EURASIAN JOURNAL OF FOOD SCIENCE AND TECHNOLOGY

Temperature dependency of sweet cherry concentrate colour: A kinetic study

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Abstract

The present study was undertaken to study degradation kinetics of visual colour of sweet cherry concentrate over temperature range of 60-80 °C during 480 minutes heat treatment. The visual colour was evaluated using a HunterLab Colourflex Colourimeter and change in visual colour was expressed in terms of total colour difference (*TCD**) which is a combination of *L** (lightness), *a** (redness/greenness) and *b** (yellowness/blueness). *TCD** was fitted to zero-order, first-order and combined kinetics model by non-linear regression iterative procedure. Correlation coefficients (R^2) ranging between 0.9040-0.9763 for zero order kinetics, 0.8232-0.9520 for first order kinetics and 0.9765-0.9898 for combined kinetics, respectively. It could be concluded that change in sweet cherry color during heating at 60, 70, 80 °C for 480 minutes can be described by either first, zero and combined kinetics, but rather better to describe with combined kinetics. Furthermore, it might be inferred that as the temperature increased, change in *TCD** could be predominantly caused by Maillard reaction rather than pigment destruction in sweet cherry concentrates.

Keywords: Colour, Concentrate, Kinetics, Sweet cherry, Thermal Degradation

Introductıon

Cherries (*Prunus* spp.) are the smallest members of the stone fruit family of Rosaceae and, *Prunus avium* L., is known as "sweet cherry"(Ferretti et al., 2010). Sweetness in the cherry fruit is mainly due to glucose and fructose, while sourness is primarily due to the presence of organic acid (malic acid). Sweet cherries are characterized by a higher content of simple sugar with respect to sour cherries (Ferretti et al., 2010). Intrinsic sweet taste of sweet cherry juice related to its sugar composition, sweet cherries contains highest amounts of glucose, followed by fructose, sorbitol and sucrose (Kelebek & Selli, 2011). Cherries contain vitamins (C, B, A, E, K), minerals (such as calcium, magnesium, phosphorous and potassium), and some carotenoids, in particular beta-carotene, and to a lower extent lutein and zeaxantine. Cherry phenolics are flavonoids (anthocyanins), non-flavonoids, flavan-3-ols and flavanols (Kelebek & Selli, 2011). Anthocyanins include cyanidin 3-glucoside, cyanidin 3-rutinoside, cyanidin 3-sophoroside, pelargonidin 3-glucoside, pelargonidin 3-rutinoside, 3-glucoside, and peonidin 3-rutinoside; non-flavonoids include phenolic acids (hydroxycinnamic and hydroxybenzoic acids) flavonols and flavan-3-ols include catechin, epicatechin, quercetin 3-glucoside, quercetin 3-rutinoside, kaempferol 3-rutinoside (Ferretti et al., 2010). Major anthocyanins in sweet cherry is cyanidin-3-rutinoside (Patras et al., 2010). Antioxidants and phenolics of cherry fruits have antioxidant, anticancer and anti-inflammation properties (Ferretti et al., 2010).

Since the colour is a major determinant for quality in red coloured fruits and vegetables, it is quite important to minimize color deterioration during processing of these

fruits. The objective of this study was to determine degradation kinetics of visual colour of sweet cherry concentrate at selected temperatures (60, 70 and 80 °C) during 480 minutes heat treatment in order to test their temperature dependency.

MATERIAL and METHODS

Materials

Sweet cherry (*Prunus avium* L.) fruits were collected in Gaziantep, Southeast Anatolia, Turkey. Pectolytic enzyme, Panzym XXL, was kindly gifted by Sinerji A.Ş., Mersin, TURKEY. All the other reagents were of analytical grade.

Preparation of concentrates

All the foreign materials such as pieces of branches and leaves and also unripe and damaged fruits were removed by hand. The cleaned fruits were washed under cold tap water, stalks and seeds were removed. Fruits were ground by using a laboratory blender. Juice was immediately filtered through muslin to remove pulp from the juice. Then the juice was depectinized with 1.0 % (v/w) Panzym XXL at 50 ^{o}C for 2 h. The depectinized juice was allowed to rest at 4^{o}C for 24 h. The juice was again filtered through five layer muslin and finally double layer filter paper to obtain a clear juice. Clear juices were concentrated using BÜCHİ Rotary Evaporator (Rotavapor R-3 model, BÜCHI Loborthechnik AG, Flawil, Switzerland) at 40 ^{o}C. The total soluble solids and pH of sweet cherry concentrate were 45.02 °Brix and 3.75, respectively.

Colour measurements

The visual colour was evaluated using a HunterLab Colourflex (A-60-1010-615 Model Colourimeter, Hunter Associates Lab. Inc. Reston VA, USA). The instrument was standardized each time with a black and a white (L = 91.10, a = 1.12, b = 1.26) tile. The colour values were expressed as *L** (lightness), *a** (redness/greenness) and *b** (yellowness/blueness). Total colour difference (*TCD**) parameter was calculated and modeled. Colour values were the means of triplicate measurements.

Degradation kinetics of visual colour

The complexity of fruit juices and derivatives implies a wide range of enzymatic and non-enzymatic browning reactions caused by thermal treatments. Consequently it is difficult to establish a reaction mechanism and to obtain a kinetic model describing the global process adequately(Ibarz et al., 1999). There are numerous references on the kinetics of colour of food materials in the literature. The majority of these works report zero-order kinetics (Eq. (1)) (Chutintrasri & Noomhorm, 2007; Tiwari et al., 2009), first-order kinetics (Eq. (2))(Ahmed et al., 2000; Shao-gian et al., 2011).

$$C = C_0 \pm k_o * t \quad (1)$$

$$C = C_o * \exp\ (\pm k_1 * t) \quad (2)$$

Sometimes the relatively simple models described do not adequately represent colour change mechanism. That is why a combined kinetics has been developed, in which the non-enzymatic colour change reactions are considered to consist of two stages. A first stage of coloured polymeric compound formation following zero order kinetics, the second stage supposes decomposition of the coloured polymers into non-coloured compounds following a

first order kinetics. According to this combined kinetics, the colour change mechanism can be expressed by (Garza et al., 1999; Ibarz et al., 1999):

$$C = \frac{k_0}{k_1} - \left[\frac{k_o}{k_1} - C_0\right] exp(\pm k_1 * t) \quad (3)$$

The terms C_o is the initial contents and C is the contents after time t (min) of heating at the given temperature while k_0 is the zero order and k_1 is the first order rate constant in Eqs. (1), (2) and (3). The parameters of zero (Eq. (1)) order, first order kinetic model (Eq. (2)) and combined kinetics model (Eq. (3)) were estimated by non-linear regression iterative procedure of the SigmaPlot (SigmaPlot 10.0 Windows version, SPSS Inc.). Total colour difference (*TCD**) was calculated by using L^*, a^*, b^* values (Eq. (4)) (Loughrey, 2002).

$$TCD^* = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (4)$$

where, L_0^* , a_0^* and b_0^* refer to initial values, and L^*, a^* and b^* refer to colour values at various times during heat treatment.

Statistical Analysis

All measurements were performed in triplicate and are reported as means and standard deviations. The parameters of kinetic models were estimated by non-linear regression iterative procedure of the SigmaPlot (SigmaPlot 10.0 Windows version, SPSS Inc.).

Table 1. Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes.

	Temperature (°C)		
	60 °C	70 °C	80 °C
Time (min)	*TDC**±*SE*	*TDC**±*SE*	*TDC**±*SE*
0	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000
60	0.2768±0.0138	0.5025±0.0251	0.6388±0.0319
120	0.3850±0.0192	0.6761±0.0338	0.8193±0.0410
180	0.5276±0.0264	0.7938±0.0397	0.9778±0.0489
240	0.6097±0.0305	0.9394±0.0470	1.2458±0.0623
300	0.7325±0.0366	1.1989±0.0599	1.3945±0.0697
360	0.8867±0.0443	1.3919±0.0696	1.5380±0.0769
480	1.0602±0.0530	1.5062±0.0753	1.6873±0.0844

SE: Standard error

RESULTS and DISCUSSION

There are numerous references on the kinetics of color of food materials in the literature. The majority of these works report zero-order kinetics (Eq. (1)) (Chutintrasri & Noomhorm, 2007; Tiwari et al., 2009), first-order kinetics (Eq. (2)) (Ahmed et al., 2000; Shao-gian et al., 2011) and combined kinetic model (Eq. (3)) [4], [9]. Combined model consist of two stages: the first one includes color formation based on Maillard reactions and it follows zero order kinetics and the second includes the color destruction (pigment destruction) which follows a first order kinetics (Garza et al., 1999; Ibarz et al., 2000).

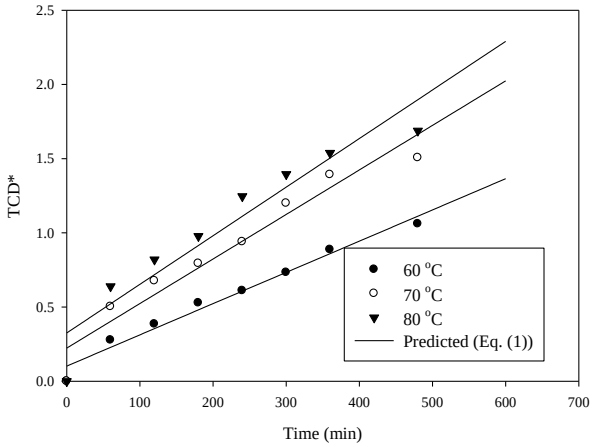

Figure 1. Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes fitted to zero order (Eq. (1)) kinetics.

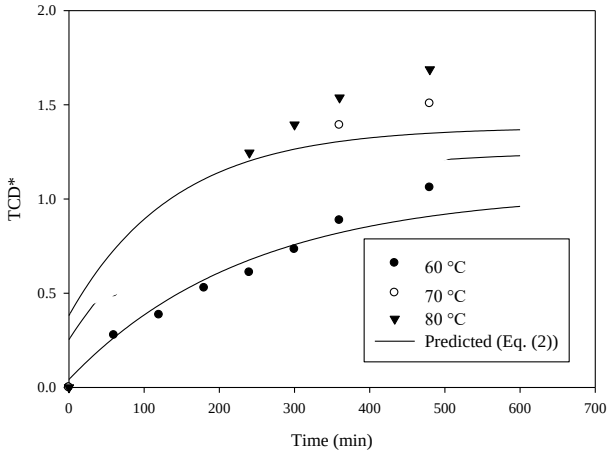

Figure 2. Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes fitted to first order (Eq. (2)) kinetics.

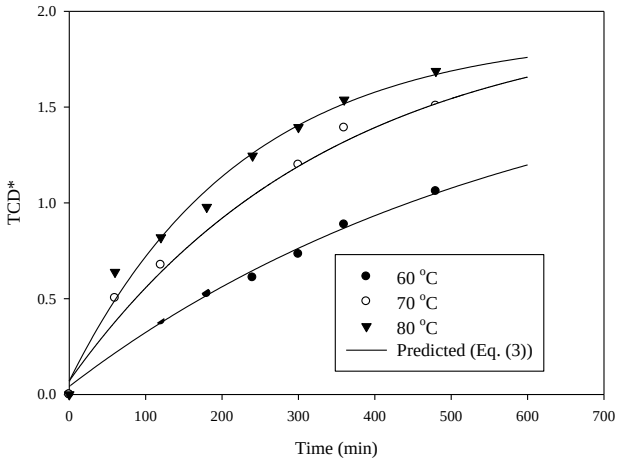

Figure 3. Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes fitted to combined model (Eq. (3)) kinetics.

Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes were given in Table 1.Variation in *TCD** value of sweet cherry concentrate was 1.0602, 1.5062 and 1.6873 at the end of 480 minutes heating at 60, 70, 80 °C, respectively (Table 1). Experimental data for change in *TCD** were fitted to zero-order (Eq. (1)), first-order (Eq. (2)) and combined kinetic model (Eq. (3)). Kinetic parameters of zero, first and combined model were given in Table 2, Table 3 and Table 4, respectively. Model graphs of zero, first and combined kinetic model were given in Figure 1, Figure 2 and Figure 3, respectively.

Table 2. Kinetics parameters of zero-order model (Eq. (1)) for *TCD** values.

Concentrate type	Temperature (°C)	$C_o \pm SE$	$ko \pm SE$	R^2
Sweet cherry	60	0.1020±0.0354	0.0021±0.0001	0.9763
	70	0.2233±0.0834	0.0030±0.0003	0.9377
	80	0.3254±0.1151	0.0033±0.0004	0.9040

SE: Standard error, R^2: correlation coefficients.

Table 3. Kinetics parameters of first-order model (Eq. (2)) for *TCD** values.

Concentrate type	Temperature (°C)	$C_o \pm SE$	$k_1 \pm SE$	R^2
Sweet cherry	60	1.0418±0.0728	-0.0042±0.0010	0.9520
	70	1.2536±0.1777	-0.0062±0.0040	0.8455
	80	1.3813±0.1965	-0.0072±0.0054	0.8232

SE: Standard error, R^2: correlation coefficients.

Table 4. Kinetics parameters of combined model (Eq. (3)) for *TCD** values.

Concentrate Type	Temperature (°C)	$C_o \pm SE$	$ko \pm SE$	$k_1 \pm SE$	R^2	ko / k_1
Sweet cherry	60	0.0420±0.0347	0.0031±0.0004	0.0017±0.0006	0.9898	1.82
	70	0.0709±0.0792	0.0058±0.0010	0.0029±0.0010	0.9765	2.00
	80	0.0702±0.0759	0.0083±0.0011	0.0044±0.0010	0.9835	1.89

SE: Standard error, R^2: correlation coefficients.

Correlation coefficients (R^2) ranging between 0.9040-0.9763 (Table 2) for zero order kinetics, 0.8232-0.9520 (Table 3) for first order kinetics and 0.9765-0.9898 (Table 4) for combined kinetics, respectively. It could be concluded that change in sweet cherry color during heating at 60, 70, 80 °C for 480 minutes can be described by either first, zero and combined kinetics due to having good correlation coefficients (R^2) and reasonable C_o values. Contrarily, it is known that there is no significant difference between zero and first order kinetics when a reaction describing any quality attribute (Labuza & Riboh, 1982). So, combination of these two models could be a good alternative to express colour change in sweet cherry concentrate. According to Ibarz et al. (2000), when the ratio of kinetic constants k_o (color formation) and k_1 (pigment destruction) is greater than unity, Maillard reaction predominates over pigment destruction. In this respect, as temperature increased, change in *TCD** may predominantly caused by Maillard reaction in sweet cherry concentrates at each temperature (Table 4). This result is correlated with the previous studies (Garza et al., 1999; Ibarz et al., 1999, 2000).

CONCLUSION

Temperature dependency of colour of sweet cherry concentrate was tested over the temperature range of 60-80 °C during 480 minutes heat treatment. Change in visual color was expressed in terms of total colour difference (*TCD*)* and *TCD** was fitted to zero-order, first-order and combined kinetics model by non-linear regression iterative procedure. Regression

analysis revealed that experimental data well fitted to all models due to having good correlation coefficients (R^2) and reasonable C_o values. So, change in sweet cherry color during heating at 60, 70, 80 °C for 480 minutes can be described by either first, zero and combined kinetics, but rather better to describe with combined kinetics. Finally, it might be inferred that as the temperature increased, change in *TCD** could be predominantly caused by Maillard reaction rather than pigment destruction in sweet cherry concentrates.

ACKNOWLEDGEMENT

A part of current study was presented as a poster presentation at International Conference on Agriculture, Forest, Food Sciences and Technologies (ICAFOF), 15-17 May 2017, Cappadocia / Turkey. Only the abstract of the study was published in the abstract book of International Conference on Agriculture, Forest, Food Sciences and Technologies (ICAFOF), 15-17 May 2017, Cappadocia / Turkey.

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