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Research Paper / Araştırma Makalesi

Kinetics of Antioxidant Activity and Color Degradation in Tomatoes during Hot Air Drying

Adeviye Rana Gokmen[1], Engin Demiray[1] ✉, Yahya Tulek[1], Yusuf Yilmaz[2]

[1]Pamukkale University, Faculty of Engineering, Department of Food Engineering, Denizli, Turkey
[2]Burdur Mehmet Akif Ersoy University, Faculty of Engineering and Architecture, Department of Food Engineering, Istiklal Campus, 15200, Burdur, Turkey

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✉ *Corresponding author (Yazışmalardan Sorumlu Yazar): edemiray@pau.edu.tr (E. Demiray)*
+90 258 296 3090 +90 258 296 3262

ABSTRACT

The antioxidant activity (AA) and color degradation were monitored in tomato quarters (*Rio Grande*) during hot air drying in a cabinet drier at five temperatures (60, 70, 80, 90 and 100°C) at an airflow rate of 0.2 m/s and 20% relative humidity. AA values of fresh tomatoes determined by total phenolic content (TPC), FRAP and DPPH assays were 85.3 mg GAE, 26.2 µmol TE and 31.3 µmol TE/100g dm, respectively. Increasing drying temperature resulted in a reduction in Hunter Lab and a/b color values of tomatoes as well as their AA values. During hot air drying, the degradation of AA and color values of tomatoes followed a first-order reaction. Activation energy values for AA degradation determined by TPC, FRAP and DPPH assays were 24.36, 22.91 and 23.67 kJ/mol, respectively. High correlations were found among the TPC, DPPH and FRAP values and lycopene and β-carotene contents of tomatoes during hot air drying. Degradation kinetic data revealed that color values and tomatoes AA are susceptible to drying temperature.

Keywords: Tomato, Hot air drying, Lycopene, β-Carotene, Antioxidant activity

Sıcak Hava ile Kurutma Sırasında Domateslerde Antioksidan Aktivite ve Renk Bozulmasının Kinetiği

ÖZ

Antioksidan aktivite (AA) ve renk bozulması, 0.2 m s^{-1} hava akış hızında, %20 bağıl nemde ve beş sıcaklıkta (60, 70, 80, 90 ve 100°C) bir kabin tipi kurutucuda çeyrek dilimler şeklinde kesilmiş domateslerde sıcak havayla kurutma sırasında incelenmiştir. Toplam fenolik madde miktarı (TPC), FRAP ve DPPH deneyleri ile belirlenen taze domateslerin AA değerleri sırasıyla 85.3 mg GAE, 26.2 µmol TE ve 31.3 µmol TE/100g yaş madde olarak hesaplanmıştır. Artan kurutma sıcaklığı ile domateslerin Hunter Lab renk değerlerinde, a/b oranında ve AA değerlerinde azalma meydana gelmiştir. Sıcak hava ile kurutma sırasında, domateslerin AA ve renk değerlerinin bozunması birinci dereceden reaksiyon modeline uyumlu olduğu belirlenmiştir. TPC, FRAP ve DPPH analizleri ile belirlenen AA bozunması için aktivasyon enerjisi değerleri sırasıyla 24.36, 22.91 ve 23.67 kJ/mol olarak hesaplanmıştır. Sıcak hava ile kurutma sırasında domateslerin TPC, DPPH ve FRAP değerleri ile likopen ve β-karoten içerikleri arasında yüksek korelasyonlar bulunmuştur. Bozunma kinetik verileri, renk değerlerinin ve domates AA'nın kuruma sıcaklığına duyarlı olduğunu ortaya çıkarmıştır.

Anahtar Kelimeler: Domates, Sıcak hava ile kurutma, Likopen, β-Karoten, Antioksidan aktivite

INTRODUCTION

Tomato production (about 165 million tons/year) is the eighth agricultural product worldwide among the commodities with the greatest value, and the leading tomato growing countries include China, the United States, India, Turkey, and Egypt [1]. Tomatoes (*Lycopersicum esculentum*) contain a number of health functional constituents such as red-colored carotenoid lycopene and other flavonoids, phenolic acids (especially chlorogenic acids) and ascorbic acid in addition to basic nutritional compounds [2, 3]. High levels of antioxidants present in tomatoes and tomato products help prevent oxidative damage that is hazardous for humans [4]. Major carotenoids present in tomato fruits include lycopene, responsible for the red color in tomatoes, and β-carotene (7% of the total carotenoid content) [5]. β-Carotene has a provitamin A activity, and lycopene acts as an antioxidant, anticarcinogenic and antimutagenic agent [6]. Lycopene concentration increases with the maturity of the tomato berries, causing the development of red color [7].

Drying provides one of the oldest and most effective means of preserving foods from spoilage. Once dried, many foods can be stored successfully for years without refrigeration, if appropriately packaged [8]. Due to its simplicity, hot air drying is frequently used to dry foods [9]. Drying kinetics of foods is generally used to describe the combined macroscopic and microscopic mechanisms of heat and mass transfer during drying, and it is influenced by several factors such as drying conditions, type of dryers and characteristics of materials to be dried. Since on-line measurement of temperature and moisture is difficult and time-consuming for drying, the drying kinetics models are essential for equipment design, process optimization and product quality improvement [10].

Tomatoes are mostly dried at high temperatures in the presence of oxygen, and dried tomato products (e.g. tomato halves, slices, quarters and powders) show the highest sensitivity to oxidative damage [11]. Drying conditions such as high temperature, long duration of exposure and the presence of oxygen may increase the degradation of total phenolics, flavonoids [12] and lycopene [13] during drying, and reduce antioxidant activity of tomatoes. Degradation of major carotenoids in tomatoes by thermal processing and non-enzymatic Maillard reaction during drying are mostly responsible for color changes of tomatoes [14]. Drying tomato quarters of three cultivars, commercially grown in New Zealand, at 42°C in a forced-air drier for 48h, Kerkhofs et al. [15] reported a decrease in total phenolic content between 8 and 33% while extractable lycopene content of tomatoes increased considerably. The authors suggested that bound lycopene in the tissue could be released at lower drying temperatures but lycopene degrades at high temperatures [14, 16, 17]. Drying process may reduce total phenolic, flavonoid and ascorbic acid contents and antioxidant activity of tomatoes [18].

Most of the studies in the literature are focused on the individual and/or combined effect of drying conditions such as pre-treatment, temperature and drying method on antioxidant activity and color values of tomatoes. These parameters are usually determined at the beginning and the end of a drying process. Drying temperature and time are two major factors influencing the degradation kinetics of tomato constituents. No study is available on the degradation kinetics of antioxidant activity and color of tomatoes during drying. Therefore, this present study was conducted to determine the degradation kinetics of antioxidant activity and color in tomato quarters during hot air drying at temperatures varying from 60 to 100°C.

MATERIALS and METHODS

Materials

Fresh tomatoes of *Rio Grande* variety with a diameter about 7 cm were obtained from a local farmer in a town of Acipayam, Denizli (Tukey) in mid-August and onwards. Healthy tomatoes, homogeneous for intense red-color and blemish- and bruise-free, were visually selected. Tomatoes in polyethylene packages were kept refrigerated until drying. The initial moisture content of samples (94.5%) was determined by the AOAC method [19]. All chemicals were of analytical grade unless stated. Solvents used in antioxidant assays were of HPLC grade. Gallic acid, 2,2 -diphenyl-1-picrylhydrazyl (DPPH), 2,4,6-tripyridyl-s-triazine (TPTZ) were purchased from Fluka (Switzerland) while iron(III) chloride hexahydrate (FeCl3.6H2O), sodium carbonate were from Riedel-de Haen (Germany). Folin-Ciocalteu reagent was purchased from Merck (Germany). Trolox® (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) and (+) catechin were obtained from Sigma (St. Louis, MO, USA).

Methods

Drying Procedure

Tomato quarters were dried in a cabinet drier (70×55×100 cm, W×D×H) manufactured by the Yücebaş Makine Ltd. Inc. (İzmir, Turkey). The cabinet had four removable stainless steel gauze trays (40×60 cm). For each drying experiment at 60, 70, 80, 90 and 100°C, 5 kg of tomatoes in uniform ripeness, color and size were used. The temperature and relative humidity of the dryer were stabilized for an hour. At all temperatures, airflow rate and relative humidity were 0.2 m/s and 20%, respectively. Relative humidity in the drying chamber was measured by a relative humidity sensor (accuracy ±2%) (Elimko, E-RHT-10, Istanbul, Turkey). The airflow rate in the drying chamber was measured with a Tri-Sense hot wire probe anemometer (accuracy ±2%) (Tri-Sense, 37000-90, Cole-Parmer Instrument Co., Illinois, USA). Air flowed vertical to the drying surfaces of samples. And hot air used in the drying process was circulated in the cabinet. Drying air used was automatically exhausted when the relative humidity was over 20%. Tomatoes were cut into quarters longitudinally, and approximately 200-250 g of quarters

was placed on each tray as a single layer with a thickness of 2.2±0.2 cm. For each temperature, one kilogram of tomatoes was used to monitor the time-dependent weight loss. The rest was either used to determine the initial dry matter (dm) content of tomato quarters or wrapped in aluminum foil in polyethylene packages that are kept at -20°C for further analyses. Tomato quarters were dried until their water content reached approximately 15 g/100 g (wet basis). Three independent measurements were taken for each experiment.

Degradation Kinetics

The relationship between the reaction rate and temperature was determined by the Eq. 1, the Arrhenius equation [20].

$$k = k_0 e^{-E_a/RT} \quad (1)$$

where k is the reaction rate constant (h^{-1}), k_0 is the pre-exponential constant (h^{-1}), Ea is the activation energy (kJ/mol), R is the universal gas constant (kJ/mol.K) and T is the absolute temperature (K).

Temperature coefficient (Q_{10}) is the criterion indicating the effect of raising the temperature by 10°C on the rate of reaction, and it was calculated by the Eq. 2 [21].

$$Q_{10} = (k_2/k_1)^{10/(T_2-T_1)} \quad (2)$$

where k_1 and k_2 are reaction rate constants at temperatures T_1 and T_2, respectively (h^{-1}).

The half time ($t_{1/2}$) is the time required for the antioxidant activity or color values of dried tomatoes to decay down to 50% of its initial concentration, and it was calculated by the Eq. 3 [17].

$$t_{1/2} = -\ln(0.5) \times k^{-1} \quad (3)$$

where k is the reaction rate constant.

The order of degradation reactions was calculated by the Eq. 4. By replacing AA with respective color values (CV), this equation was also used to determine the reaction order for color degradation during drying.

$$\ln AA = \ln AA_0 - k.t \quad (4)$$

where AA is the antioxidant activity (μmol TE or mg GAE /g dm) at time *t*, AA_0 is the initial antioxidant activity of lipophilic extracts, and *k* is the reaction rate constant.

Color Measurements

The Hunterlab MiniScan XE colorimeter (Hunter Associates Laboratory, USA) was used to monitor the changes in Hunter color values of tomatoes during drying. Color readings were taken at three different points of tomatoes for better representation of average color values, and expressed in Hunter Color Scale (Lab). The red–yellow ratio (a/b) was reported to indicate the redness of tomatoes [22].

Extraction of Lipophilic Constituents

For the extraction of lipophilic constituents from tomatoes, the method suggested by Lin and Chen [23] was used with some modifications. Fresh or dried tomato samples were mixed with ethanol-hexane solution (4:3, v/v) containing 1% BHT (w/v) at a ratio of 1:10 (w/v). The mixture was homogenized by a homogenizer (Miccra D-8, ART Prozess- & Labortechnik GmbH & Co. KG, Müllheim, Germany), and then transferred into a polypropylene centrifuge tube. After centrifuging (Universal 30RF, Hettich Zentrifugen, Tuttlingen, Germany) at 11,000*g* at 5°C for 15 min, supernatants were transferred into amber bottles by using glass Pasteur pipettes. The use of extract in ethanol-hexane mixture created cloudiness in the working solutions of antioxidant activity assays. Therefore, 0.5 mL of the extract was fully evaporated with nitrogen flash, and then the residue was redissolved in 0.2 mL of the appropriate working solutions in the antioxidant activity assays. The samples were vortexed briefly and sonicated for 5 min to dissolve the residue completely.

Antioxidant Activity Assays

Total phenol contents (TPC) of tomato extracts were determined by the Folin-Ciocalteu method [24]. Gallic acid was used as a standard. A UV-Vis spectrophotometer with 8 cells (T80 Model, PG Instruments, England) was used to determine the total phenol contents of extracts in terms of gallic acid equivalents (GAE). The FRAP and DPPH assay procedures described by Thaipong et al. [25] were used to determine antioxidant activities of tomato extracts. For FRAP assay, absorbance of ferrous tripyridyltriazine complex was measured at 593 nm with a spectrophotometer. For DPPH assay, the absorbance readings of extracts were taken at 515 nm wavelength. The linear standard curves used in both FRAP and DPPH assays were between 10 and 50 μM Trolox®. Antioxidant activity of tomato extracts in FRAP and DPPH assays were expressed in μmol TE/g dry matter.

Statistical Analysis

Drying experiments were performed in triplicates and the measurements were performed in duplicates. Data were analyzed using the Statistical Analysis System software [26]. PROC CORR was used to determine Pearson's correlation coefficients (R) among the parameters studied. Lycopene and β-carotene contents of processed tomatoes reported in a study by Demiray et al. [17] were used to determine correlation coefficients among total phenolic content, antioxidant activity, and lycopene and β-carotene contents of tomatoes during drying.

RESULTS and DISCUSSION

Degradation Kinetics of Total Phenolic Content

Drying is used to preserve foods, and food components like phenolics may degrade during this process. With drying, the time taken to reduce the moisture content of tomatoes from the initial value 95.2±0.2% (w.b.) to a final value 10±0.2% (w.b.) was 20, 14, 12, 10 and 8 h at 60, 70, 80, 90 and 100°C, respectively. In this study, degradation in TPC during drying of tomatoes followed a first-order reaction. Plot of natural logarithm of TPC against time for each temperature is shown in Fig. 1A. Equations used to explain the time-dependency of antioxidant activity are indicated in Table 1, and coefficients of determinations (R^2) were higher than 0.95, confirming that the reaction of antioxidant activity degradation is a first order.

Table 1. Linear equations for the antioxidant activity and color degradation of tomatoes during hot air drying at five different temperatures (y, natural logarithm of either antioxidant activity or color values; x, the drying time in h; R^2, the coefficients of determination, are shown in parenthesis).

Parameter	Temperature (°C)				
	60	70	80	90	100
TPC	y = -0.1689x + 7.4360 (0.9984)	y = -0.2331x + 7.3234 (0.9974)	y = -0.3262x + 7.4570 (0.9973)	y = -0.3556x + 7.4048 (0.9994)	y = -0.4418x + 7.3270 (0.9989)
FRAP	y = -0.1863x + 6.1276 (0.9972)	y = -0.2359x + 6.0987 (0.9910)	y = -0.2844x + 6.0636 (0.9955)	y = -0.3426x + 6.1275 (0.9922)	y = -0.4696x + 6.2292 (0.9943)
DPPH	y = -0.1632x + 5.6361 (0.9963)	y = -0.2549x + 5.7112 (0.9977)	y = -0.2900x + 5.6914 (0.9971)	y = -0.3480x + 5.7279 (0.9966)	y = -0.4368x + 5.7070 (0.9918)
Hunter color L	y = -0.0067x + 3.4092 (0.9929)	y = -0.0137x + 3.2830 (0.9893)	y = -0.0186x + 3.3542 (0.9981)	y = -0.0287x + 3.3462 (0.9972)	y = -0.0432x + 3.3355 (0.9951)
Hunter color a	y = -0.0111x + 3.2509 (0.8980)	y = -0.0230x + 3.2901 (0.9943)	y = -0.0322x + 3.2898 (0.9740)	y = -0.0502x + 3.3247 (0.9699)	y = -0.0699x + 3.2522 (0.9898)
Hunter color b	y = -0.0037x + 2.5814 (0.9822)	y = -0.0071x + 2.5755 (0.9233)	y = -0.0118x + 2.5560 (0.9851)	y = 0.0123x + 2.5623 (0.9919)	y = -0.0126x + 2.5576 (0.8992)
a/b	y = -0.0074x + 0.6694 (0.8118)	y = -0.0107x + 0.7275 (0.9591)	y = -0.0205x + 0.7336 (0.9386)	y = -0.0431x + 0.7489 (0.9667)	y = -0.0467x + 0.7209 (0.7612)

Calculated rate constants (k) and other kinetic parameters of antioxidant activity loss in tomatoes during various drying conditions are given in Table 2. Reaction rate constants for the loss of TPC in tomato quarters were in the range of 0.17-0.44 h^{-1} and significantly affected by drying temperature. Temperature dependence of reaction rate constants followed the Arrhenius relationship.

Results of this present study were in good agreement with the data reported in the literature. Indeed, a first order kinetic model was suggested for the thermal degradation of lycopene in tomatoes paste [21] and in model systems [27]. Activation energy for TPC was 24.36 kJ/mol. The effect of increasing temperature from 60 to 70ºC was similar to temperature increase from 70 to 80°C, which is reflected by similar Q_{10} values for the total phenolic contents of tomatoes (Table 2). Half-life times for TPC degradation in Table 2 support that at elevated drying temperatures TPC loss in tomatoes becomes faster. Results indicated that the drying temperature of 70°C is more suitable to minimize the degradation of TPC in tomato quarters during hot air drying even though the drying takes place longer. Studying eight different dried tomato (*Lycopersicum esculentum*) samples (preserved in oil) marketed in Brazil, de Abreu et al. [28] reported that total phenolic contents of hydrophilic extracts of processed tomatoes ranged from about 338 to 836 mg GAE/100 g dm. In a recent study by Aktürk Gümüşay et al. [29], TPC of fresh tomatoes reduced from 792 mg to 314, 346, 356 and 654 mg GAE/100 g dm for sun-dried, oven-dried, vacuum oven-dried and freeze-dried tomatoes, respectively. They reported that oxidative enzymes like polyphenoloxidase and peroxidase could be activated during drying and lead to a loss in TPC values of tomatoes. Studying the degradation kinetics of TPC, antioxidant capacity and vitamin C content of mandarin slices during drying (oven and vacuum) at 55, 65 and 75°C, Akdas and Baslar [30] reported that degradation kinetics for TPC were of a first-order model and activation energy values for the TPC degradation of oven and vacuum dried mandarin slices were about 53 and 55 kJ/mol, respectively.

Tomatoes contain a number of flavonoids and phenolic acids that can contribute to a healthy diet, and besides flavonoids, stilbenoids and other phenolics, tomato is the most important source of lycopene, a red-colored carotenoid associated with several health benefits [2]. Flavonoids are regarded as potentially useful compounds, with implications for inflammation, cardiovascular diseases and cancer [31]. Chlorogenic acids and related compounds are the main phenolic compounds besides flavonoids in tomatoes, which may also be responsible for an astringent taste [32]. Food processing conditions may result in a reduction in total phenolic contents and antioxidant activity of tomatoes [33]. In a study by Toor and Savage [18], total phenolic content of three tomato cultivars (Excell, Tradiro, and Flavourine) reduced from 404 to 300 mg GAE/100 g dm at the end of a drying process at 42°C for 18h in a forced-air drier.

Degradation Kinetics of Ferric Reducing Antioxidant Power

The degradation rate of FRAP values in tomato quarters increased with temperature (Table 2). In this present study, when tested in the FRAP assay, the antioxidant

activity of tomatoes dried at 60ºC changed from 305.24 to 58.02 mg/100 g dm at the end of drying. But at 100ºC, it dropped to 12.96 mg. The kinetics of degradation of antioxidant activity with the FRAP assay followed a first-order reaction like TPC. The reaction constants of AA in dried tomatoes were determined by plotting the natural logarithm of AA (µmol TE / g dm) against time for each temperature (Fig. 1B). Depending on drying temperature, AA degradation rate increased. Half life time was calculated as 3.72 h at 60ºC, which dropped to 1.48 h at 100ºC. Activation energy was 22.91 kJ/mol. When temperature increased from 90 to 100ºC, the degradation rate of AA in tomatoes was affected more than other temperatures ranges (i.e. Q_{10} value was the highest for the temperature increase from 90 to 100°C). Studying the antioxidant capacity of several tomato varieties, Martinez-Valverde et al. [34] reported that the antioxidant activity of tomato extracts is mostly dependent on the tomato variety and the assay method used. The authors stated that lycopene and ferulic and caffeic acids are distinctive compounds that are highly related to the antioxidant capacity of tomatoes.

Table 2. Reaction rate constants and other kinetic parameters[a] for antioxidant activity loss in tomatoes during drying at five different temperatures

Antioxidant Activity Method	Temperature (ºC)	Q_{10} Value	k (h^{-1})	$t_{1/2}$ (h)	E_a (kJ/mol)
TPC	60		0.1689	4.10	24.36
	70	1.38	0.2331	2.97	
	80	1.40	0.3262	2.12	
	90	1.09	0.3556	1.95	
	100	1.24	0.4418	1.57	
FRAP	60		0.1863	3.72	22.91
	70	1.27	0.2359	2.94	
	80	1.21	0.2844	2.44	
	90	1.20	0.3426	2.02	
	100	1.37	0.4696	1.48	
DPPH	60		0.1632	4.25	23.67
	70	1.56	0.2549	2.72	
	80	1.14	0.2900	2.39	
	90	1.20	0.3480	1.99	
	100	1.26	0.4368	1.59	

[a]: Q_{10}, k, $t_{1/2}$ and E_a: temperature coefficient, reaction rate constant, reaction half life time and activation energy, respectively.

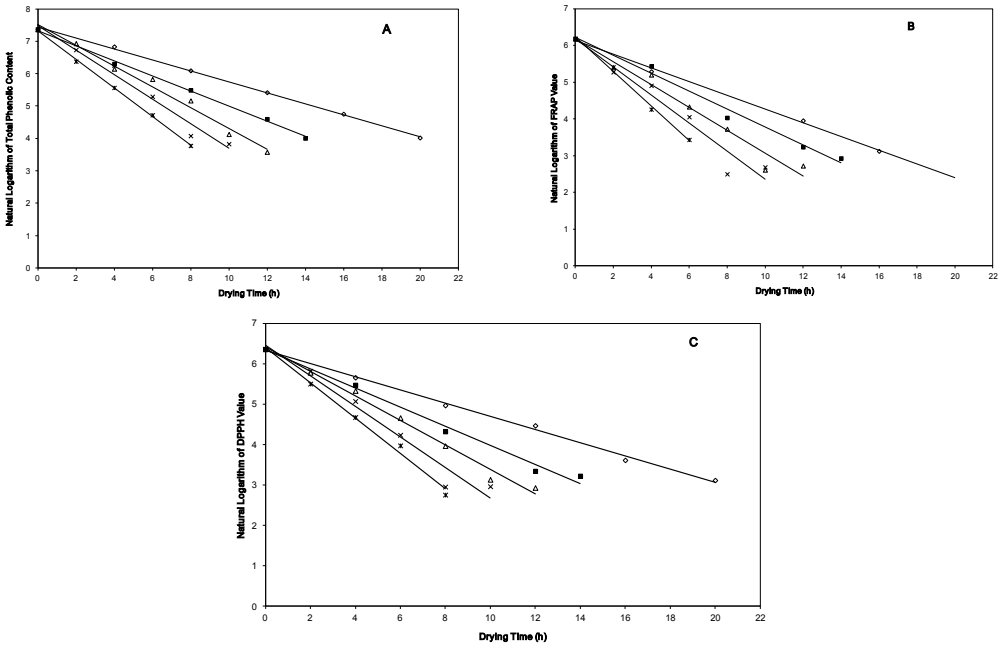

Figure 1. Degradation kinetics of antioxidant activity (A, TPC; B, FRAP and C, DPPH values) in tomatoes dried at 60°C (♦), 70°C (□), 80°C (△), 90°C (×) and 100°C (∗). Lines indicate linear regression for each drying temperature, and each point reflects the average of triplicates

Degradation Kinetics of DPPH

Higher DPPH radical scavenging activity of hydrophilic extracts of tomato and tomato products than hydrophobic extracts were previously reported by several authors [28, 35, 36] although conflicting results were also present in the literature [37]. Using the ABTS assay, Toor and Savage [18] reported that drying tomatoes at 42°C for 18h in a forced air drying reduced the total antioxidant activity of fresh tomatoes from 2.73 to 1.78 mmol TE/100 g dm. Similar reductions in the total antioxidant activity of different cultivars were also reported by Kerkhofs et al. [15]. In this present study, DPPH radical scavenging activity of dried tomatoes was determined in hydrophobic extracts. The degradation kinetics of DPPH values followed a first-order reaction like TPC and FRAP. Reaction constants for DPPH values in dried tomatoes were determined by plotting the natural logarithm of DPPH values (µmol TE/g dm) versus time for each temperature (Fig. 1C). The plots were mostly linear (R^2 = 0.904–0.980), confirming that the reaction of DPPH value degradation is towards a first order. Kinetic data at various drying conditions are shown in Table 2. Reaction rate constants for antioxidant activity loss in terms of DPPH values were in the range of 0.1632-0.4368 h^{-1} and significantly influenced by drying temperature. As drying temperature increased, the degradation of DPPH values also increased. For example, half life time ($t_{1/2}$) of DPPH values in tomatoes during drying was 4.25 h at 60ºC; however, it decreased to 1.59 h at 100ºC. Results indicated that DPPH values are highly influenced by drying temperature, and results were similar to total phenolic contents and FRAP values of tomatoes during drying. Akdas and Baslar [30] dried mandarin slices in oven or vacuum drying conditions at 55, 65 and 75°C, and determined the degradation kinetics of DPPH radical scavenging activity of slices. They suggested a first-order reaction for antioxidant activity degradation and reported that activation energy values for the degradation of antioxidant activity in oven and vacuum dried mandarin slices were about 40 and 42 kJ mol^{-1}, respectively. In this present study, the degradation of DPPH values in tomato quarters during hot air drying was a first-order reaction, and activation energy was 23.67 kJ mol^{-1}.

Degradation Kinetics of Color Values

Degradation of color values followed a first-order reaction ($ln\ CV = lnCV_0 - k.t$) where CV is the color value (Hunter L, a, b or a/b value) at time t, CV_0 is the respective initial color value of processed tomatoes, and k is the reaction rate constant). Plots of natural logarithm of color values against time for each temperature are shown in Fig. 2A-D while the equations explaining the time-dependency of color values of processed tomatoes are indicated in Table 1. Coefficients of determinations (R^2) were in the range of 0.90 to 0.99, which is a good indicator for a first order reaction. The calculated rate constants (k) and other kinetic parameters of color values in tomatoes during various drying conditions are given in Table 3. The reaction rate constants for the color values of tomato quarters during drying were in the range of 0.01-0.07 h^{-1} and significantly affected by drying temperature. Temperature dependence of the reaction rate constants followed the Arrhenius relationship.

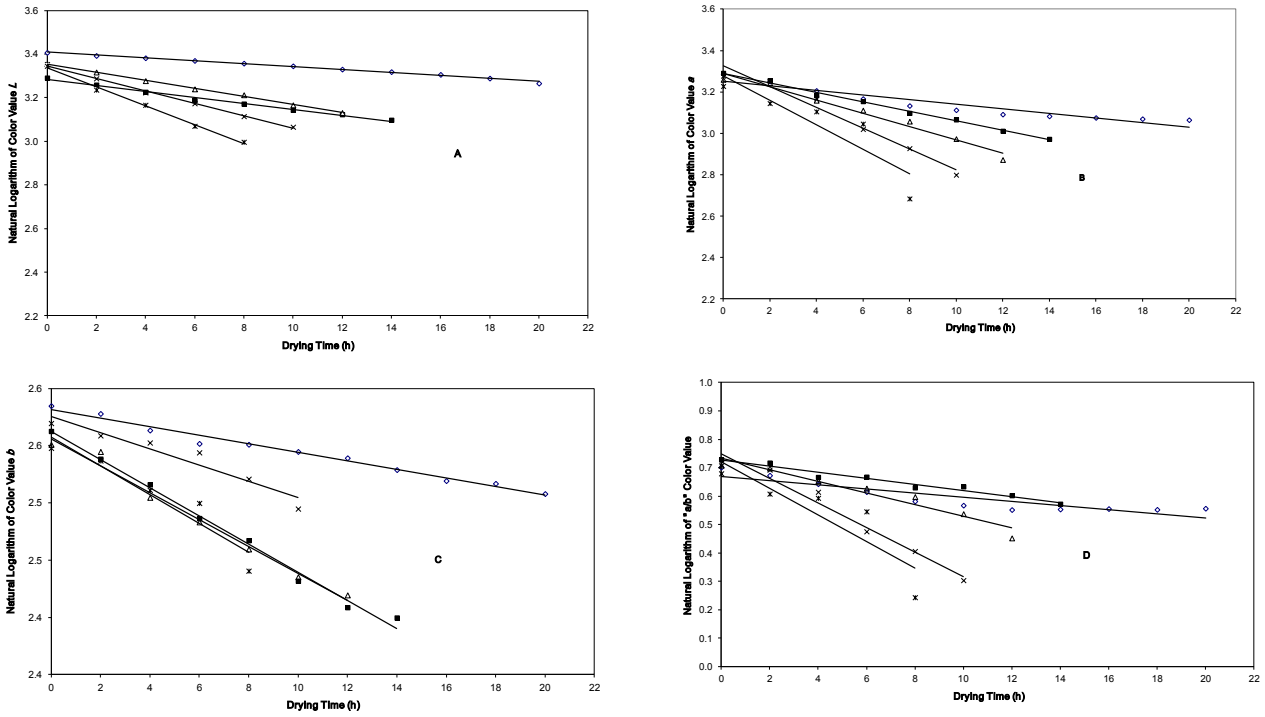

Figure 2. Degradation kinetics of color values (A, Hunter L; B, Hunter a; C, Hunter b and D, a/b values) in tomatoes dried at 60°C (♦), 70°C (□), 80°C (△), 90°C (×) and 100°C (∗). Lines indicate linear regression for each drying temperature, and each point reflects the average of triplicates.

Changing drying temperature from 60 to 70°C resulted in the highest Q_{10} value of Hunter L, a and b color parameters in processed tomatoes in comparison to other temperature changes. On the other hand, the highest Q_{10} value (2.102) was determined in a/b values of processed tomatoes when temperature was increased from 80 to 90°C. Color variation in tomatoes is mostly related to a/b value and a low a/b value represents an orange to brown color due to the breakdown of lycopene and the formation of the Maillard reaction products by the intensive heat treatment [38, 39]. Half-life time for a/b value was calculated as 51 min at 60ºC, which dropped to 9 min at 100ºC. The activation energy was 52.58 kJ/mol.

Drying method itself has a significant influence on color values of tomatoes [40]. In a study by Izli and Isik [41], tomato halves were dried at microwave, convective, and microwave-convective driers to determine changes in color and microstructure of tomatoes. Authors reported that both drying temperature and drier type influenced tomato color, and reduction in drying temperature resulted in a better retention of color. Similarly, studying the effect of drier type (microwave, vacuum-microwave and hot air) on drying kinetics, antioxidant activity and color changes of tomato quarters, Orikasa et al. [42] reported that the use of a vacuum-microwave drier increased the retention of antioxidant activity in tomato quarters while leading to a lighter color than other two methods. Kerkhofs et al. [15] drying tomato quarters of three cultivars (Aranka, Encore and Flavourine) in a forced-air drier at 42°C for 18 h to a final moisture content of 23% resulted in a reduction of $a*/b*$ ratio by 25%. Under similar drying conditions, Toor and Savage [15] reported that drying reduced CIE L* values while increasing a*/b* ratios of tomatoes (Excell, Tradiro and Flavourine). Demiray and Tulek [43] drying red pepper slices in a vacuum dryer at three different temperatures (45, 55 and 65°C) and two absolute pressures (21.5 kPa and 48.0 kPa). Authors reported that the color values (Hunter L, a and b) decreased, while ΔE (The color difference) increased during drying. Mathematical modeling of color degradation kinetics indicated that both the zero-order and first-order kinetic model were found to describe the Hunter L, a and b values. However, ΔE followed zero-order kinetic model.

Table 3. Reaction rate constants and other kinetic parameters[a] for color values in tomatoes during drying at five different temperatures

Hunter Color Value	Temperature (ºC)	Q_{10} Value	k (h^{-1})	$t_{1/2}$ (h)	E_a (kJ/mol)
L	60		0.0067	1.72	46.29
	70	2.044	0.0137	0.84	
	80	1.357	0.0186	0.62	
	90	1.543	0.0287	0.40	
	100	1.505	0.0432	0.27	
a	60		0.0111	1.04	46.28
	70	2.019	0.0230	0.50	
	80	1.332	0.0322	0.36	
	90	1.522	0.0502	0.23	
	100	1.392	0.0699	0.17	
b	60		0.0037	3.12	31.49
	70	1.920	0.0071	1.63	
	80	1.662	0.0118	0.98	
	90	1.042	0.0123	0.94	
	100	1.024	0.0126	0.92	
a/b	60		0.0074	0.85	52.58
	70	1.445	0.0107	0.56	
	80	1.915	0.0205	0.31	
	90	2.102	0.0431	0.16	
	100	1.083	0.0467	0.15	

[a]: Q_{10}, k, $t_{1/2}$, k_0 and E_a: temperature coefficient, reaction rate constant, reaction half life time, preexponential constant and activation energy, respectively.

Correlation among Color Values, Antioxidant Activity, Lycopene and β-Carotene Contents

In this present study, significant correlation coefficients ($p<0.001$) were found among the parameters studied (Table 4). Total phenolic content, DPPH and FRAP values and lycopene and β-carotene contents of tomatoes during hot air drying were highly correlated with each other (i.e. Pearson correlation coefficients > 0.90). Arias et al. [44] reported a good correlation between color of hydroponic tomatoes and their lycopene content, and they proposed an equation explaining the relation between the lycopene content and the ratio of a*/b* color values during maturity. Studying the changes in carotenoids, phenolic

compounds and vitamin C contents of red and yellow tomatoes during technical processing and lyophilization, George et al. [45] reported lower a*/b* ratios and β-carotene contents in yellow tomatoes than in red tomatoes. The authors stated that the parameter b* was higher in yellow tomato than in red tomato, and they concluded that the b* parameter was not a good indicator of the β-carotene content. Insignificant correlation between total phenolic content and CIE Lab color values of 167 tomato samples of five different cultivars was reported by Hernandez et al. [46] However, the authors reported that correlation between lycopene content and color value a*, which represents red color, was significant. Ilahy et al. [47] reported that antioxidant activity (ABTS and FRAP values) of hydrophilic extracts of high-lycopene tomato cultivars was significantly correlated with total phenolic contents of extracts while antioxidant activity of lipophilic extracts was highly and significantly correlated with total carotenoid and lycopene contents of tomato extracts. Kim et al. [48] reported the highest correlation (r= 0.893) between the total phenolic content and reducing power of hydrothermal extracts of watermelons and the lowest correlation between ABTS values and reducing power (r= 0.605). The authors also reported high correlation between the TPC and DPPH values of hydrothermal extracts of watermelons. In this present study, all parameters studied were correlated with each other, and the main reason for this could be the fact that the correlations were determined during hot air drying of tomatoes. Drying process had a significant effect on the parameters including color values, total phenolic contents and antioxidant activity of tomatoes.

Table 4. Pearson correlation coefficients among color values, lycopene and β-carotene contents, TPC, DPPH and FRAP values of air-dried tomatoes (n=26). Lower values in parentheses (p values) indicate that parameters are highly correlated with each other. Coefficients higher than 0.90 are shown in bold.

Parameters	L	a	b	a/b	TPC	DPPH	FRAP	Lycopene	β-Carotene
L	1.000	0.837 (<0.0001)	0.727 (<0.0001)	0.721 (<0.0001)	0.798 (<0.0001)	0.780 (<0.0001)	0.751 (<0.0001)	0.819 (<0.0001)	0.698 (<0.0001)
a		1.000	0.736 (<0.0001)	**0.936** (<0.0001)	0.878 (<0.0001)	0.875 (<0.0001)	0.846 (<0.0001)	**0.919** (<0.0001)	0.890 (<0.0001)
b			1.000	0.452 (0.0200)	0.717 (<0.0001)	0.711 (<0.0001)	0.681 (<0.0001)	0.764 (<0.0001)	0.750 (<0.0001)
a/b				1.000	0.774 (<0.0001)	0.773 (<0.0001)	0.751 (<0.0001)	0.824 (<0.0001)	0.793 (<0.0001)
TPC					1.000	**0.994** (<0.0001)	**0.982** (<0.0001)	**0.949** (<0.0001)	**0.917** (<0.0001)
DPPH						1.000	**0.992** (<0.0001)	**0.946** (<0.0001)	**0.924** (<0.0001)
FRAP							1.000	**0.927** (<0.0001)	0.896 (<0.0001)
Lycopene								1.000	**0.954** (<0.0001)
β-Carotene									1.000

CONCLUSION

This study indicated that degradation kinetics of antioxidant activity and color values in tomato quarters during hot air drying followed a first-order reaction. Reaction rate constants for these constituents of tomatoes were highly dependent on the drying temperature, and activation energy values for antioxidant activity determined by three TPC, FRAP and DPPH assays were 24.36, 22.91 and 23.67 kJ/mol, respectively. Prolonged drying time increased the degradation rate of antioxidant activity of tomatoes during hot air drying. In lipophilic extracts, significant correlations were found among the TPC, DPPH and FRAP values and lycopene and β-carotene contents of tomatoes during hot air drying. Main reason for high correlations could be the fact that hot air drying has a significant influence on parameters studied including color values and antioxidant activity of tomatoes. Kinetic data revealed that color values and antioxidant activity of tomatoes are susceptible to drying temperature. Under the conditions studied, tomatoes should be dried at temperatures lower than 70°C in order to obtain better retention of antioxidant activity and color in final products. Results of this present study could be useful to optimize drying conditions for tomatoes with superior total phenolic content and antioxidant activity as well as desired color values.

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