | | $1.42\times10^{-3}$ | | 0.8596 | 0.12 |
| | | Hend.andPabis | 1.17 | | $1.72\times10^{-3}$ | | 0.9056 | 0.10 |
| | | Wang and Sing | $-6.92\times10^{-4}$ | $-3.40\times10^{-7}$ | | | 0.9691 | 0.05 |
| | 65 | Page | | | $1.18\times10^{-6}(\pm0.06)^{b,x}$ | $2.15(\pm0.02)^{a,x}$ | 0.9841 | 0.04 |
| | | Modified Page | | | $1.86\times10^{-3}$ | 2.15 | 0.9841 | 0.04 |
| | | Newton | | | $1.77\times10^{-3}$ | | 0.8616 | 0.13 |
| | | Hend.andPabis | 1.18 | | $2.12\times10^{-3}$ | | 0.9033 | 0.11 |
| | | Wang and Sing | $-1.14\times10^{-3}$ | $1.00\times10^{-7}$ | | | 0.9308 | 0.09 |
| | 75 | Page | | | $2.76\times10^{-6}(\pm0.03)^{c,x}$ | $2.14(\pm0.03)^{a,x}$ | 0.9697 | 0.06 |
| | | Modified Page | | | $2.53\times10^{-3}$ | 2.14 | 0.9697 | 0.06 |
| | | Newton | | | $2.49\times10^{-3}$ | | 0.8867 | 0.12 |
| | | Hend.andPabis | 1.17 | | $2.90\times10^{-3}$ | | 0.9174 | 0.10 |
| | | Wang and Sing | $-1.96\times10^{-3}$ | $1.01\times10^{-6}$ | | | 0.9229 | 0.10 |
| Vacuum | 55 | Page | | | $7.31\times10^{-4}(\pm0.02)^{a,y}$ | $1.71(\pm0.02)^{a,y}$ | 0.9950 | 0.02 |
| | | Modified Page | | | $5.90\times10^{-3}$ | 1.71 | 0.9950 | 0.02 |
| | | Newton | | | $5.77\times10^{-3}$ | | 0.9254 | 0.09 |
| | | Hend.andPabis | 1.11 | | $6.49\times10^{-3}$ | | 0.9465 | 0.08 |
| | | Wang and Sing | $-4.05\times10^{-3}$ | $2.95\times10^{-6}$ | | | 0.9722 | 0.05 |
| | 65 | Page | | | $9.34\times10^{-4}(\pm0.03)^{b,y}$ | $1.28(\pm0.01)^{a,y}$ | 0.9858 | 0.04 |
| | | Modified Page | | | $7.25\times10^{-3}$ | 1.28 | 0.9858 | 0.04 |
| | | Newton | | | $7.41\times10^{-3}$ | | 0.9692 | 0.06 |
| | | Hend.andPabis | 1.05 | | $7.80\times10^{-3}$ | | 0.9734 | 0.05 |
| | | Wang and Sing | $-5.51\times10^{-3}$ | $7.64\times10^{-6}$ | | | 0.9902 | 0.03 |
| | 75 | Page | | | $1.57\times10^{-3}(\pm0.08)^{c,y}$ | $1.09(\pm0.02)^{a,y}$ | 0.9875 | 0.03 |
| | | Modified Page | | | $9.32\times10^{-3}$ | 1.09 | 0.9875 | 0.03 |
| | | Newton | | | $9.45\times10^{-3}$ | | 0.9857 | 0.04 |
| | | Hend.andPabis | 1.02 | | $9.59\times10^{-3}$ | | 0.9860 | 0.04 |
| | | Wang and Sing | $-7.04\times10^{-3}$ | $1.30\times10^{-5}$ | | | 0.9839 | 0.04 |

Means in the same column with different superscript letters are significantly different, a to c (temperature), x to y (dryer), and $p \leq 0.05$. Values in parentheses are standard deviations.

Furthermore, the experimental-predicted plot was close to linear, indicating a good model fit to the Page and Weibull models in describing the drying characteristics of red peppers (Fig. 3).

From the Page model, N was found to be greater than 1.0 (the lowest value was 1.09), which means that the relationship between the moisture ratio and time was unlikely to be first order kinetics. Thus, Page's model offered improved predictability of drying kinetics over other models. For Page's model, *k* for the pepper samples increased from $8.73\times10^{-7}$ min$^{-1}$ to $2.76\times10^{-6}$ min$^{-1}$ (a 68.37% increase) when drying temperature changed from 55°C to 75°C for hot air drying. Also, a 97.52% increase was obtained in the value of *k* for vacuum drying within the same temperature range. When comparing hot air and vacuum drying of peppers at 55°C temperature, the *k* value for the Page model increased from $8.73\times10^{-7}$ min$^{-1}$ to $7.31\times10^{-4}$ min$^{-1}$, a 99.88% increase. Vacuum drying produced a similar percentage increase in the *k* value at 65°C and 75°C (99.87 and 99.82%). These results are supported with results in Section 3.1, which is related to the increased drying rate and decreased drying time with vacuum drying.

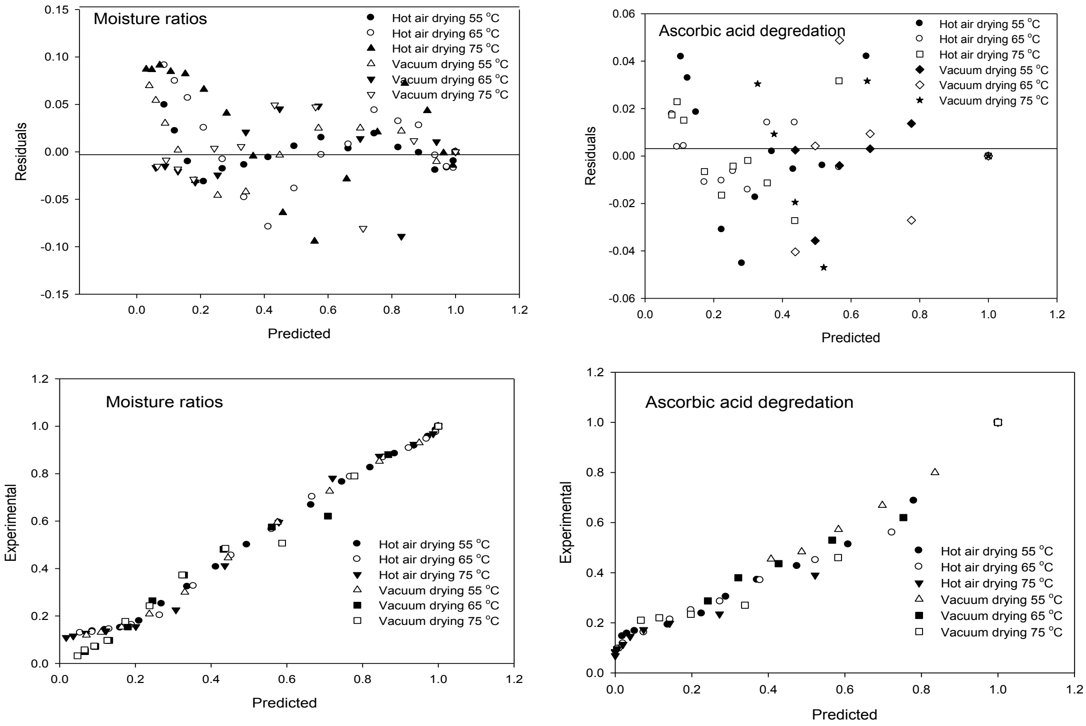


**Figure 3**. Residual-predicted and experimental-predicted plots for Page and Weibull models at different temperatures (55, 65 and 75°C) for hot air and vacuum drying

### 3.2.2 A general model to describe the moisture ratio ($M_t/M_o$) as a function of drying time and temperature

Arrhenius plots of the natural logarithm of the rate constant (*k*) versus the inverse of *T* (K) (Eq. 9) for both hot air and vacuum drying of peppers are superposed in Fig. 4. The activation energy, $E_a$, is related to the slope of this graph, and shows that the temperature dependence of the drying rate constant (*k*) was fitted to a linear model. The computed values of $E_a$ were found to be 54.4 kJ mol$^{-1}$ for hot air and 36.0 kJ mol$^{-1}$ for vacuum drying of peppers, respectively. Compared to the hot air drying, the activation energy decreased when the vacuum drying was applied for drying red pepper. This corresponds to the increase of the drying rate and decrease of the drying time. A similar comparable result was obtained by THERDTHAI and ZHOU (2009) for mint leaves for both hot air and vacuum drying. Also, the activation energy is shown to be sensitive to the drying rate constant against temperature. The greater activation energy value, the higher sensitivity of the *k* value of pepper to the temperature. In general, activation energy values for food and agricultural crops lie in the range of 12.7 to 110.0 kJ mol$^{-1}$ (AGHBASHLO *et al.*, 2008).

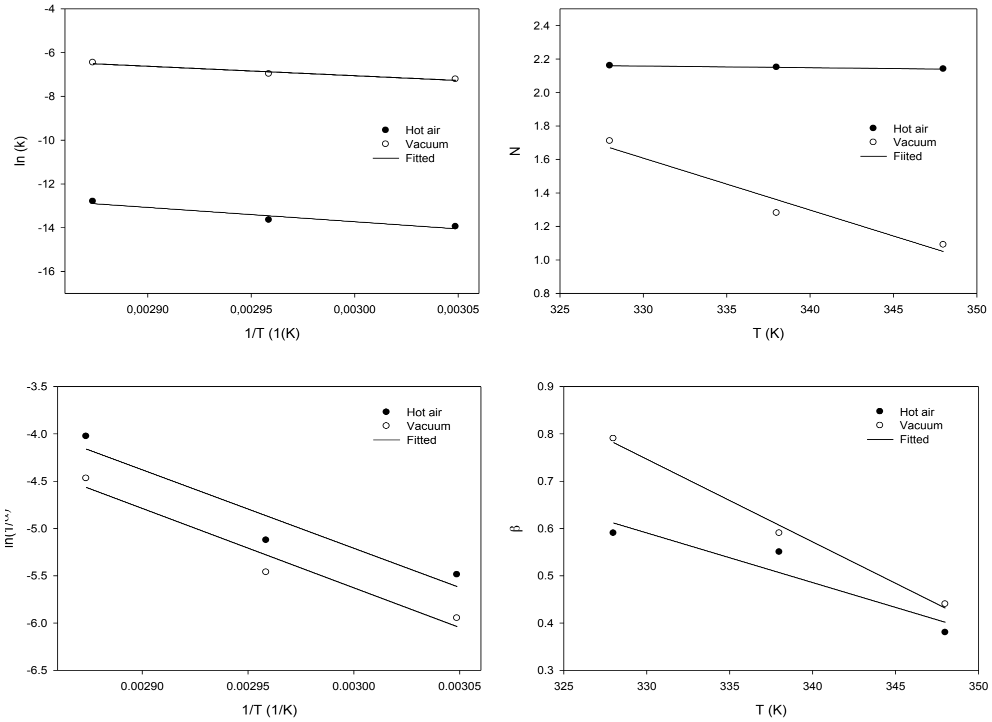


**Figure 4**. Arrhenius plot of the Page (drying rate constant, *k* and *N*) and Weibull (kinetic reaction rate constant for ascorbic acid, $1/\alpha$ and β) models for temperatures of 55, 65 and 75°C for hot air and vacuum drying of peppers.

The activation energy of pepper for the present study compares satisfactorily with similar data for red pepper reported in published literature by TURHAN *et al.* (1997), KAYMAK-ERTEKIN (2002) and DI SCALA and CRAPISTE (2008), at 28.4, 42.8 and 33.8 kJ mol$^{-1}$, respectively.

The parameter values of Page's model obtained for *k* and *N* by the least square fit of experimental points are given below for both hot air and vacuum drying:

Hot air drying $\ln(k) = 5.8966 - \frac{6540.9601}{T}$ ($R^2$=0.9211) (10)

$N = 2.488 - 0.001 * T$ (R2=0.9999) (11)

Vacuum drying $\ln(k) = 5.9359 - \frac{4331.2057}{T}$ (R2=0.9524) (12)

$N = 11.838 - 0.031 * T$ (R2=0.9524) (13)

Combining Page's model with Equations 10 to 13, the following general models can be derived to describe the drying kinetics of pepper as a function of time and temperature:

$$MR = \exp[-363.798 * \exp(-6540.9601 \frac{1}{T}) * t^{2.488-0.0010*T}] \quad \text{(for hot air drying)} \quad (14)$$

$$MR = \exp[-378.380 * \exp(-4331.2057 \frac{1}{T}) * t^{11.838-0.031*T}] \quad \text{(for vacuum drying)} \quad (15)$$

These expressions can be used to estimate the moisture ratio of red pepper and for temperature at any time with great accuracy during the hot air and vacuum drying processes. Similar expressions were also obtained by several researchers for different agricultural products (AKPINAR *et al.*, 2003; KAYMAK-ERTEKIN, 2002; GOWEN *et al.*, 2007; YILDIRIM *et al.*, 2011; CHAYJAN *et al.*, 2011).

### 3.3.1 Ascorbic acid degradation kinetics for pepper during drying

Ascorbic acid degradation was modeled using first order and Weibull models (Eq. 16 and 17). The Weibull model is flexible owing to the inclusion of a shape constant in addition to the rate constant and has been employed to describe microbial, enzymatic and chemical degradation kinetics (CUNHA *et al.*, 1998; MANSO *et al.*, 2001).

$$\frac{C_t}{C_o} = \exp(-k_1 * t) \quad (16)$$

$$\frac{C_t}{C_o} = \exp(-(\frac{t}{\alpha})^{\beta}) \quad (17)$$

where $C_t$ is the ascorbic acid concentration at a time $t$, $C_o$ is the initial ascorbic acid concentration, $C_t/C_o$ is the ascorbic acid degradation ratio at any time, $k_1$ is the rate constant, $\beta$ (dimensionless) is the shape constant (first order kinetics model is applicable when $\beta=1$) and $\alpha$ is the scale parameter in minutes.

In general, according to the literature, the average vitamin C content for red peppers is around 23.84-78.67 mg/100g (ANDREWS, 1995; TEODORO *et al.*, 2013). The vitamin C content for the red peppers used in this study was 54.35 mg/100 g. Red pepper is known to be one of the richest sources of vitamin C compared with other fruits and vegetables (MARIN *et al.*, 2004; SARKER and GOHDA, 2013), thus vitamin C was selected as the quality parameter for this study. A graphical representation of the experimental and predicted vitamin C degradation in the pepper samples during vacuum and hot air drying at 55, 65 and 75°C is shown in Fig. 5. As seen in the figure, at any time during drying, the loss of vitamin C increased with increasing temperature ($p<0.05$) in both drying conditions due to the heat-sensitive nature of vitamin C. The heated air inherently exposes the products to oxidation, reducing their ascorbic acid content (VEGA-GALVEZ *et al.*, 2008).

The degradation kinetics of vitamin C was assessed with first order and Weibull models. The Weibull distribution function has an interesting potential for describing microbial, enzymatic and chemical degradation kinetics (CUNHA *et al.*, 1998; OMS-OLIU *et al.*, 2009). Table 3 shows the results of fitting vitamin C retention in red pepper to the first order model and Weibull model distribution. The Weibull model (Eq. 17) yielded a good fit to the vitamin C experimental data, and the Weibull distribution seemed to be suitable considering the high determination coefficients ($R^2 = 0.9904$ to $0.9975$) and the low RMSEs (0.01 to 0.03). The values of kinetic constants ($\alpha$) and ($\beta$) of the Weibull model were obtained by fitting Eq. 17 to the experimental data. The $\alpha$ and $\beta$ values obtained from the Weibull model were directly affected by drying temperature. The $\beta$ values for hot air drying were 0.59, 0.55 and 0.38 at 55, 65 and 75°C, respectively, and 0.79, 0.59 and 0.44 for vacuum drying at the same temperature levels. The constant $\beta$ represents a behavior index, and if $\beta < 1$ the reaction rate decreases with time and a degradation rate higher than the exponential is observed at the beginning of the process (CUNHA *et al.*, 1998; MARFIL *et al.*, 2008). Fig. 5 supports this idea as there was an initial high rate of vitamin C loss at relatively higher moisture contents, followed by a period of less rapid degradation as the moisture content decreased. Similar tendencies in vitamin C degradation during drying were also observed in other studies (DI SCALA and CRAPISTE 2008; ERENTURK *et al.*, 2005). Therefore, retention of vitamin C is not only dependent on drying conditions but also on the sample moisture content. The $\alpha$ values were 241.83, 168.08 and 56.07 at 55, 65 and 75°C, respectively for hot air drying, and 383.05, 235.79 and 87.45 for vacuum drying at the same temperature levels (Table 3). Higher $\alpha$ values indicate lower degradation rates or, in other words, a longer time before nutrient collapse (MARFIL *et al.*, 2008). The parameter $\alpha$ was dependent on both temperature and dryer type in this study. The degradation rate was less in vacuum drying and for lower drying temperatures. An oxygen-deficient medium and less drying time could be reasons for the lower degradation rate of the vitamin C in vacuum drying (YILMAZ *et al.*, 2017).

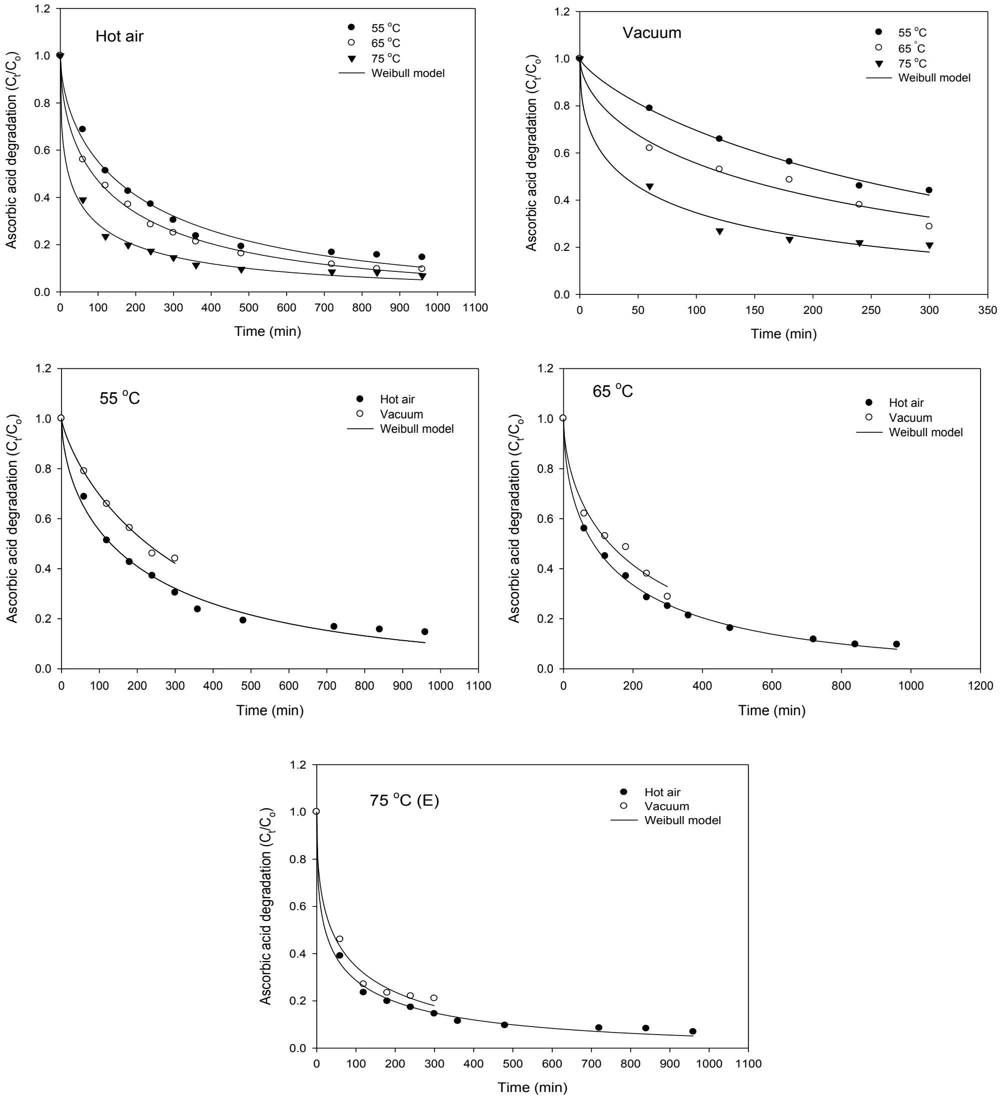


**Figure 5**. Ascorbic acid degradation curves for pepper samples using the Weibull model for hot air and vacuum drying at 55, 65 and 75°C.

The final vitamin C contents of the vacuum dried peppers were 45, 43 and 28% of the initial value at 55, 65 and 75°C respectively, as the drying operation was terminated at 12.50% moisture content (w.b.). Vitamin C retention for hot air drying was 20, 19 and 15% at 55, 65 and 75°C, respectively. As seen in these results, the degradation rate was higher for hot air drying and elevated temperatures. VEGA-GALVEZ *et al.* (2008) reported the ratio of final to initial vitamin C was in the range 0.18, 0.17, 0.15 and 0.16 for the Lamuyo variety red pepper dried at 50, 60, 70 and 80°C, respectively. SIGGE *et al.* (1999) reported 25 to 40% retention of vitamin C during dehydration of green peppers processed between 55 and 75°C. Indeed, drying at 55 and 65°C in this study produced similar vitamin C degradation. The results from DI SCALA and CRAPISTE (2008) also showed the same nutritional degradation level for red peppers from the ascorbic acid retention standpoint at 60 and 70°C. Vitamin C degradation rates during drying depended mostly on the combination of temperature and time parameters. In addition to that, air composition, sample shape and also food composition ($a_w$, enzymes, pH) are directly related to vitamin C retention (SANTOS and SILVA, 2008).

**Table 3**. First order and Weibull model parameters for drying pepper samples at different temperatures during hot air and vacuum drying.

| Process | Temp. (°C ) | Model | α | (1/α) | β | $k_1$ | $R^2$ | RMSE |
|---|---|---|---|---|---|---|---|---|
| Hot air | 55 | First order | | | | $4.13\text{x}10^{-3}$ | 0.9024 | 0.08 |
| | | Weibull | $241.83(\pm1.35)^{c,x}$ | $4.14\text{x}10^{3}(\pm0.04)^{a,y}$ | $0.59(\pm0.01)^{c,x}$ | | 0.9883 | 0.03 |
| | 65 | First order | | | | $5.39\text{x}10^{-3}$ | 0.9048 | 0.08 |
| | | Weibull | $168.08(\pm0.87)^{b,x}$ | $5.95\text{x}10^{3}(\pm0.02)^{b,y}$ | $0.55(\pm0.02)^{b,x}$ | | 0.9975 | 0.01 |
| | 75 | First order | | | | $10.80\text{x}10^{-3}$ | 0.8926 | 0.08 |
| | | Weibull | $56.07(\pm2.22)^{a,x}$ | $17.83\text{x}10^{3}(\pm0.05)^{c,y}$ | $0.38(\pm0.01)^{a,x}$ | | 0.9955 | 0.02 |
| Vacuum | 55 | First order | | | | $3.00\text{x}10^{-3}$ | 0.9790 | 0.03 |
| | | Weibull | $383.05(\pm3.84)^{c,y}$ | $2.61\text{x}10^{-3}(\pm0.03)^{a,x}$ | $0.79(\pm0.04)^{c,y}$ | | 0.9972 | 0.01 |
| | 65 | First order | | | | $4.73\text{x}10^{-3}$ | 0.9226 | 0.06 |
| | | Weibull | $235.79(\pm2.45)^{b,y}$ | $4.24\text{x}10^{-3}(\pm0.03)^{b,x}$ | $0.59(\pm0.02)^{b,y}$ | | 0.9940 | 0.02 |
| | 75 | First order | | | | $9.02\text{x}10^{-3}$ | 0.8897 | 0.09 |
| | | Weibull | $87.45(\pm3.42)^{a,y}$ | $11.43\text{x}10^{3}(\pm0.05)^{c,x}$ | $0.44(\pm0.01)^{a,y}$ | | 0.9904 | 0.03 |

Means in the same column with different superscript letters are significantly different, a to c (temperature), x to y (dryer), and $p \leq 0.05$. Values in parentheses are standard deviations.

### 3.2.3 A general model to describe ascorbic acid degradation as a function of drying time and temperature

The temperature dependence of ascorbic acid degradation on the basis of Weibull's model can be described by an Arrhenius type equation where plots of $\ln(1/\alpha)$ Eq. (18) versus the reciprocal of drying temperature in absolute degrees resulted in straight lines (Fig. 4).

$$\ln(1/\alpha) = \ln(1/\alpha_o) - \frac{E_a}{RT} \tag{18}$$

Where, $T$, $E_a$ and $R$ are the drying temperature in K, the activation energy in kJ mol$^{-1}$ and the ideal gas constant of $8.314\times10^{-3}$ mol$^{-1}$ K$^{-1}$, respectively. The parameter values obtained by Weibull's model ($\alpha$ and $\beta$) by least square fit of the experimental points are given below for both hot air and vacuum drying:

Hot air drying $$\ln(1/\alpha) = 19.68 - \frac{8298.00}{T} \quad (R^2=0.9131) \tag{19}$$

$$\beta = 4.06 - 0.0105 * T \quad (R^2=0.8867) \tag{20}$$

Vacuum drying $$\ln(1/\alpha) = 19.57 - \frac{8398.94}{T} \quad (R^2=0.9555) \tag{21}$$

$$\beta = 6.52 - 0.0175 * T \quad (R^2=0.9932) \tag{22}$$

The high activation energies for both hot air (68.99 kJ mol$^{-1}$) and vacuum drying (69.83 kJ mol$^{-1}$) obtained in this study based on Weibull's model suggest that vitamin C is highly susceptible to temperature changes (OMS-OLIU *et al.*, 2009; MARFIL *et al.*, 2008; KARAASLAN *et al.*, 2014). The degradation rates of ascorbic acid during vacuum drying was lower than that of hot air drying, but its activation energy was higher. These results indicate that vacuum drying was more stable than hot air drying.

From the regression of linear fit of Arrhenius curves for Weibull's model, the following general model can be derived to describe the ascorbic acid degradation kinetics of pepper during drying as a function of time and temperature:

Hot air: $$\frac{C_t}{C_o} = \exp[-(3.54x10^8 * \exp(-8298\frac{1}{T}) * t)^{4.0557-0.0105*T}] \tag{23}$$

Vacuum: $$\frac{C_t}{C_o} = \exp[-(3.15x10^8 * \exp(-8398.9383\frac{1}{T}) * t)^{6.5217-0.0175*T}] \tag{24}$$

With the models developed (Eqs. 23 to 24), the time and temperature dependent (instantaneous) ascorbic acid content can be estimated for both the dryer types. This study revealed the effects of dryer type, drying temperature, drying time and moisture removal on the vitamin C content of the red pepper. Also, our findings demonstrated that the Weibull distribution is likely to be a useful tool for describing vitamin C changes in red pepper under different drying conditions.

## 4. CONCLUSIONS

The drying rate of peppers increased under vacuum drying by 76.6% at 55°C, 73.6% at 65°C and 70.2% at 75°C, respectively. Vacuum drying could reduce the drying time of peppers by 74.1% at 55oC, 69.3% at 65°C and 67.0% at 75°C, compared to hot air drying. The drying time is shorter when the temperature is higher due to the increase of the drying rate, which means an enhanced heat transfer potential between the air and the peppers, therefore favoring the evaporation of water from the peppers. The Page model provided the best fit of five drying kinetic models with the highest $R^2$ values (0.9697 to 0.9996) and the lowest RMSE values (0.06 to 0.02). Weibull's model yielded a good fit with ascorbic acid degradation data, and the model distribution seemed to be suitable considering the high determination coefficients ($R^2 = 0.9904$ to 0.9975) and low RMSE values (0.01 to 0.03). Increases in drying temperature increased the percentage of the *k* value in Page's model to 68.37% for hot air drying and 97.52% for vacuum drying. Vacuum drying increased the *k* value of the Page model with a 99.88% increase at 55°C, 99.87% at 65°C and 99.82% at 75°C. The activation energy of peppers based on drying kinetics decreased from 54.4 kJ mol$^{-1}$ to 36.0 kJ mol$^{-1}$ with vacuum drying. This confirms the increase in drying rate and decrease in drying time. On the other hand, high activation energies for both hot air (68.99 kJ mol$^{-1}$) and vacuum drying (69.83 kJ mol$^{-1}$), based on ascorbic acid degradation that were obtained in this study, suggest that vitamin C is highly susceptible to temperature changes. The degradation rates of ascorbic acid during vacuum drying were lower than that of hot air drying, while its activation energy was higher. These results indicate that vacuum drying was more stable than hot air drying. New general expressions obtained for both drying and ascorbic acid degradation kinetics can be used to estimate the moisture ratio and the ascorbic acid degradation ratio of red pepper at any time and temperature with a great accuracy during the hot air and vacuum drying processes. We concluded that vacuum drying can be more advantagoeus over hot air drying with respect to drying time and ascorbic acid degradation.

## ACKNOWLEDGEMENTS

The authors would like to thank Harran University Scientific Research Council for financial support, and Uğur KESKIN for technical assistance.

## ABBREVIATIONS

| | |
|---|---|
| Co | Initial ascorbic acid concentration in mg 100g$^{-1}$ |
| Ct | Ascorbic acid concentration at any time in mg 100g$^{-1}$ |
| DAD | Diode Array Detector |
| d.b. | Dry base |
| DR | Drying rates |
| Ea | Activation energy in kJ mol$^{-1}$ |
| HMF | Hydroxymethylfurfural |
| K | Drying temperature in K (Kelvin) |
| ko | Pre-exponential factor |
| k, N | Parameter values of Page's model |
| M.C. | Moisture content |
| MR | Moisture ratio |
| Mt | Moisture content at any time |
| Mo | Initial Moisture content |
| Me | Equilibrium Moisture content |
| R2 | Coefficient of determination |
| RMSE | Root mean square error |
| R | Ideal gas constant: 8.314×10$^{-3}$ mol$^{-1}$ K$^{-1}$ |
| w.b. | Wet base |
| α, β | Kinetic constants of the Weibull model |

## REFERENCES

Aghbashlo M., Kianmehr M.H. and Samimi-Akhljahani H. 2008. Influence of drying conditions on the effective moisture diffusivity, energy of activation and energy consumption during the thin-layer drying of barberries fruit (Berberidaceae). Energ. Convers. Manage. 49:2865-2871.

Akpınar E.K., Bicer Y. and Yildiz C. 2003. Thin layer drying of red pepper. J. Food Eng. 59:99-104.

Andrews J. 1995. Peppers: The Domesticated Capsicums (4th ed., pp. 81). University of Texas Press, Austin, TX.

Chayjan R.A., Parian A.J. and Esna-Ashari M. 2011. Modeling of moisture diffusion, activation energy and specific energy consumption of high moisture corn in a fixed and fluidized bed convective dryer. Span. J. Agric. Res. 9:28-40.

Cunha L.M., Oliveira F., and Oliveira J.C. 1998. Optimal experimental design for estimating the kinetic parameters of processes described by the Weibull probability distribution function. J. Food Eng. 37(2):175-191.

Darvishi H., Asl A.R., Asghari A., Azadbakht M., Najafi G., and Khodaei J. 2014. Study of the drying kinetics of pepper. J. Saudi Soc. Agric. Sci. 13(2):130-138.

Di Scala K.C. and Crapiste G.H. 2008, Drying kinetics and quality changes during drying of red pepper. LWT- Food Sci. Technol. 41:789-795.

Erenturk S., Gulaboglu M.S., and Gultekin S. 2005. The effects of cutting and drying medium on the vitamin C content of rosehip during drying. J. Food Eng. 68(4):513-518.

Fazaeli M., Yousefi S. and Emam-Djomeh Z. 2011. Investigation on the effects of microwave and conventional heating methods on the phytochemicals of pomegranate (*Punica granatum* L.) and black mulberry juices. Food Res. Int. 50:568-573.

Giri S.K., and Prasad S. 2007. Drying kinetics and rehydration Characteristics of microwave-vacuum and convective hot-air dried mushrooms. J. Food Eng. 78(2):512-521.

Gowen A., Abu-Ghannam N., Frias J., and Oliveira J. 2007. Modeling the water absorption process in chickpeas (Cicer arietinum L.)-The effect of blanching pretreatment on water intake and texture kinetics. J. Food Eng. 78, 810-819.

Gogus F., and Maskan M. 1998. Water transfer in potato during air drying. Drying Technol. 16:1715-1728.

Henderson S.M. 1974. Progress in developing the thin layer drying equation. T. ASAE. 17:1167-1172.

Henderson S.M. and Pabis S. 1961. Grain drying theory: I Temperature eff ect on drying coefficient. J. Agr. Eng. Res. 6:169-174.

Hiwilepo-van Hal P., Bosschaart C., van Twisk C., Verkerk R., and Dekker M. 2012. Kinetics of thermal degradation of vitamin C in marula fruit (*Sclerocarya birrea* subsp. *caffra*) as compared to other selected tropical fruits. LWT- Food Sci. Technol. 49(2):188-191.

Kamiloglu S., Pasli A.A., Ozcelik B., and Capanoglu E. 2014. Evaluating the in vitro bioaccessibility of phenolics and antioxidant activity during consumption of dried fruits with nuts. LWT- Food Sci. Technol. 56:284-289.

Karaaslan M.,Yılmaz F. M., Cesur Ö., Vardin H., İkinci A., and Dalgıç A. C. 2014. Drying kinetics and thermal degradation of phenolic compounds and anthocyanins in pomegranate arils dried under vacuum conditions. Int. J. Food Sci. Tech. 49:595-605.

Kaymak-Ertekin F., and Gedik A. 2005. Kinetic modeling of quality deterioration in onions during drying and storage. J. Food Eng. 68(4):443-453.

Kaymak-Ertekin F. 2002. Drying and rehydrating kinetics of green and red peppers. J. Food Sci. 67:168-175.

Kumar O.A., and Sape S.T. 2009. Ascorbic Acid Contents in Chili Peppers (*Capsicum* L.). Not. Sci. Biol. 1:50-52,

Lee Y., Howard L.R. and Villalon B. 1995. Flavonoids and antioxidant activity of fresh pepper (*Capsicum annuum*) cultivars. J. Food Sci. 60:473-476.

Manso C.M., Oliveira F.A.R., Oliveira J.C. and Frías J.M. 2001. Modelling ascorbic acid thermal degradation and browning in orange juice under aerobic conditions. Int. J. Food Sci. Tech. 36:303-312.

Marfil P., Santos E., and Telis V. 2008. Ascorbic acid degradation kinetics in tomatoes at different drying conditions. LWT- Food Sci. Technol. 41(9):1642-1647.

Marin A., Ferreres F., Tomás-Barberán F.A., and Gil M.I. 2004. Characterization and quantitation of antioxidant constituents of sweet pepper (*Capsicum annuum* L.). J. Agric. Food Chem. 52:3861-3869.

Midilli A. 2001. Determination of pistachio drying behavior and conditions in a solar drying system. Int. J. Energ. Res. 25:715-725.

Midilli A., Olgun H., and Ayhan T. 1999. Experimental studies on mushroom and pollen drying. Int. J. Energ. Res. 23(13):1143-1152.

Mujumdar A.S. 2012. Industrial Transfer Processes, (pp. 12-13). NUS, Singapore.

Nadeem M., Anjum F.M., Khan M.R., Saeed A.R. 2011. Antioxidant Potential of Bell Pepper (*Capsicum annum* L.)-A Review, Pakistan Journal of Food Science 21:(1-4).

Oms-Oliu G., Odriozola-Serrano I., Soliva-Fortuny R.,and Martin-Belloso O. 2009. Use of Weibull distribution for describing kinetics of antioxidant potential changes in fresh-cut watermeon. J. Food Eng. 95(1):99-105.

Pere C. and Rodier E. 2002. Microwave vacuum drying of porous media: Experimental study and qualitative considerations of internal transfers. Chem. Eng. Proc. 41:427-436.

Puwastien P., Siong E.T., Kantasubrata J., Craven G., Feliciano R.R., and Judprasong K. 2011. ASEAN Manual of Food Analysis, Regional Centre of ASEAN Network of Food Data System, 141.

Santos P.H.S. and Silva M.A. 2008. Retention of Vitamin C in Drying Processes of Fruits and Vegetables-A Review. Drying Technol. 26:1421-1437.

Sarker M.R. and Gohda E. 2013. Promotion of anti-keyhole limpet hemocyanin IgM and IgG antibody productions *in vitro* by red bell pepper extract. J. Funct. Food. 5:1918-1926.

Sarsavadia P.N., Sawhney R.L., Pangavhane D.R., and Singh S.P. 1999. Drying behaviour of brined onion slices. J. Food Eng. 40:219-226.

Stefanelli D., Winkler S., Frisina Jones, and C.R. 2014. Reduction in Nitrogen Prior to Harvest Increases Phenolic Content of Baby Red Lettuce Leaves, Agricultural Sciences 5:546-554.

Sigge G.O., Hansmann C.F. and Joubert E. 1999. Optimizing the dehydration conditions of green bell peppers (*Capsicum annuum* L.): quality criteria. J. Food Quality. 22:439-452.

Teodoro A.F.P., Alves R.B.N., Ribeiro L.B., Reis K., Reifschneider F.J.B., Fonseca M.E.N., Silva J.P., and Costa T.S.A. 2013. Vitamin C content in Habanero pepper accessions (*Capsicum chinense*). Hort. Bras. 31:59-62.

Therdthai N. and Zhou, W. 2009. Characterization of microwave vacuum drying and hot air drying of mint leaves (*Mentha cordifolia Opizex* Fresen). J. Food Eng. 91: 482-489.

Togrul I.T., and Pehlivan D. 2002. Mathematical modeling of solar drying of apricots in thin layers. J. Food Eng. 55:209-216.

Turhan M., Turhan K.N. and Şahbaz F. 1997. Drying Kinetics of Red Pepper. J. Food Process. Preserv. 21:209-223.

Vega-Galvez A., Lemus-Mondaca R., Bilbao-Sáinz C., Fito P. and Andrés A. 2008. Effect of drying temperature on the quality of rehydrated dried red bell pepper (var. Lamuyo). J. Food Eng. 85(1):42-50, 2008.

Veras A.O.M., Béttega R., Freire F.B., Barrozo M.A.S. and Freire J.T. 2012. Drying kinetics, structural characteristics and vitamin C retention of *dedode-moça* pepper (*Capsicum baccatum*) during convective and freeze drying. Braz. J. Chem. Eng. 29:741-750.

Villota R. and Hawkes J.G. 1986. Kinetics of nutrients and organoleptic changes in foods during processing. In: Physical and chemical properties of food. ASAE (pp.266-366). Michigan, USA.

Wang C.Y. and Singh R.P. 1978. Use of variable equilibrium moisture content in modeling rice drying. T. ASAE. 11:668-672.

White G.M., Ross I.J. and Ponelert R. 1981. Fully exposed drying of popcorn. T. ASAE. 24:466-468.

Yaldiz O. and Ertekin C. 2001. Thin layer solar drying of some vegetables. Drying Technol. 19:583-596.

Yaldiz O., Ertekin C. and Uzun H.I. 2001. Mathematical modelling of thin layer solar drying of sultana grapes. Energ. Int. J. 26: 457-465.

Yıldırım A., Öner M.D., and Bayram M. 2011. Fitting Fick's model to analyze water diffusion into chickpeas during soaking with ultrasound treatment. J. Food Eng.104:134-142.

Yılmaz F.M., Yüksekkaya S., Vardin H. and Karaaslan M. 2017. The effects of drying conditions on moisture transfer and quality of pomegranate fruit leather (pestil). J. Saudi Soc. Agric. Sci. 16:33-40.

Zhang Q. and Litchfield J.B.1991. An optimization of intermittent corn drying in a laboratory scale thin layer dryer. Drying Technol. 9:383-395.

Paper Received November 3, 2017 Accepted April 14, 2018