

Drying characteristics and some quality parameters of whole jujube (*Zizyphus jujuba* Mill.) during hot air drying

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Abstract

Drying kinetics, water-soluble vitamins, total phenolic content (TPC), antioxidant capacity (AC) of the jujube fruits dried at 50, 60, and 70°C, and degradation kinetics of the quality parameters were investigated. The models fitted to drying were determined as Page at 50 and 70°C, Parabolic at 60°C. Increment in the drying temperature increased the drying rate and decreased the drying time. Water-soluble vitamins, TPC, and AC were significantly reduced by the drying process. Degradation of water-soluble vitamins increased with the drying temperature, although TPC and AC were not significantly affected by temperature. Thermal degradations of quality parameters were fitted to first-order kinetic.

Keywords: antioxidant capacity; degradation kinetics; drying kinetics; total phenol content; water-soluble vitamins

Introduction

Jujube fruit (*Zizyphus jujuba* Mill.), belonging to the *Rhamnaceae* family, is a drupe, which has a round-elliptic shape, apple-like taste, and is rich in various bioactive compounds and nutrients such as vitamin C, polysaccharides, minerals (especially potassium), and phenolic compounds (Chen *et al.*, 2015; Gao *et al.*, 2011; Wojdylo *et al.*, 2016). The jujube fruit has higher vitamin C content than the fruits that are known as sources of vitamin C such as kiwi, strawberry, and lemon (Frenich *et al.*, 2005; Wu *et al.*, 2012). In addition, the jujube fruit is a good source for thiamine, riboflavin, niacin, and pyridoxine as B complex vitamins (Gao *et al.*, 2013). B complex vitamins have an important role as coenzymes for enzymatic reactions in different biological systems (Calderón-Ospina and Nava-Mesa, 2020). Moreover, the jujube fruit has been considered as a good source of phenolic compounds compared to common fruits, which are widely known for being a source of phenolic compound such as berries

(Gao *et al.*, 2011). In traditional Chinese medicine, the jujube fruits have been used as a crude drug for analeptic, palliative, and antitumor purposes for thousands of years (Li *et al.*, 2007; Rostami and Gharibzahedi, 2017). The jujube fruits are also used for pharmaceutical benefits such as antioxidant, anticancer, anti-inflammatory, antiepileptic, hepatoprotective, and neuroprotective effects (Choi *et al.*, 2012; Ji *et al.*, 2017). The pharmaceutical benefits of the jujube fruit have been associated with chemical ingredients, which mainly consist of vitamin C, phenolics, polysaccharides, triterpenic acids, and nucleosides (Ji *et al.*, 2017).

The jujube fruits have been consumed as fresh, dried, tea, alcoholic beverages, pickle, jam, compote, or candy (Elmas *et al.*, 2019; Wang *et al.*, 2016; Wojdylo *et al.*, 2016). Although the jujube fruits are generally consumed as fresh, the postharvest shelf-life of the jujube fruit is very short. Thus, the commercial value of the jujube fruits is less (Wang *et al.*, 2016; Zozio *et al.*, 2014). Chemical

reactions, microbiological activity, and physical alterations in the pre- or post-harvest period of many plant-based foods mostly require high water content (Tepe and Tepe, 2020). Therefore, some preservation methods such as drying can be suggested to extend their shelf-life.

Drying, which is also called dehydration, is one of the oldest methods of food preservation, used since ancient times. The beneficial properties of drying can be ordered as reducing the water activity to microbiological safety zone and transport costs, providing easier process and extending shelf life (Elmas *et al.*, 2019). Selection of drying methods has great importance for the preservation of quality parameters such as the content of phenolic compounds, vitamins, and antioxidant capacity (AC). Sun drying and hot air drying are traditional methods for jujube drying (Wang *et al.*, 2016). The main mechanism of hot air drying is mass and heat transfer and phase transition (Tepe and Tepe, 2020). Hot air drying provides some advantages such as being free from the climate effects, reducing the drying cycle, and hygienic conditions in comparison to sun drying (Elmas *et al.*, 2019). However, long drying time, loss of nutritional and bioactive value, and changes in sensory properties are disadvantages of hot air drying (Elmas *et al.*, 2019; Onwude *et al.*, 2017; Wang *et al.*, 2019). In addition to the hot air drying method, microwave, vacuum, and freeze drying methods have been regarded as alternative drying methods. Conurso *et al.* (2019) notified that decrement in drying time and better product quality could be provided by microwave drying. In addition, vacuum drying is useful for drying of easily oxidizing foods. Besides, freeze drying has also many advantages such as preserving food quality, especially in heat-sensitive foods. These drying methods can be used alone or combined with each other such as microwave-hot air or vacuum-microwave drying. The combined drying methods may be useful for increasing the efficiency (energy efficiency, environment friendly, product quality) of these drying methods (Sun *et al.*, 2019). To select the most appropriate drying method, mathematical modeling is needed along with the determination of product quality, energy efficiency, etc. In this context, thin-layer drying has been used for the determination of the drying kinetics of fruits and vegetables. The most appropriate drying conditions can be selected by using thin-layer drying technology, a kind of mathematical modeling. Thus, a drying process can be designed and optimized (Onwude *et al.*, 2016).

There are some recent researches on the drying of jujube fruits in the literature. Elmas *et al.* (2019) have reported that moisture content, water activity, and the total phenolic content (TPC) decreased as the drying temperature increased in hot air drying. In addition, Anjum *et al.* (2020) have investigated the effects of drying methods (sun and hot air drying) on several physical properties,

AC, content of vitamin C, and TPC. In that study, it was notified that the highest AC and TPC were observed in jujube fruits dried at 70°C, while the highest vitamin C content was obtained at 50°C (Anjum *et al.*, 2020). The effects of different drying methods (convective, vacuum-microwave, convective pre-drying, and vacuum-microwave combination) on phenolic compounds, AC, and the color of jujube fruits were investigated by Wojdyło *et al.* (2019). Convective drying carried out at 50°C has been reported to be the best method in terms of polyphenol content, AC, and color parameters.

In this study, it was aimed to: (i) determine the drying characteristics of whole jujube fruits at different air temperatures (50, 60, 70°C); (ii) investigate the effect of drying on vitamin C and B complex content, TPC, and AC of fresh and dried whole jujube fruits; and (iii) determine thermal degradation kinetics of these bioactive compounds during the drying process.

Materials and Methods

Sample preparation

Fresh jujube fruits (*Zizyphus jujuba* Mill.) were provided from a local producer in Denizli, a province in Turkey. The fresh jujube fruits were carefully selected in terms of the same ripening stage (fully mature) and the same size. Before the analysis, fresh jujube fruits were washed to remove foreign materials. The fresh jujube fruits were stored at 4°C in a refrigerator. Determination of the initial moisture content of the samples was carried out in a drying oven at 105°C till any changes in the sample weight. The initial moisture content of whole jujube fruits was 65.26% ± 0.6.

Drying experiment

A cabinet dryer (Yücebas, Makine Ltd. Inc., Izmir, Turkey) was used for the drying experiments. For the condition stabilization, the cabinet dryer was turned on approximately 30 min before drying. Samples (500 g) were weighted on a drying tray and placed in a cabinet dryer for each drying experiment. Drying temperatures were selected as 50, 60, and 70°C, similar to other researches on the drying of jujube fruits (Fang *et al.*, 2009a; Motevali *et al.*, 2012; Wojdyło *et al.*, 2016, 2019). Besides, air velocity and relative humidity were 2 m s⁻¹ and 20%, respectively. In practical application, the moisture content of the dried jujube fruits needs to be below 25% on wet basis (WB) (Fang *et al.*, 2009a). Therefore, the drying experiments were continued until the moisture content of the samples achieved to 21% on WB, similar to the results of the studies by Fang *et al.* (2009a)

and Yi *et al.* (2012). All of drying experiments were performed in triplicate.

Drying characteristics of whole jujube fruits

To design the best drying conditions, thin-layer drying models are very important. The thin-layer mathematical models selected in the current study are listed in Table 1. Significant information about drying temperature and time can be provided with these models (Demiray *et al.*, 2017).

Moisture ratio (MR) of whole jujube fruits was calculated using Eq. (1):

$$MR = \frac{M_t - M_e}{M_i - M_e} \quad (1)$$

M_i : initial moisture content of the samples (g water g⁻¹ dry matter);

M_t : moisture content at any point of time (g water g⁻¹ dry matter);

M_e : equilibrium moisture content (g water g⁻¹ dry matter).

M_e can be ignored because of its insignificant value in comparison to M_i and M_t (Fang *et al.*, 2009a).

Drying rate (DR) was determined using Eq. (2):

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

$M_{t+\Delta t}$: moisture content at time difference;

Δt : difference of time between two measuring points.

The relation between the predicted and the experimental data of whole jujube fruits dried at different drying temperatures is explained with determination coefficient

(R²), root-mean square error (RMSE), and reduced chi-square (χ^2). RMSE is a statistical parameter, which expresses the deviation between the predicted and the experimental values. The best equation predicting experimental data is determined according to the lower values of χ^2 and RMSE, and the higher value of R². The RMSE (Eq. 3) and chi-square (χ^2) (Eq. 4) values were calculated as follows:

$$RMSE = \left[\frac{1}{N} \sum_{i=0}^N (MR_{pre,i} - MR_{exp,i})^2 \right]^{\frac{1}{2}} \quad (3)$$

$$\chi^2 = \frac{\sum_{i=0}^N (MR_{pre,i} - MR_{exp,i})^2}{N - n} \quad (4)$$

$MR_{pre,i}$: predicted MR;

$MR_{exp,i}$: experimental MR;

N: number of observation data;

n: constants of thin layer drying models.

Thin-layer modeling and statistical parameters were calculated using the MATLAB software (R2015a, version 8.5) non-linear curve fitting toolbox with the trust-region algorithm.

Determination of effective moisture diffusivity and activation energy in hot-air drying

Fick's diffusion equation has been accepted to describe the drying characteristics of biomaterials. Crank (1975) has suggested a solution to this equation, which can be used for spherical products. Eq. (5) has been recommended for spherical products by assuming constant effective diffusivity and no shrinkage (Doymaz, 2006).

$$MR = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2 \pi^2 D_{eff} t}{r^2}\right) \quad (5)$$

D_{eff} : effective moisture diffusivity (m² s⁻¹);

r: arithmetical average of radius of samples at measured intervals (m).

Eq. (5) can be simplified for the first term of the series (Saravacos and Raouzeos, 1986). The new equation is written as given below, Eq (6):

$$\ln(MR) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff}}{r^2} t\right) \quad (6)$$

Table 1. Thin-layer mathematical models.

Model name	Model	References
Logarithmic	$a \exp(-kt) + c$	Demiray <i>et al.</i> (2017)
Lewis	$\exp(-kt)$	Demiray <i>et al.</i> (2017)
Henderson and Pabis	$a \exp(-kt)$	Tepe and Tepe (2020)
Page	$\exp(-kt^n)$	Demiray <i>et al.</i> (2017)
Parabolic	$a + bt + ct^2$	Bi <i>et al.</i> (2015)
Wang and Sing	$1 + at + bt^2$	Tepe and Tepe (2020)

The plot gives a straight line with a slope as follows, Eq. (7):

$$\text{Slope} = -\frac{\pi^2}{r^2} D_{\text{eff}} \quad (7)$$

Arrhenius equation in hot air drying process was used for the calculation of activation energy (Fang *et al.*, 2009a):

$$D_{\text{eff}} = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

R: universal gas constant (8.314 J mol⁻¹ K⁻¹ or 1.987 cal mol⁻¹ K⁻¹);

T: absolute temperature (K);

E_a: activation energy (kJ mol⁻¹ or kcal mol⁻¹);

D₀: pre-exponential constant (m² s⁻¹).

After regulation of the natural logarithm of Eq. (8), Eq. (9) can be written as given below:

$$\ln D_{\text{eff}} = \ln D_0 - \frac{E_a}{RT} \quad (9)$$

Natural logarithm of effective moisture diffusivity versus T⁻¹ gives a straight line with a slope, which represents activation energy.

Analysis of water-soluble vitamins

An extraction method, recommended by Dönmez (2015), was used for water-soluble vitamins. In order to determine the water-soluble vitamins, 5 g of each sample was weighted. After homogenization with distilled water (1:9, w:v), the homogenate was centrifuged at 2355 × g for 10 min (Nüve NF 800R). The supernatant obtained from centrifugation was filtrated using a 0.45 µm filter to be injected into the high performance liquid chromatography (HPLC).

A micro syringe was used for injecting 20 µL of the last filtrate into the HPLC column. Mobile phase consisted of 0.1 M HPLC grade KH₂PO₄ at pH 7. An HPLC device (SHIMADZU), column oven at 25°C (SHIMADZU CTO-20A), Column ACE C18 (7.8 × 300 mm), pump (SHIMADZU LC-20AD), degasser (SHIMADZU DGU-20A3), photo-diode array (PDA) detector (SPD-M20A) at 254, 261, 324, 234 nm for ascorbic acid, niacin, pyridoxine, and thiamin, respectively were used for analysis. The mobile phase was isocratic with 0.7 mL min⁻¹ flow rate. For riboflavin analysis, the column is Macherey-Nagel NH₂ (4.6 × 250 mm), column oven temperature is 40°C, and the wave length is 266 nm. The same mobile phase was isocratic with 1 mL min⁻¹ flow rate.

The content of water-soluble vitamins was calculated using an equation obtained from a calibration curve consisting of different concentrations of stock solutions (5, 10, 25, 50, 75, and 100 ppm) with a high R² (0.9999). Results were given as mg 100 g⁻¹ in dry weight (DW) for vitamin C and µg 100 g⁻¹ for niacin, pyridoxine, thiamine, and riboflavin. Each analysis was performed in triplicate.

Analyzes of TPC and AC

Analyses of TPC and AC were performed with methanolic extraction with a slight modification, as suggested by Choi *et al.* (2012). Jujube fruit samples (5 g) and 45 mL of 90% methanol were homogenized using a laboratory-type blender. The homogenate was centrifuged at 2355 × g for 10 min. After centrifugation, the supernatants were collected and filtrated using a filter paper.

TPC analysis was performed according to Singleton and Rossi (1965) with a slight modification. Folin-ciocalteu solution (1500 µL) (10% v/v) was added into 300 µL of the extract, and the mixture was kept in a dark place for 5 min. After adding 1200 µL of aqueous 7.5% Na₂CO₃ into the mixture, the mixture was incubated at room temperature in a dark place for 2 h. At the end of the incubation, the absorbance of samples was measured at 760 nm using a spectrophotometer (T80, PG Ins. UK.). Each analysis was carried out in triplicate, and TPC was expressed as mg gallic acid equivalent (GAE) 100 g⁻¹ in DW.

The AC analysis was carried out using a method suggested by Thaipong *et al.* (2006) with slight modification. Extracts (150 µL) and DPPH methanolic solution (2850 µL), whose absorbance is 1.1 at 515 nm, were mixed. After incubation for 60 min at room temperature in a dark place, the absorbance of samples was measured at 515 nm. Each sample was analyzed in triplicate, and AC was expressed as mmol trolox equivalent (mmol TE) g⁻¹ in DW.

Color measurement

Reflectance color value of the whole jujube fruit skin was measured using Hunter Lab Color Miniscan XE (45/0-L, USA). The samples were placed on a white background, and the measurement was done by covering a transparent glass. ΔE was calculated with the equations below (Horuz *et al.*, 2017):

$$\Delta E = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2} \quad (10)$$

ΔE: Total color differences;

L: Lightness (0 = black, 100 = white) value at the end of the drying process;

L_0 : Initial lightness value of the fresh jujube fruits;

a: Redness (a+ = red, a- = green) value at the end of the drying process;

a_0 : Initial redness value of the fresh jujube fruits;

b: Yellowness (b+ = yellow, b- = blue) value at the end of the drying process;

b_0 : Initial yellowness value of the fresh jujube fruits.

R: universal gas constant (8.314×10^{-3} kJ mol⁻¹ K⁻¹ and 1.987×10^{-3} kcal mol⁻¹ K⁻¹);

T: absolute temperature (K);

E_a : activation energy (kcal mol⁻¹ or kJ mol⁻¹).

Quotient indicator (Q_{10}) expresses the temperature-dependence of reaction rate and is calculated with Eq. (16) (Kadalkal *et al.*, 2017):

$$Q_{10} = \left(\frac{k_2}{k_1} \right)^{\left(\frac{10}{T_2 - T_1} \right)} \quad (16)$$

Calculation of kinetic parameters

Labuza and Riboh (1982) and Kadalkal *et al.* (2017) have suggested Eq. (11) as the general equation to describe the reaction rate of compounds degrading or forming:

$$\frac{dC}{dt} = k[C]^m \quad (11)$$

For the zero-order kinetic model, Eq. (12) can be written as below:

$$C = C_0 - kt \quad (12)$$

When Eq. (1) is integrated, if m equals one, Eq. (3) is written as follows:

$$\ln C = \ln C_0 - kt \quad (13)$$

$\ln C$: natural logarithm of the residual vitamin C, B complex vitamins, TPC, and AC;

$\ln C_0$: initial content of vitamin C, B complex vitamins, TPC, and AC;

k: rate constant (h⁻¹);

t: time.

Temperature dependence of vitamin C, B complex vitamins, TPC, and AC can be calculated with Eq. (14) (Kadalkal *et al.*, 2017; Labuza and Riboh, 1982):

$$k = k_0 \times e^{-\frac{E_a}{RT}} \quad (14)$$

When the Eq. (14) is regulated, Eq. (15) is written as follows:

$$\ln k = \left(-\frac{E_a}{R} \right) \times \left(\frac{1}{T} \right) + \ln k_0 \quad (15)$$

k_0 : frequency factor (h⁻¹);

Half-life time, a time required for half of the concentration, for each temperature is calculated with Eq. (17) for the first-order kinetic (Kadalkal *et al.*, 2017);

$$t_{1/2} = -\ln(0.5) \times k^{-1} = 0.693 \times k^{-1} \quad (17)$$

D represents the time that it takes for the compound or quality criterion to lose 90% of its quality and is calculated for first-order kinetics as written below (Eq. 18):

$$D = 2.303 \times k^{-1} \quad (18)$$

Statistical analysis

All of the data were statistically analyzed using the SPSS software (ver. 22 SPSS Inc., Chicago, IL, USA) and expressed as mean \pm standard deviation (SD). Analysis of variance (ANOVA) was used to evaluate differences between treatments, with a significance level of $p = 0.05$. The differences between groups were determined using the Duncan test.

Results and Discussion

Drying characteristics of whole jujube fruits during hot air drying

MR and DR of whole jujube fruits during hot air drying are shown in Figure 1. As understood from Figure 1, drying temperature has statistically affected DR and the drying time of whole jujube fruits. It was clearly observed that DR increased with the increment in drying temperature. Accordingly, the drying time was reduced and found to be 48, 30, and 18 h for 50, 60, and 70°C, respectively. Likewise, Yi *et al.* (2012) reported that drying times of whole jujube fruits at 45, 55, and 65°C for constant air velocity (2 m s⁻¹) were about 45, 25, and 20 h, respectively. It could be explained with increasing of the heat transfer coefficient by increment in drying temperature. Generally, two periods as constant rate and falling rate are the main

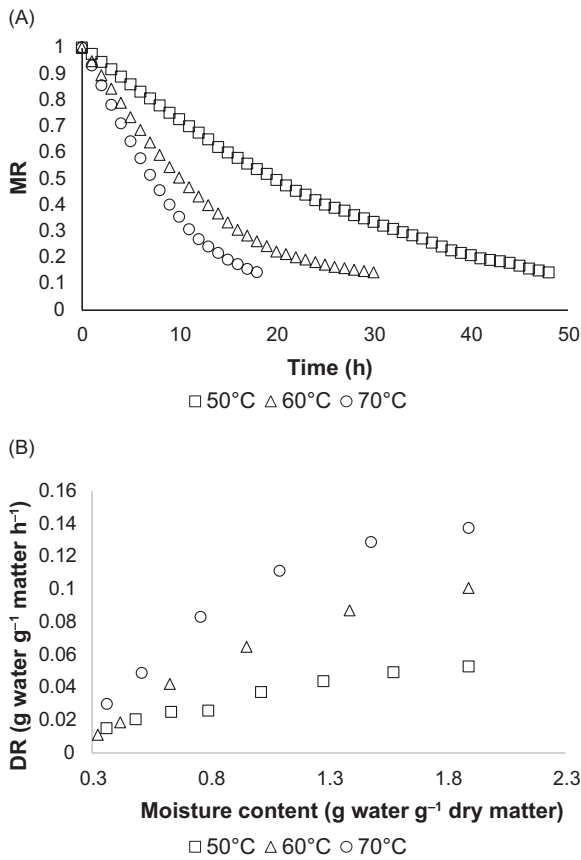


Figure 1. Moisture ratio and drying rate of whole jujube fruits during hot air drying.

Table 2. Models, constants, and statistical parameters of thin-layer drying curves.

Models	Temperature	Model constants			χ^2	RMSE	R ²
Lewis	50°C	k = 0.03638			0.00043784	0.020710	0.9936
	60°C	k = 0.06996			0.000355573	0.018550	0.9953
	70°C	k = 0.10140			0.000841207	0.028230	0.9899
Page	50°C	k = 0.02349	n = 1.135		2.00099E-05	0.004381	0.9997
	60°C	k = 0.05734	n = 1.074		0.00022413	0.014480	0.9972
	70°C	k = 0.06731	n = 1.182		5.10587E-05	0.006759	0.9995
Henderson and Pabis	50°C	k = 0.03820	a = 1.041		0.000225899	0.014720	0.9968
	60°C	k = 0.07249	a = 1.032		0.00024309	0.015080	0.9970
	70°C	k = 0.10720	a = 1.049		0.000524835	0.021670	0.9944
Logaritmik	50°C	k = 0.05256	a = 0.9309	c = 0.1427	0.001495566	0.037470	0.9794
	60°C	k = 0.10390	a = 0.9326	c = 0.1428	0.001457264	0.036280	0.9825
	70°C	k = 0.14750	a = 0.9333	c = 0.1439	0.002635481	0.047110	0.9733
Wang and Singh	50°C	a = -0.03016	b = 0.0002595		2.90427E-05	0.005278	0.9995
	60°C	a = -0.05971	b = 0.0010510		4.66771E-05	0.006608	0.9994
	70°C	a = -0.08348	b = 0.0019720		0.000105507	0.009716	0.9988
Parabolic	50°C	a = 1.003	b = -0.03039	c = -0.0002634	2.92706E-05	0.005242	0.9996
	60°C	a = 1.008	b = -0.06080	c = 0.0010800	3.94992E-05	0.005973	0.9995
	70°C	a = 1.017	b = -0.08723	c = 0.0021410	6.1355E-05	0.007188	0.9994

RMSE, root-mean square error.

constituents of the drying process of agricultural products such as fruits and vegetables. In the current study, the falling rate period was observed. This statement was found to in sync with other studies, in which the jujube fruits were dried with hot air, by Fang *et al.* (2009a), Yi *et al.* (2012), Baomeng *et al.* (2014), and Chen *et al.* (2015).

MR of whole jujube fruits during hot air drying was used to be fitted mathematical models that are listed in Table 1. Statistical parameters to describe the most suitable model are presented in Table 2. Demiray *et al.* (2017) reported that the lower RMSE and χ^2 and the higher R² are required for goodness of the fit. As seen from Table 2, the parabolic model was the best model for predicting the experimental MR of whole jujube fruits for 60°C, while experimental MRs of jujube dried at 50 and 70°C were described with Page model with the lowest RMSE and χ^2 and the highest R² values.

Effective moisture diffusivity and activation energy of whole jujube fruits during hot air drying

D_{eff} and E_a values of whole jujube fruits are presented in Table 3. D_{eff} values of whole jujube fruits were calculated in the range of 6.43 × 10⁻¹¹ and 1.80 × 10⁻¹⁰ m² s⁻¹. In comparison to the other drying temperatures, the highest value of D_{eff} was obtained from the drying process

Table 3. D_{eff} and E_a values of whole jujube fruits.

Temperature	D_{eff} ($\text{m}^2 \text{s}^{-1}$)	E_a (kJ mol^{-1})	E_a (kcal mol^{-1})
50°C	6.43×10^{-11}		
60°C	1.11×10^{-10}	47.41	11.33
70°C	1.80×10^{-10}		

performed at 70°C. It is a fact that drying temperature is one of the most important factors affecting the D_{eff} value. Increment in D_{eff} value means more easy evaporation of moisture content of the sample and consequently an increment in DR. In addition, a proportional relationship between D_{eff} and DR was reported by Demiray *et al.* (2017). Elmas *et al.* (2019) and Fang *et al.* (2009a) notified D_{eff} values of jujube fruits ranging from 1.27×10^{-9} to 3.55×10^{-9} and 5×10^{-11} to $2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively. When compared to these studies, the result of the current study was less than that reported by Elmas *et al.* (2019) and very similar to the findings notified by Fang *et al.* (2009a). This difference might be because of drying conditions, equipment, and the shape of dried fruits (sliced or whole). Arrhenius relation between D_{eff} and T^{-1} is presented in Figure 2. E_a value of whole jujube fruits was found to be 47.11 kJ mol^{-1} and 11.33 kcal mol^{-1} . Various E_a values were reported for drying of the jujube fruit. Fang *et al.* (2009a) have reported that the E_a value of the jujube fruit was 54.51 kJ mol^{-1} . On the contrary, Elmas *et al.* (2019) have found the E_a value of sliced jujube fruit to be 28.183 kJ mol^{-1} . Besides, Motevali *et al.* (2012) have notified that the E_a value of the jujube fruit ranged from 34.97 to 74.20 kJ mol^{-1} .

Color properties of whole jujube fruits during hot air drying

Color properties of fresh and dried whole jujube fruits are shown in Table 4. When compared to the initial L,

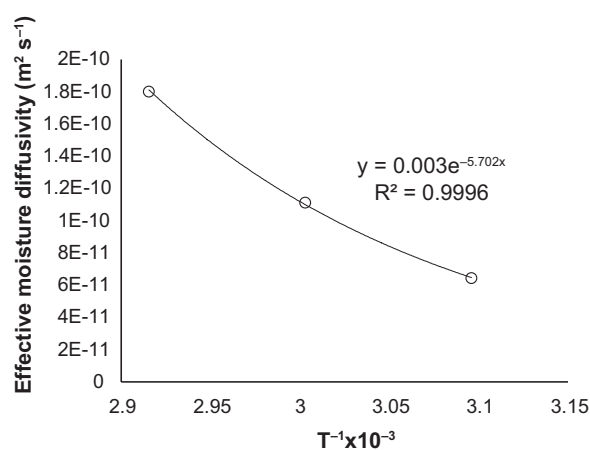
Figure 2. Arrhenius type relation between D_{eff} and T^{-1} .

Table 4. The color properties of whole jujube fruits.

	L	a	b	ΔE
Fresh	21.92 ± 0.01^a	15.95 ± 0.12^a	9.91 ± 0.12^a	0.00
50°C	10.31 ± 0.05^b	2.04 ± 0.04^b	1.04 ± 0.02^b	20.17
60°C	11.09 ± 0.03^c	2.23 ± 0.02^c	1.34 ± 0.07^c	19.47
70°C	12.25 ± 0.04^d	4.57 ± 0.02^d	2.12 ± 0.08^d	16.84

*The different letters in the same column are significantly different ($p < 0.05$).

a, and b values of whole jujube fruits, these parameters were significantly decreased depending on the drying process ($p < 0.05$). The lowest L, a, and b values were obtained at 50°C. It could be because of the longer time of the drying process at 50°C. ΔE represents differences between the colors of the samples (Horuz *et al.*, 2017). ΔE values of dried whole jujube fruits depending on drying temperature and time ranged from 16.84 to 20.17.

The effect of the drying process on the water-soluble vitamins, TPC, and AC

The effect of the drying process on the water-soluble vitamins of whole jujube fruits is given in Table 5. Water-soluble vitamins were significantly affected by the drying process. Vitamin C content of the jujube fruit differs depending on some factors such as geographical conditions and cultivars. In the current study, vitamin C content of fresh whole jujube fruits was determined as $78.90 \pm 0.96 \text{ mg } 100 \text{ g}^{-1} \text{ DW}$. Vitamin C content of the whole jujube fruit was considerably reduced by the drying process, mainly the drying temperature ($p < 0.05$). Fang *et al.* (2009b) have similarly reported decrement in vitamin C content of the whole jujube fruit during hot air drying. Reduction in vitamin C content of sliced jujube fruit during hot air drying was also notified by Chen *et al.* (2015). Vitamin C is a heat-sensitive compound and, thus, might be degraded by a heating process such as drying (Chin *et al.*, 2015). In addition, vitamin C oxidation can occur more rapidly at higher temperatures (Orikasa *et al.*, 2014; Santos and Silva, 2008). The highest loss of vitamin C content of whole jujube fruits was 81.91% at 70°C, while the lowest loss was 55.51% at 50°C. Loss of vitamin C content of whole jujube fruits increased with the increment in drying temperature. This result was similar to Chen *et al.* (2015) but contrary to Fang *et al.* (2009b). In other fruits, vitamin C has been reported to be more degraded with the increasing air temperature (Chin *et al.*, 2015; Kaya *et al.*, 2010; Orikasa *et al.*, 2014; Vega-Galvez *et al.*, 2009).

Initial content of thiamine (B1), riboflavin (B2), niacin (B3), and pyridoxine (B6) in fresh whole jujube fruits were determined as 27.33 ± 1.52 , 41.00 ± 1.00 , $883.33 \pm$

Table 5. The effect of the drying process on water-soluble vitamins of whole jujube fruits.

	Vitamin C	% Loss	Thiamine (B1)	% Loss	Riboflavin (B2)	% Loss	Niacin (B3)	% Loss	Pyridoxine (B6)	% Loss
Fresh	78.90 ± 0.96 ^a	0	27.33 ± 1.52 ^a	0	41.00 ± 1.00 ^a	0	883.33 ± 15.27 ^a	0	80.33 ± 2.08 ^b	0
50°C	35.10 ± 0.36 ^b	55.51	19.93 ± 0.21 ^b	27.07	19.73 ± 0.15 ^b	51.88	761.67 ± 4.04 ^b	13.77	ND*	100
60°C	20.93 ± 0.64 ^c	73.47	18.63 ± 0.15 ^b	31.83	18.13 ± 0.15 ^c	55.78	689.33 ± 4.16 ^c	21.96	ND	100
70°C	14.27 ± 0.55 ^d	81.91	16.47 ± 0.21 ^c	39.74	15.43 ± 0.15 ^d	62.37	631.00 ± 2.00 ^d	28.57	ND	100

*ND, not detected; Vitamin C was expressed as mg 100 g⁻¹ DW, B complex vitamins were expressed as µg 100 g⁻¹ DW. The different letters in the same column are significantly different (p < 0.05).

15.27, and 80.33 ± 2.08 µg 100 g⁻¹ DW, respectively. Yaşa (2016) had reported thiamine (B1), riboflavin (B2), niacin (B3), and pyridoxine (B6) content of jujube cultivated in Denizli, a province of Turkey, to be 0.018, 0.036, 0.82, and 0.076 mg 100 g⁻¹, respectively. Results of the current study were in good agreement with those reported by Yaşa (2016). In addition, Li *et al.* (2007) have reported thiamine and riboflavin content of five Chinese jujube cultivars in the range of 0.04–0.09 mg 100 g⁻¹ and 0.05–0.09 mg 100 g⁻¹, respectively. These values were also similar to those reported by Gao *et al.* (2013), Pareek (2013), Yaşa (2016), and Li *et al.* (2007). Drying temperature has a great impact on B complex vitamins. As seen from Table 5, B complex vitamins of whole jujube fruits remarkably decreased at the end of the drying process (p < 0.05). The highest losses in thiamin (B1), riboflavin (B2), and niacin (B3) content occurred at 70°C as 39.74, 62.37, and 28.57% (p < 0.05), respectively, whereas the drying process at 50°C resulted in the lowest losses with the percentages of 27.07, 51.88, and 13.77 (p < 0.05), respectively. On the other hand, pyridoxine was the highest affected compound among B complex vitamins. No pyridoxine content of whole jujube fruits was determined at the end of the drying process (p < 0.05). It could be under the limit of detection. It was similarly notified by Yaşa (2016) that thiamin (B1), riboflavin (B2), and niacin (B3) content of whole jujube fruits decreased during drying. In addition, no pyridoxine content was reported at the end of the drying process by Yaşa (2016).

The effect of the drying process on TPC and AC of whole jujube fruits are presented in Table 6. As seen in Table 6, TPC and AC of fresh whole jujube fruits were found to be 1911.4 ± 47.32 mg GAE 100 g⁻¹ DW and 0.214 ± 0.001 mmol TE g⁻¹ DW. TPC and AC of whole jujube fruits significantly decreased with hot air drying (p < 0.05). The loss percentages of TPC in whole jujube fruits dried at 50, 60, and 70°C were calculated as 78.10, 76.26, and 74.68, respectively. In the current study, the increment in the drying temperature has no significant effect on the reduction in TPC (p > 0.05). Likewise, Vega-Galvez *et al.* (2009) noted no significant change in the TPC of red pepper during hot air drying. Similarly, TPC of sour cherries was also notified to have decreased during

drying; however, there were no significant differences between the drying temperatures (Horuz *et al.*, 2017). On the contrary, Yaşa (2016) has reported that the TPC of whole jujube fruits was reduced by hot air drying and the loss of TPC increased with an increment in the drying temperature. Likewise, Elmas *et al.* (2019) notified more decrement in the TPC of sliced jujube fruits based on an increment in the drying temperature. Furthermore, AC of whole jujube fruits dried at 50, 60, and 70°C decreased with the percentage of 61.22, 60.75, and 59.35, respectively. No significant difference was found between the drying temperatures (p > 0.05). Long drying times might decrease AC of foods (Garau *et al.*, 2007). On the contrary, Wojdylo *et al.* (2016) have notified that AC of three different jujube cultivars decreased with hot air drying, and an increment in the drying temperature increased the reduction of AC in these cultivars. A decrement in AC of hot-air-dried red pepper was reported by Vega-Galvez *et al.* (2009). However, no significant differences between drying temperatures were notified in the same study.

Kinetic parameters of vitamin C

To the best of our knowledge, degradation of vitamin C in whole dried jujube fruits was investigated for the first time. Thermal degradation of vitamin C in whole dried jujube fruits is shown in Figure 3. As seen in Figure 3, thermal

Table 6. The effect of the drying process on TPC and AC of whole jujube fruits.

	TPC	% Loss	AC	% Loss
Fresh	1911.40 ± 47.32 ^a	0	0.214 ± 0.001 ^a	0
50°C	418.59 ± 12.18 ^b	78.10	0.083 ± 0.001 ^b	61.22
60°C	453.71 ± 4.61 ^b	76.26	0.084 ± 0.001 ^b	60.75
70°C	484.03 ± 6.21 ^b	74.68	0.087 ± 0.001 ^b	59.35

*TPC was expressed as mg GAE 100 g⁻¹ DW; AC was expressed as mmol TE g⁻¹ DW. The different letters in the same column are significantly different (p < 0.05). TPC, total phenolic content; AC, antioxidant capacity.

degradation of vitamin C in whole dried jujube fruits followed the first-order kinetic model. Thermal degradation of vitamin C is reported to frequently fit to the first-order reaction model in different dried foods by Demiray *et al.* (2013), Kadakal *et al.* (2017), Orikasa *et al.* (2014), and Kurozawa *et al.* (2014). Kinetic parameters of vitamin C are listed in Table 7. The rate constant of vitamin C thermal degradation increased depending on an increment in the drying temperature. Accordingly, the values of $t_{1/2}$ and D decreased. Likewise, Demiray *et al.* (2013) and Akdaş and Başlar (2015) have reported an increment in the degradation rate constant of vitamin C in tomato and mandarin, respectively, as drying temperatures were raised. In addition, the values of $t_{1/2}$ decreased with an increase in the degradation rate constant. Kadakal *et al.* (2017) have notified an increment in degradation rate constant and decrement in the values of $t_{1/2}$ and D of vitamin C thermal degradation in rosehip nectar during thermal treatment. Also, in another study, vitamin C degradation in hot-air-dried kiwi fruits showed an increment with an increase in the drying temperature (Orikasa *et al.*, 2014). Kurozawa *et al.* (2014) have indicated a rate constant of vitamin C thermal degradation in papaya with an increment in temperature during the drying process. The result of the current study is in good agreement with other reports.

Activation energy reflects the reaction's temperature sensitivity. Higher E_a indicates higher sensitivity to temperature changes. Besides, higher E_a means higher stability to thermal degradation (Bell, 2020; Kadakal *et al.*, 2017). Arrhenius equation, which was used for the calculation of the E_a of vitamin C thermal degradation, is given in Figure 4. The E_a of vitamin C thermal degradation in whole dried jujube fruits was calculated as 80.87 kJ mol⁻¹. This value was higher than 46.248 and 46.99 kJ mol⁻¹ by Akdaş and Başlar (2015) and Demiray *et al.* (2013), respectively, meaning that vitamin C was more stable to thermal degradation, and its thermal degradation reaction was more sensitive to temperature changes in whole dried jujube fruits. Q_{10} value, a criterion reflecting the effect of raising temperature by 10°C on the rate of reaction, is also used as an indicator of the reaction's temperature sensitivity. Higher Q_{10} values denote greater temperature sensitivity (Bell, 2020; Kadakal *et al.*, 2017). In the current study, the value of Q_{10} from 50 to 60°C was found to be slightly higher than from 60 to 70°C. This means that the thermal degradation of vitamin C was more affected by an increment of temperature from 50 to 60°C than from 60°C to 70°C. Kadakal *et al.* (2017) and Demiray *et al.* (2013) have similarly reported that the Q_{10} value of vitamin C thermal

Table 7. First-order kinetic parameters of water-soluble vitamins, TPC, and AC of whole dried jujube fruits.

Compound	Temperature	k (h ⁻¹)	$t_{1/2}$ (h)	D (h)	R ²	E_a (kcal mol ⁻¹)	E_a (kJ mol ⁻¹)	Q_{10} (50–60°C)	Q_{10} (60–70°C)
Vitamin C	50°C	0.0170	40.76	135.47	0.9865	19.33	80.87	2.62	2.21
	60°C	0.0445	15.57	51.75	0.9894				
	70°C	0.0983	7.05	23.43	0.9890				
Thiamine	50°C	0.0066	105.00	348.94	0.9798	16.23	67.90	1.89	2.31
	60°C	0.0125	55.44	184.24	0.9776				
	70°C	0.0289	23.98	79.69	0.9869				
Riboflavin	50°C	0.0162	42.78	142.16	0.9810	13.23	55.37	1.70	1.96
	60°C	0.0275	25.20	83.75	0.9817				
	70°C	0.054	12.83	42.65	0.9918				
Niacin	50°C	0.0034	203.82	677.35	0.9733	18.83	78.78	2.47	2.24
	60°C	0.0084	82.50	274.17	0.9856				
	70°C	0.0188	36.86	122.50	0.9922				
Pyridoxine	50°C	0.0505	13.72	45.60	0.9898	15.63	65.41	1.75	1.72
	60°C	0.0886	7.82	25.99	0.9886				
	70°C	0.1524	4.55	15.11	0.9999				
TPC	50°C	0.0332	20.87	69.37	0.9815	9.33	39.02	1.51	1.54
	60°C	0.0503	13.77	45.78	0.9648				
	70°C	0.0775	8.94	29.72	0.9796				
AC	50°C	0.0194	35.72	118.71	0.9619	10.68	44.68	1.62	1.63
	60°C	0.0314	22.07	73.34	0.9683				
	70°C	0.0512	13.54	44.98	0.9684				

TPC, total phenolic content; AC, antioxidant capacity.

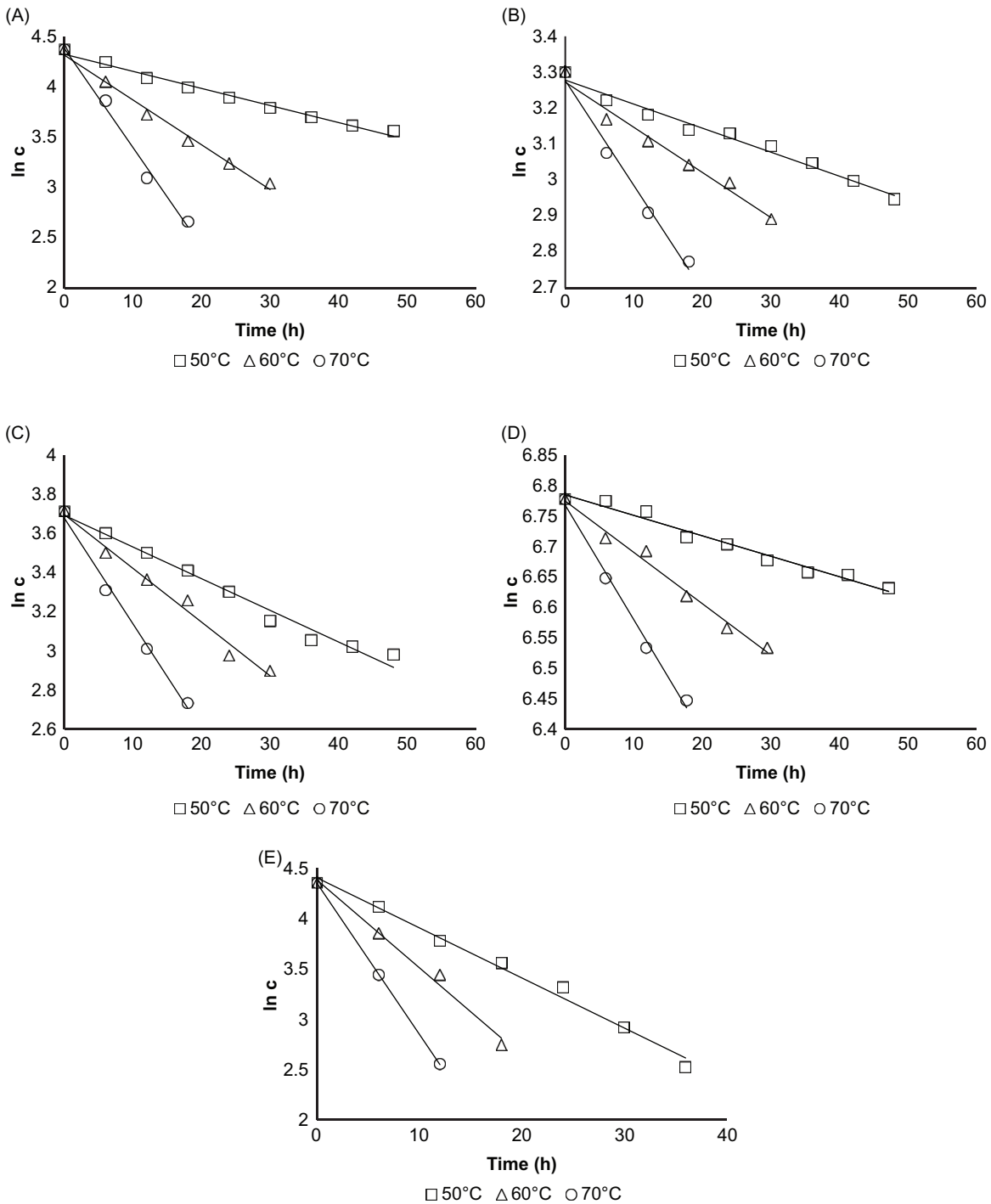


Figure 3. First-order plots of (A) vitamin C, (B) thiamine, (C) riboflavin, (D) niacin and (E) pyridoxine during drying of the whole jujube fruits

degradation decreased with an increment in the process temperature.

Kinetic parameters of B complex vitamins

To the best of our knowledge, no data on B complex vitamin degradations in jujube fruits during hot air-drying

process have been published as yet. Thermal degradation kinetics of B complex vitamins in jujube fruits during hot air-drying process was investigated for the first time in this study. Thermal degradation of B complex vitamins is given in Figure 3. However, no pyridoxine content was determined at the end of the process. Therefore, kinetic modeling of pyridoxine thermal degradation was conducted until the last point where pyridoxine was

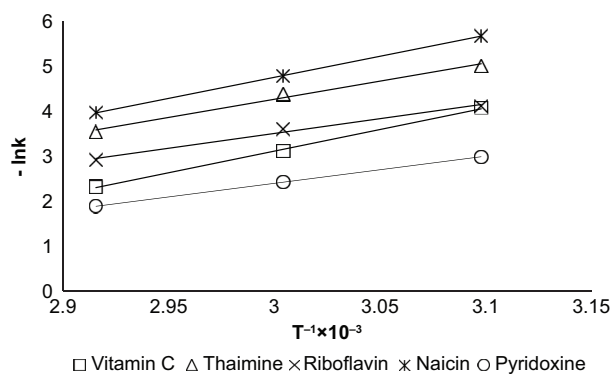


Figure 4. Arrhenius plots of water-soluble vitamins of whole dried jujube fruits.

detected. Thermal degradation of B complex vitamins followed the first-order kinetic model. Likewise, Kadakal *et al.* (2017) have reported that thermal degradation of thiamine and riboflavin in rosehip nectar fitted to the first-order kinetic model during thermal treatment for 30 min. Thermal degradation of niacin in cooked potato for 60 min in the temperature range of 50–120°C was notified to follow the first-order kinetic model by Nisha *et al.* (2009). Nisha *et al.* (2005) and Rekha *et al.* (2004) have reported a first-order kinetic of thermal degradation of riboflavin and thiamin in cooked spinach and red gram splits at a temperature range of 50–120°C for 60 min, respectively. Kinetic parameters of B complex vitamins' thermal degradation are presented in Table 7. In the current study, degradation rate constants of B complex vitamins increased with the increment in drying temperature. Accordingly, degradation rapidly occurred at higher temperatures. In consequence, the values of $t_{1/2}$ and D of B complex vitamins decreased. In the current study, degradation rate constants of thiamine, riboflavin, niacin, and pyridoxine ranged from 0.0066 to 0.0289 h⁻¹, 0.0162 to 0.054 h⁻¹, 0.0034 to 0.0188 h⁻¹, and 0.0505 to 0.1524 h⁻¹, respectively. Kadakal *et al.* (2017), Nisha *et al.* (2009), Nisha *et al.* (2005), and Rekha *et al.* (2004) have also reported an increment in degradation rate constant of B complex vitamins in different foods with an increase in process temperatures.

Figure 4 shows Arrhenius equation of B complex vitamins' thermal degradation. The E_a s of thiamine, riboflavin, niacin, and pyridoxine were found to be 67.90, 55.37, 78.78, and 65.41 kJ mol⁻¹, respectively. Sensitivity of a reaction to temperature change can be explained with the E_a as stated before. Accordingly, niacin was more sensitive to temperature changes but shows the highest stability due to the highest E_a value in comparison to other B complex vitamins in jujube fruits. Nisha *et al.* (2005) have found the E_a of riboflavin thermal degradation in cooked spinach to be 21.72 kJ mol⁻¹. Kadakal *et al.* (2017) have also reported that the E_a s of thiamine

and riboflavin thermal degradation in rosehip were 36.38 and 37.15 kJ mol⁻¹, respectively. Nisha *et al.* (2009) have notified the E_a of niacin in cooked potato cubes to be 16.70 kJ mol⁻¹. The E_a s of thiamine, riboflavin, niacin, and pyridoxine of jujube fruits were found to be higher than those reports. This means that thiamine, riboflavin, niacin, and pyridoxine in jujube fruits were more sensitive to temperature changes; however, they were more stable to thermal degradation when compared to those reports. On the other hand, niacin was the highest affected compound by 10°C temperature increment from 50 to 60°C due to the highest Q_{10} value when compared to Q_{10} values.

Kinetic parameters of TPC and AC

The current study presented the first data on TPC thermal degradation in whole dried jujube fruits. TPC thermal degradation is shown in Figure 5. It was found that TPC thermal degradation followed the first-order kinetic model. Akdaş and Başlar (2015) have similarly reported a first-order reaction of TPC of mandarin during the oven drying process. Sarpong *et al.* (2018) have notified that TPC thermal degradation in banana samples during convective drying was described using the first-order kinetic model. The result of the current study was in good agreement with reports by Akdaş and Başlar (2015) and Sarpong *et al.* (2018). Kinetic parameters of TPC thermal degradation are listed in Table 7. Rate constant of TPC thermal degradation showed an increment as drying temperatures increased. It was obvious that this increment caused a decrement in the values of $t_{1/2}$ and D. Rate constant of TPC thermal degradation ranged from 0.0332 to 0.0775 h⁻¹. Akdaş and Başlar (2015), Sarpong *et al.* (2018), and Kadakal and Duman (2018) have reported an increment in TPC thermal degradation in different foods with an increase in temperature. TPC thermal degradation was slightly affected by 10°C temperature increment. E_a was calculated using the Arrhenius equation as given in Figure 6. The E_a of TPC thermal degradation was calculated as 39.02 kJ mol⁻¹. Sarpong *et al.* (2018) have reported the E_a of convective dried banana at 60, 70, and 80°C as 14.29 kJ mol⁻¹. Likewise, The E_a s of TPC thermal degradation in Starking Delicious, Golden Delicious, and Granny Smith apple cultivars dried at 65, 70, and 75°C were notified as 27.52, 29.84, and 32.48 kJ mol⁻¹, respectively (Ertekin Filiz and Seydim, 2018). Akdaş and Başlar (2015) have reported the E_a as 55.037 kJ mol⁻¹ for oven-dried mandarin at 55, 65, and 75°C. The result of the current study was higher than those reported by Sarpong *et al.* (2018) and Ertekin Filiz and Seydim (2018); however, it was lower than those reported by Akdaş and Başlar (2015). On the other hand, thermal degradation of TPC was not affected by the 10°C temperature increment.

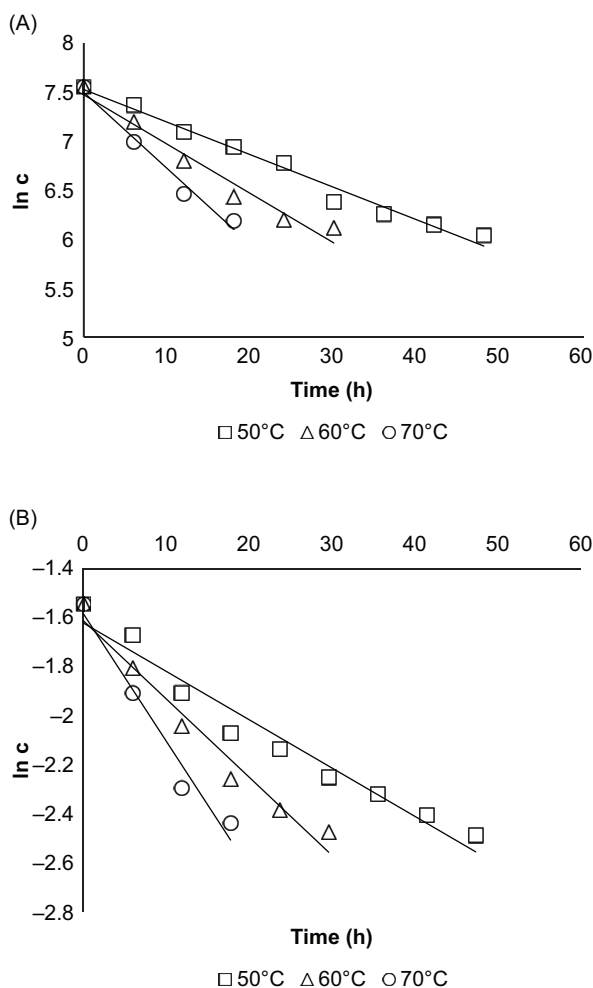


Figure 5. First-order kinetics of total phenolic content (A) and antioxidant capacity (B) of whole dried jujube fruits.

AC thermal degradation could be described using the first-order kinetic model (Başlar *et al.*, 2014; Oancea *et al.*, 2017; Sarpong *et al.*, 2018). In contrast to this, Orikasa *et al.* (2014) and Ertekin Filiz and Seydim (2018) have reported that zero-order kinetic model may also be used to describe AC thermal degradation. To the best of our knowledge, AC thermal degradation in whole dried jujube fruits was investigated for the first time. AC thermal degradation is given in Figure 5. In the current study, AC thermal degradation followed the first-order kinetic model. Oancea *et al.* (2017), Başlar *et al.* (2014), and Sarpong *et al.* (2018) have reported the first-order kinetic of AC in sour cherry extracts, oven-dried pomegranate, and convective dried banana during the thermal process. Kinetic parameters of AC thermal degradation are given in Table 7. Rate constants of AC thermal degradation increased with an increment in the drying temperature as expected. Rate constant of AC thermal degradation was reported to increase with process temperature by Oancea *et al.* (2017), Başlar *et al.* (2014), and Sarpong *et al.* (2018). Accordingly, the values of $t_{1/2}$ and D were reduced. On the

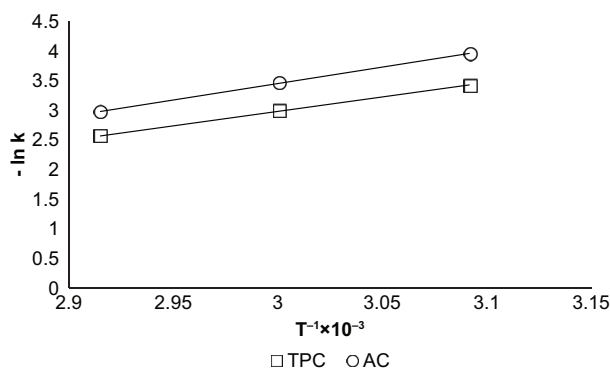


Figure 6. Arrhenius plots of total phenolic content and antioxidant capacity of whole dried jujube fruits.

other hand, a 10°C temperature increment had no significant effect on AC thermal degradation. Figure 6 presents the Arrhenius equation of AC thermal degradation that was used for the calculation of the E_a . The E_a of AC thermal degradation was 44.68 kJ mol⁻¹.

Conclusions

In the current study, drying characteristics and some quality parameters of the health-promising fruit, jujube (*Zizyphus jujuba* Mill.), in Turkey were investigated under different drying conditions.

1. DR of jujube was highly influenced by the drying temperature. The longest drying time was found to be 48 h at 50°C, and the shortest was 18 h at 70°C.
2. The best predicting models of experimental MR were determined as Parabolic model for 60°C and Page model for 50 and 70°C.
3. Effective moisture diffusivity showed an increment with an increase in the drying temperature. The most effective moisture diffusivity was obtained at 70°C.
4. When compared to dried jujube fruits regardless of the drying temperature, water-soluble vitamins, TPC, and AC of fresh jujube fruits were determined to be higher. While the highest loss of water-soluble vitamin occurred at 70°C because of a more rapid enzymatic and nonenzymatic degradation, TPC and AC were not significantly affected by the drying temperature.
5. Vitamin C and B complexes, TPC, and AC thermal degradation were fitted to the first-order kinetic model.
6. Vitamin C and niacin were very susceptible to temperature change. On the contrary, TPC and AC were the lowest sensitive compounds.

7. Vitamin C and B complexes were strongly temperature dependent, while TPC and AC were not significantly affected by increment in temperature.

In further studies, the effect of different drying methods, such as microwave, vacuum, combinations of vacuum–microwave, microwave–hot air, should be investigated for dehydration of jujube fruits. Thus, the most suitable conditions and methods may be optimized by observing the loss of nutritional compounds during the process.

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