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β-carotene and lycopene degradation kinetics of tarhana dough during convective air drying and traditional drying methods

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Abstract

In this study, tarhana doughs were dried with convective air drying at 30, 40 and 50 °C temperatures and 0.5, 1.25 and 2 m/s air velocities, and with traditional drying (sun-drying method). By this way effects of drying air temperature and velocity on degradation kinetics of β-carotene and lycopene during air drying of tarhana samples were investigated and the results compared with traditional drying method. The degradation reaction of β-carotene and lycopene was found to be following the first-order kinetic model. The reaction rate constant values of the β-carotene degradation were determined in the range of 0.0003-0.0025 min^{-1}, and the activation energy values were determined in the range of 6.15-49.05 kJ/mol. The reaction rate constant values of the lycopene degradation were determined in the range of 0.0001-0.0007 min^{-1}, and the activation energy values were determined in the range of 20.5-34.3 kJ/mol. β-carotene and lycopene content of tarhana samples decreased with the increase in drying temperature, and the rate of degradation reactions of these components increased with the increase in temperature and air velocity. As a result, it was determined that β-carotene and lycopene were better preserved at 1.25 m/s air velocity at 30 °C.

Keywords: tarhana; β-carotene; lycopene; kinetics; modeling; convective air drying.

Practical Application: Traditionally sun drying method is used in tarhana production. Quality losses in this method is high and the production is done at uncontrolled conditions. Higher quality tarhana can be produced under controlled temperature, relative humidity and air velocity conditions in industrial hot air drying systems. This work studied the hot air drying of tarhana dough under controlled conditions and the degradation kinetics of β-carotene and lycopene contents of tarhana were investigated.

1 Introduction

Tarhana is a traditional fermented Turkish food produced with wheat flour, yoghurt, red pepper, tomato, onion, salt, mint, and yeast. However, the ingredients vary depending on where it is produced. As a result of kneading the mixed tarhana components, tarhana dough is obtained. Tarhana dough is fermented until it reaches a certain acidity which differes depending on the region of production. After the fermentation process, the properly dried dough is ground, and powdered tarhana is obtained (Hayta et al., 2002; Turkish Standardization Institute, 2004). Tarhana specifically has a low pH (3.8-4.2) and moisture (6-9%) resulting in a naturally safe product with a long shelf life. It also has a high amount of protein, vitamins, and minerals which increase its nutritional importance, especially for infants and children. Other important characteristics of tarhana, including its production and properties, were comprehensively reviewed by some researchers (Dağlıoğlu, 2000; Özdemir & Onur Devres, 1999; Kabak & Dobson, 2011).

Food processing changes the nutritional and sensory quality of foods and drying is an important food process (Vasconcelos et al., 2021). The drying stage of tarhana production is usually done under sun traditionally. Sun-drying is effected by weather conditions and requires a longer time. In this method, tarhana dough is dried in open air under uncontrolled conditions such as drying at ambient temperature, relative humidity and air velocity. For these reasons, some physical, chemical and microbiological deteriorations may occur in tarhana produced by drying under sun. As a result, losses in color and important nutrients such as vitamins and carotenoids and microbiological contamination may occur (Jiang et al., 2023; Altun, 2015).

The drying process is important in terms of the product's physical, chemical, and microbiological properties in tarhana production. Hot air drying is often used for food producing due to its simplicity (Guo et. al. 2023). It is reported in the literature that methods such as hot air drying, vacuum drying, microwave and freeze-drying can be used in tarhana drying process as an alternative to the traditional drying method. In this way, higher quality products can be produced under more economical and more optimized process conditions, in which important drying parameters such as temperature, relative humidity and air velocity are applied in a controlled manner (Hayta et al., 2002; Dağlıoğlu, 2000).

In some studies examined in the literature, it was seen that the effects of industrial tarhana production process conditions

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on important nutrients were examined only in terms of changes in the final product (Hayta et al., 2002; Dağlıoğlu, 2000). In order to improve the food quality and optimize the drying conditions, it is considered important to develop an affective kinetic model that can explain the change in foods during drying (Jiang et al., 2023).

No studies were found on the degradation kinetics of important nutritional elements such as β-carotene and lycopene during tarhana drying process. Therefore, this study aimed to investigate the effects of drying air temperature and velocity on the degradation kinetics of β-Carotene and lycopene in tarhana during air drying and compare the results with traditional drying method. In this way, it is thought that important contributions will be made to the literature and the industrial tarhana production sector.

2 Materials and methods

2.1 Materials

The wheat flour used in tarhana production was supplied from a local business, and red peppers, dried mint, onion, tomato, salt, S. Cerevisiae fresh baker's yeast (Pakmaya, Izmir) and commercial yoghurt produced from set type full-fat cow's milk (Aynes Gıda San. ve Tic. Aş., Denizli, Turkey) were obtained from the local market in Denizli, Turkey.

2.2 Method

Tarhana dough production and fermentation

Tarhana production consists of mixing wheat flour (40%), red pepper (20%), yoghurt (16%), dried onion (12%), tomato (10%), salt (1%), dried mint (0.5%) and fresh yeast (0.5%). The red pepper to be used in the production of tarhana was ground in a blender and kept at -18 °C. Tomatoes and onions were also crushed in a blender and mashed. Wheat flour was added gradually after the purees (red peper, tomato and onion), yoghurt, dried mint, yeast, and salt were mixed in a kneader (Kenwood KMM02, United Kingdom) for 25 minutes. After the kneading process, the tarhana dough was left to fermentation at 30 °C in an oven (WiseCube, Fuzzy Control System, Wisd Laboratory Instruments, Germany). Acidity measurements were made daily during fermentation. 10 g of tarhana dough sample and 50 mL of ethanol (67%) were mixed in a flask. After filtration of the dough-ethanol mix, titration was made with 0.1 N NaOH. Acidity values were calculated by multiplying the amount of sodium hydroxide used in the titration (mL) with the dilution factor of 5 (Şimşek et al., 2017). On the 6th day of fermentation, the acidity reached 21 then the fermentation process was finished (Göncü & Çelik, 2020). The initial moisture content of tarhana dough samples after the end of fermentation processes were measured. As a result of the measurements, the initial moisture conten of tarhana dough samples were determined as 50 ± 2%.

Drying the tarhana dough samples

Tarhana samples were dried in a specifically produced PLC controlled laboratory cabinet dryer. Production and installation of the dryer were performed by Eksis Industrial Drying Systems (Isparta, Turkey). The cooling system connected to perform the drying process at 30 °C. By this way the drying air temperature can be adjusted between 30 °C and 85 °C. Workable air velocity in the device ranges from 0.5-2.0 m/s. The product's weight change (due to moisture loss) during drying can be detected with the load cell located at the bottom of the dryer.

Tarhana dough samples, whose initial moisture content was determined, were placed on perforated wire trays in the form of cylindrical discs obtained with the help of a 1 cm thick and 4 cm diameter stainless steel molds. The drying process of tarhana samples was carried out with dry air at constant relative humidity (12 ± 2%) at 30, 40, and 50 °C, and 0.5, 1.25, and 2 m/s air velocities using the cabinet dryer. The tarhana dough was also dried with the traditional drying method (TM). During the traditional drying method, air temperature, air velocity and relative humidity measurements were taken at every two hours. The average of these values is given in Table 1. The weight change (moisture loss) of the product during drying was measured at regular intervals. The drying processes were continued until the moisture content of the tarhana dough samples reached 8%. The study was carried out in three parallel and two replications. Sample codes and drying conditions are given in Table 1.

β-carotene and lycopene determination

β-carotene and lycopene analyzes were carried out in 2 stages as extraction and identification-calculation. In the analysis, the method determined by Demiray (2009) was taken as a basis.

4 g of dried tarhana samples were taken into centrifuge tubes and mixed with 40 mL of ethanol/hexane (4v/3v) mixture solution containing 1% BHT. The mixture, which was homogenized for 1 minute in the homogenizer (IKA T18), was centrifuged for 15 minutes at 11000xg at 5 °C. The clear ethanol-hexane phase collected at the top of the centrifuge tubes was transferred to amber bottles with a Pasteur pipette. Supernatants transferred to amber bottles were passed through a 0.45 µm membrane filter and injected into the HPLC device (Thermo-fischer, USA) equipped with C18 (ACE) column and Diode Array Dedector (DAD).

The flow conditions of HPLC was 0.45 mL/min at the temperature of 25 °C and the analysis duration was 20 min. Detection wavelength was 445 nm for β-carotene and 470 nm for

Table 1. Drying conditions with sample codes.

Sample Code	Drying Temperature (°C)	Air velocity (m/s)	Relative Humidity (%) (±2)
301	30	0.5	12
302	30	1.25	12
303	30	2.0	12
401	40	0.5	12
402	40	1.25	12
403	40	2.0	12
501	50	0.5	12
502	50	1.25	12
503	50	2.0	12
TM	32	1.08	16

TM: Traditional Drying Method.

lycopene. The mobile phase contained the mixture of acetonitrile, methanol, dichloromethane and hexane (40:20:20:20, v/v/v/v) (Demiray, 2009). The amounts of β-carotene and lycopene were determined according to the standard curves which were constructed with six points (1, 5, 10, 25, 50 and 100 ppm concentrations of standards).

Calculations of β-carotene and lycopene degradation kinetic parameters in tarhana samples

To determine the model equations of the degradation kinetics of β-carotene and lycopene during drying, the graphs were drawn according to the zero degrees kinetic model and the first-degree kinetic model. The model in which the highest coefficient of determination (R^2) was obtained in the graphs was defined as the kinetic model representing the degradation of β-carotene and lycopene.

The formula for the zero-order kinetic model of β-carotene and lycopene degradations is given in Equation 1;

$$C = Co \pm kt \quad (1)$$

Where, C is the amount of component at any time t, C_0, the amount of component at $t=0$, k is the kinetic constant (concentration/time), and t defines the drying time (min).

The formula for the first order kinetic model of β-carotene and lycopene degradations is given in Equation 2;

$$C / Co = exp(-kt) \quad (2)$$

Where, C defines the amount of component at any time t, C_0, is the amount of component at $t=0$, k defines the kinetic constant (min^{-1}), t defines the drying time (min).

The formula used to calculate the half-life period ($t_{1/2}$), which expresses the time required for the β-carotene and lycopene initial concentrations of the tarhana samples to decrease by half during drying, is given in Equation 3;

$$\frac{t_1}{2} = \ln 0.5 / k \quad (3)$$

The activation energy value, which expresses the effect of temperature on the β-carotene and lycopene degradation reaction occurring during the drying was calculated using the Arhenius Equation (Equation 4):

$$k = k_0 \, e^{E_a / RT} \quad (4)$$

In these equations; Ea (kj/mol) is the activation energy, k (min^{-1}) is the reaction rate constant, k_0 (min^{-1}) is the exponential constant, R (kj/mol.K) is the gas constant, T (°K) is the temperature.

The Q_{10} value showing the effect of temperature change was calculated by Equation 5;

$$Q_{10} = (k_2 / k_1)^{10/(T_2 - T_1)} \quad (5)$$

Where, k_1 and k_2 represent reaction rate constants at temperatures T_1 and T_2, respectively (Demiray, 2015).

Statistical analysis

Two replicates were taken for each tarhana drying experiments. β-carotene and lycopene analysis were made in three parallels. While calculating the kinetic parameters, the average of the β-carotene and lycopene analysis results of the samples obtained from the repeated drying trials was used. Means and standard deviations were calculated with the software SPSS 16.0.

3 Results and discussion

3.1 β-Carotene and lycopene degradiation kinetics in tarhana samples

To determine the degree of of β-carotene and lycopene degradation reactions during the drying process compatibility of tarhana samples with the zero and first order kinetic models were tested. Correlation coefficients (R^2) obtained from time-dependent graphs of β-carotene and lycopene concentrations for the zero-order kinetic model were in the range of 0.70-0.96 for the β-carotene degradation reaction and 0.74-0.89 for the lycopene degradation reaction. However, the R^2 values obtained from natural logarithm of β-carotene and lycopene concentrations versus time graphs for testing the first-order kinetic model were ranged between 0.92 and 0.99 (the graphs are given in Figure 1) and 0.88 and 0.97 (the graphs are given in Figure 2), respectively. Therefore, it was concluded that experimental data of the β-carotene and lycopene degradation reactions fits the first-order kinetic model. It was also determined that the increase in drying temperature for all different air velocity conditions caused a decrease in the β-carotene and lycopene content of tarhana samples. Similarly, some researchers reported that the amount of lycopene decreased with the increase in drying temperature (Santos-Sanchez et al., 2012). In another study, researchers applied heat treatment to tomato pulp at 50, 60, 70, 80, and 90 °C for 20, 40, 60, 80, and 100 minutes. And they found that the lycopene degradation reaction was suitable for the first-order kinetic model under these conditions (Goula et al., 2006).

To the best of our knowledge, this study will be the first in literature that is examinig the β-Carotene and lycopene degradations during the drying process of tarhana doughs. However, there are some other studies examined the effects of drying conditions on β-carotene and lycopene degradations during the drying of other foods (Santos-Sanchez et al., 2012; Goula et al., 2006; Demiray & Tülek, 2016). It is also revealed by other researchers that there are losses in the amount of some phenolic substances such as β-carotene and lycopene in the drying process. Similarly, in a study examining the effects of drying methods on the total amount of phenolic substances in tarhana samples, it was reported that the changes in the amount of phenolic substances resulting from changes in drying conditions could be attributed to the dependency of the stabilities of phenolic compounds to the drying conditions (Değirmencioğlu et al., 2016).

The kinetic data (k value, Q_{10} value, E_a value, and half-life value) related to the β-carotene and lycopene degradation reactions

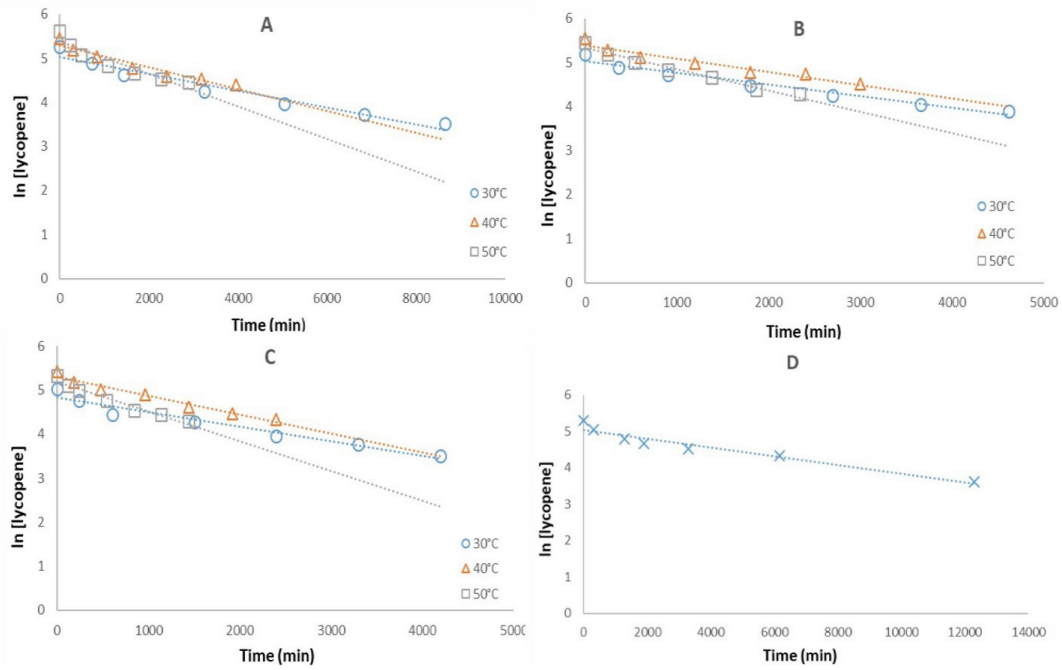

Figure 1. β-carotene degradation kinetics graphs of tarhana samples dried at 30, 40 ve 50 °C; A) 0.5 m/s air velocity, B) 1.25 m/s air velocity, C) 2 m/s air velocity, D) Drying with the traditional method.

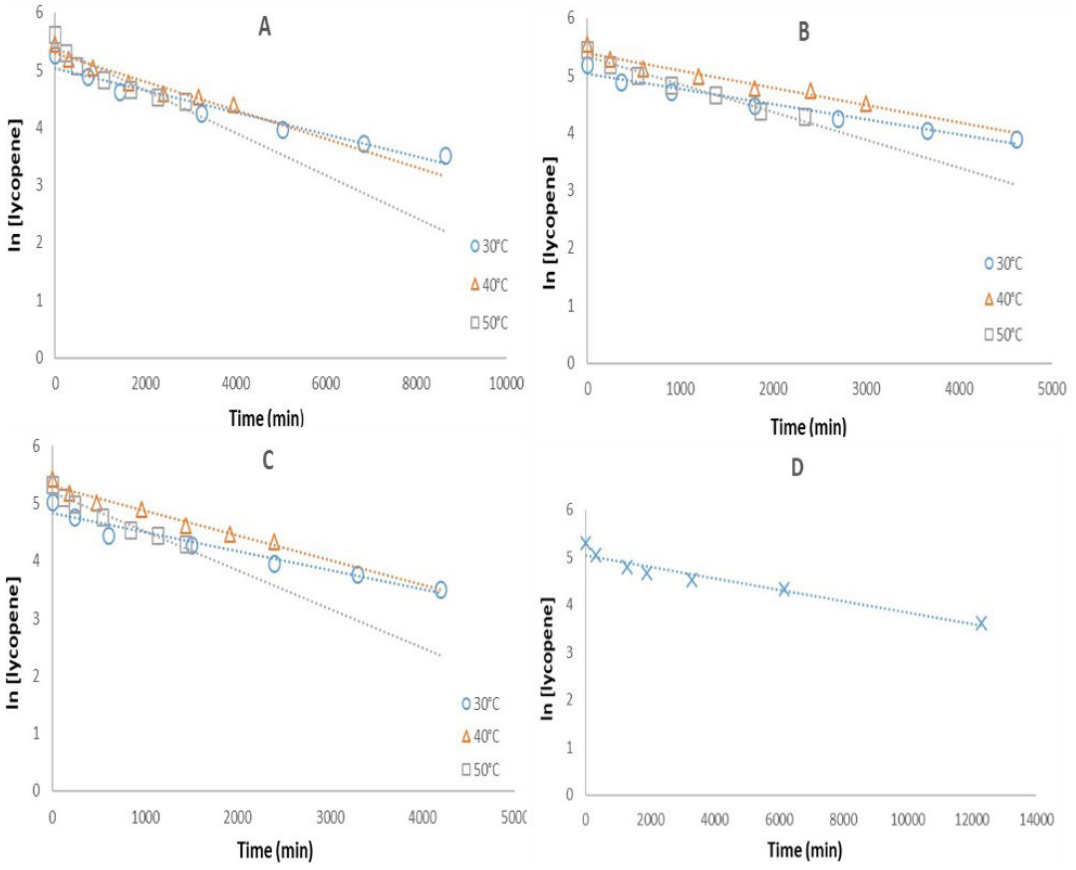

Figure 2. Lycopene degradation kinetics graphs of tarhana samples dried at 30, 40 ve 50 °C; A) 0.5 m/s air velocity, B) 1.25 m/s air velocity, C) 2 m/s air velocity, D) traditional method.

during the drying of tarhana samples under different temperature and air velocity are given in Tables 2 and 3, respectively.

The rate constants of the β-carotene degradation reaction in the drying process of tarhana dough were changed between 0.0003 min^{-1} and 0.0014 min^{-1}. Drying temperature and air velocity affected the rate constant significantly. The rate constants of the β-carotene degradation reaction increased with the increase in the drying temperature and air velocity. The lowest k value was determined for tarhana samples dried at 30 °C at 0.5 m/s air velocity. This value is the same as the value obtained by the traditional drying method. However, the half-life of the β-carotene degradation reaction tended to decrease with increasing the temperature and air velocity parameters applied in the drying process. Additionally, the activation energy value of the β-carotene degradation reaction decreased with the increase in drying air velocity.

When the Q_{10} values expressing the effect of each 10 °C change in the drying temperature on the changing reactions of components are examined, it was seen that increasing the drying temperature from 30 °C to 40 °C (Q_{10} = 2.00) affected the β-carotene degradation more than increasing the drying temperature from 40 °C to 50 °C (Q_{10} = 1.67) for the tarhana dough samples dried at 0.5 m/s air velocity. Contrary to this, increasing the drying temperature from 40 °C to 50 °C was more effective on the β-carotene degradation reaction for 1.25 and 2 m/s air velocities. In this study, the Q_{10} values obtained for the β-carotene degradation reaction for the tarhana drying process were in the range of 1.14 to 3.57. In the study of Demiray & Tülek (2016); they were determined the similar Q_{10} values (1.4-1.5) for β-carotene degradation reaction in tarhana. In both studies, it was observed that the Q_{10} value was lower at at higher temperatures.

Lycopene degradation reaction rate constants for the drying process of tarhana dough were in the 0.0001-0.0007 min^{-1} range. It was determined that the lycopene degradation reaction rate constants increased with increasing drying temperature and air velocity. The lowest k value for lycopene degradation reaction was determined for the tarhana samples dried with the traditional drying method. However, during the drying process of tarhana dough, the activation energy value of the lycopene degradation reaction decreased with the increase in air velocity. In addition, it was determined that the half-life of the lycopene degradation reaction decreased with increase in temperature and air velocity. When the Q_{10} values obtained for lycopene degradation reactions are examined, for all air velocity conditions, it was found that increasing the drying temperature from 40 °C to 50 °C was more effective on the degradation reactions.

Physical, chemical and enzymatic changes during processing may affect the structure of sensitive components of foods (Vasconcelos et al., 2021). Drying processes are carried out at different temperatures and times depending on the food's

Table 2. Kinetic data of β-carotene degradation for tarhana samples.

Sample Code	Drying Temperature (°C)	Air Velocity (m/s)	k (min^{-1})	$t_{1/2}$ (min)	Q_{10} (30-40 °C)	Q_{10} (40-50 °C)	E_a (kj/mol)
301	30	0.5	0.0003	2310			
401	30	1.25	0.0006	1155	2.00	1.67	49.05
501	30	2.0	0.0010	693			
302	40	0.5	0.0007	990			
402	40	1.25	0.0008	866	1.14	1.75	28.00
502	40	2.0	0.0014	495			
303	50	0.5	0.0007	990			
403	50	1.25	0.0007	990	2.00	3.57	6.15
503	50	2.0	0.0025	277			
TM	32	1.08	0.0003	2310	-	-	-

TM: Traditional Drying Method.

Table 3. Kinetic data of Lycopene degradation for tarhana samples.

Sample Code	Drying Temperature (°C)	Air Velocity (m/s)	k (min^{-1})	$t_{1/2}$ (min)	Q_{10} (30-40 °C)	Q_{10} (40-50 °C)	E_a (kj/mol)
301	30	0.5	0.0002	3465			
401	30	1.25	0.0002	3465	1.00	2.00	27.89
501	30	2.0	0.0004	1732			
302	40	0.5	0.0003	2310			
402	40	1.25	0.0003	2310	1.00	1.66	20.50
502	40	2.0	0.0005	1386			
303	50	0.5	0.0003	2310			
403	50	1.25	0.0004	1732	1.33	1.75	34.30
503	50	2.0	0.0007	990			
TM	32	1.08	0.0001	6930	-	-	-

TM: Traditional Drying Method.

physical structure, chemical composition and moisture content. The temperature-time combinations applied during drying affect vitamins, carotenoids and phenolic compounds, which are important nutrients in food. High temperatures and long process times can cause significant damage to these important components. Enzyme activities such as polyphenol oxidase and thermal degradation of sensitive components are important problems encountered in drying processes (Tumer & Tulek, 2022; Wojdylo et al., 2014; Mrkic et al., 2006).

The loss of bioactive components in foods might be due to oxidative or non-oxidative changes (Tumer & Tulek, 2022). During drying, the oxygen in the environment can also cause oxidative changes in these important bioactive components, which are sensitive to oxidation. Since changes in air velocity in the drying environment also affect the oxygen movement, it is important in oxidation and degradation processes (Mrkic et al., 2006). For all these reasons, this study which was carried out to determine the effects of temperature and air velocity in the drying processes of tarhana, which has important bioactive components for human health, will make important contributions to both tarhana producers and literature.

However, the primary limitation in generalizing these results is the lack of similar kinetic studies to which these results can be compared. As we mentioned in the previous paragraphs, to the best of our knowledge, this study will be the first in the literature to examine the degradation of β-Carotene and lycopene during drying of tarhana dough. For this reason, it is important to contribute to the literature by making researches on lycopene and β-carotene change during tarhana drying process. Besides this, the changes in other costituents (e.g. aroma compouns, B group vitamins and etc.) and optimization of industrial tarhna drying process can be examined in future studies.

4 Conclusion

The study investigated the effects of different temperatures and air velocities on the β-Carotene content, and lycopene content of tarhana samples during drying. The β-Carotene and lycopene content of tarhana samples decreased with increasing drying temperature. When the β-Carotene and lycopene degrediaton kinetic data of the tarhana samples were examined, it was determined that the lowest k values were obtained from the tarhana produced by the traditional drying method. For the β-Carotene degrediaton reaction, the closest reaction rate constant values to the conventional method were obtained in the samples dried at 30 °C at 0.5 m/s air velocity. The lycopene degrediaton reaction rate constant values obtained were similar for the tarhana samples dried at 30 and 40 °C and traditional method.

As seen in this study, hot air drying was successfully applied in drying of tarhana with minimal β-carotene and lycopene loss. However, as can be seen in the literature, its use in the tarhana drying processes is very limited. In this regard, the application of hot air drying and other industrial drying technologies, which can preserve the quality features of tarhana, can contribute to the development of production process of traditional food product tarhana.

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