Kinetic modelling of non-enzymatic browning and changes of physio-chemical parameters of peach juice during storage

Jian Lyu¹ · Xuan Liu¹ · Jinfeng Bi¹ · Xinye Wu¹ · Linyan Zhou¹ · Weihong Ruan¹ · Mo Zhou¹ · Yi Jiao¹

Revised: 24 November 2017 / Accepted: 18 December 2017 / Published online: 30 January 2018
© Association of Food Scientists & Technologists (India) 2018

Abstract Kinetics of non-enzymatic browning and loss of free amino acids during different storage temperature (4, 25, 37 °C) were investigated. Changes of browning degree (A_{420}), color parameters, Vitamin C (V_c), free amino acids and 5-hydroxymethylfurfural (5-HMF) were analyzed to evaluate the non-enzymatic browning reactions, which were significantly affected by storage temperature. The lower temperature (4 °C) decreased the loss of V_c and the generation of 5-HMF, but induce the highest loss of serine. At the end of storage, loss of serine, alanine and aspartic acid were mainly lost. Results showed that zero-order kinetic model ($R^2 > 0.859$), the first-order model ($R^2 > 0.926$) and the combined kinetic model ($R^2 > 0.916$) were the most appropriate to describe the changes of a^* and b^* values, the degradation of V_c and the changes of A_{420} , L^* and 5-HMF during different storage temperatures. These kinetic models can be applied for predicting and minimizing the non-enzymatic browning of fresh peach juice during storage.

Keywords Non-enzymatic browning · Kinetic model · Peach juice · Color · 5-HMF

Introduction

Browning, resulting in dark appearance, was the most important reaction during processing and storage of fruit juices (Rattanathanalerk et al. 2005). Non-enzymatic browning, including caramelisation, Maillard reaction, degradation of Vitamin C and phenols oxidation and polymerization, was reported to perform an important role in fruit juice browning (Quevedo et al. 2010; Cornwell and Wrolstad 1981). Attribute to oxidation and degradation, Vitamin C in fruit juice was identified to decrease during storage (Roig et al. 1999). Damasceno et al. (2008) reported that the degradation of Vitamin C was the main factor affecting non-enzymatic browning during apple juice storage. In addition, Maillard reactions between reducing sugars and amino acids caused the decline of juice sensory and nutritional qualities, which widely observed in fruit juice (Martins et al. 2000; Koca et al. 2007; Özhan et al. 2010). Besides, Amino acids could trigger a range of reactions and produce browning pigments named melanoidins. Buedo et al. (2001) found that total amino acid content was lost by 8, 35 and 60% when peach juice stored at 15, 30 and 37 °C after 112 days, respectively. Moreover, Maillard reaction and degradation of Vitamin C could produce harmful substances to human's body and unwanted components such as furfural and 5-hydroxymethylfurfural.

Kinetic models such as zero and first order model, have been adopted to predict the changes of Critical quality indicators of juice during storage, which could be used to characterize non-enzymatic browning reactions (Labuza and Tannenbaum 1972; Saguy et al. 1978; Vaikousi et al. 2008). Garza et al. (1999) reported that both browning degree and 5-HMF content were well fitted to the first-order kinetic model in peach puree during heat treatment, respectively. However, the non-enzymatic browning

Jian Lyu and Xuan Liu have contributed equally to the present work.

✉ Jinfeng Bi
bjfcaas@126.com

¹ Institute of Food Science and Technology, Chinese Academy of Agricultural Sciences, Key Laboratory of Agro-Products Processing, Ministry of Agriculture, No. 2 Yuan Ming Yuan West Road, Haidian District, Beijing 100193, China

comprises a series of complex reactions due to various components in different food matrix. Therefore, non-enzymatic browning kinetics may vary for different juices.

Peach juice is one of the most important fruit juices for its pleasant flavor and nutritional value. Peach juice concentrates and peach puree are the main products for peach beverage processing. However, typical flavor compounds may lose and be diluted during concentration and formulation. The objective of this paper is to investigate the non-enzymatic browning characteristics, which have high effect on the appearance of fresh peach juice (not from concentrated) during storage. The information obtained from this study would facilitate the fresh peach juice as a potential long-shelf life product.

Materials and methods

Samples

Preparation of fresh peach juice

Fresh peaches (*Prunus persica* L. cv. Jiubao, widely planted in north of China) were harvested from a standard commercial orchard (Pinggu district, Beijing, China) at commercial maturity. Peaches were washed, removed the stones, cut into pieces and juiced by adding Vitamin C (0.8% weight of the peach mass), and filtered with 200 mesh cloth to obtain the crude peach juice. Then the crude peach juice was homogenized, sterilized and packed into PET bottles (standard volume of 500 mL). The above packed juice was regarded as the fresh peach juice.

Storage treatments

The fresh peach juice samples were stored at the temperature of 4, 25 and 37 °C for 40 days, respectively. Browning degree, color parameters, Vitamin C content, free amino acids and 5-HMF were determined every 10 days. All the measurements were conducted within 24 h at each tenth day.

Analytical determinations

Browning degree evaluation

Browning degree (A_{420}) of the stored samples was expressed as the values of A_{420} , which was measured using a UV-1800 Spectrophotometer (Shimadzu), reported by Chutintrasri and Noomhorm (2007). Peach juice was centrifuged at 9000 rpm for 15 min and the supernatant was collected and filtered through 0.45 μ m membrane, then measured for absorbance at 420 nm.

Color measurement

Color changes of peach juice were analyzed by Color Quest XT system (Hunter Lab, USA). Three Hunter parameters, named L^* , a^* and b^* were measured. L^* stood for lightness (black = 0, white = 100), a^* represented for greenness and redness (+ a^* , redness; − a^* , greenness), b^* indicated blueness and yellowness (− b^* , blueness; + b^* , yellowness).

Vitamin C

Vitamin C was determined according to AOAC (1984) method.

Free amino acids

Free amino acids were determined by the method of Chinese National Standard GB/T 30987-2014. Determination of free amino acids in plants. 50 mL of each juice sample were mixed with 35 mL aqueous solution of sulfosalicylic acid (5%), agitated by ultrasonic for 10 min, diluted to 100 mL, filtered by 0.45 μ m membrane then determined by an automatic amino acid analyser system of L-8900 (Hitachi, Japan). The resin column 2619 (4.6 $\times$ 60 mm) was used for analyze with the temperature of 57 °C and column 2650 (4 $\times$ 50 mm) was used for reaction with the temperature of 135 °C. The pH values of four standard buffer were 3.30, 3.20, 4.00 and 4.90, respectively. The flow rate was 0.400 mL/min for pump A and 0.350 mL/min for pump B. The gradient program was recommended by the column manufacturer. Total amino acids (TAA) were determined by the titration method, as recommended by AOAC (1980). The free amino acid and TAA for samples were expressed as the relative content (%) of initial sample.

5-HMF

5-HMF contents of stored peach juice samples were determined by following the procedure described by Burdurlu and Karadeniz (2003). Barbituric acid and *p*-toluidine could react with 5-HMF and form red compounds. The contents of 5-HMF could be calculated by the absorbance values at 550 nm monitored by a UV-1800 Spectrophotometer (Shimadzu).

Kinetic model analysis

Browning degree, color parameters, Vitamin C content and 5-HMF content were analyzed by zero-order, first-order and combined kinetic models, which were applied to describe non-enzymatic changes of peach juice during

storage. The equations are as follows (Damasceno et al. 2008):

$$C = C_0 + k_0 t \quad (1)$$

$$C = C_0 + \exp(k_1 t) \quad (2)$$

$$C = k_0/k_1 - (k_0/k_1 - C_0) \exp(-k_1 t) \quad (3)$$

where Eq. (1) is the zero-order kinetic model, Eq. (2) is the first-order kinetic model and Eq. (3) is the combined kinetic model. C_0 and C are the initial value of each non-enzymatic indicator and the value of that at storage time of t , respectively. k_0 and k_1 were the kinetic rate constants, respectively. The changes of kinetic constant with storage temperatures were represented by the Arrhenius equation,

$$k = k_0 \exp(-E_a/RT) \quad (4)$$

where k is the equilibrium constant, k_0 is the exponential coefficient; E_a is the activation energy (kJ/mol); R is the universal gas constant (8.314 J/mol K); T is the absolute temperature (K).

Statistical analysis

Analysis of variance (ANOVA) was applied to the experiment data, $p < 0.05$ was considered as differences, the statistical program (Origin 8.0, Origin Lab Company) was used for data analysis. All the experiments were performed in triplicate.

Results and discussion

Browning degree

The changes of A_{420} were shown in Fig. 1. Obviously, the A_{420} values increased with the extension of storage time. The storage time showed a significant influence on the browning degree ($p < 0.05$) of peach juice. After 40 days, the browning degree value increased by 0.212, 0.382 and 0.533 for the storage temperature of 4, 25 and 37 °C, respectively. Changes of A_{420} values were found to be well fitted to the combined kinetic model and the kinetic parameters were listed in Table 1. The kinetic constants increased with the rise of storage temperatures, which illustrated that browning degree increased faster under high temperature (25 and 37 °C).

Color parameters

The changes of L^* , a^* and b^* values were shown in Fig. 2. During the storage, the color of peach juice samples turned to dark gradually, which could be interpreted by the decrease of L^* values. With the increase of temperature, the

Fig. 1 Change in absorbance of peach juice during storage at different temperature

L^* values reduced by 4.67, 5.17 and 10.18 at 4, 25 and 37 °C, respectively. However, a^* values increased by 0.93, 2.56 and 3.70 and b^* values increased by 1.35, 2.02 and 5.36, respectively. The values of L^* , a^* and b^* values changed with the extension of storage period, meanwhile, the reaction rate constant increased to high levels with the elevated storage temperature.

As shown in Table 1, changes of L^*/L_0^* values could be well described by the combined kinetic model ($R^2 > 0.916$). However, both changes of a^*/a_0^* and b^*/b_0^* could be characterized by the zero-order kinetic model ($R^2 > 0.859$). Activation energy (E_a) was defined as the minimum energy required starting a chemical reaction. Therefore, the E_a values for the change of color parameter during storage could be regarded as indicators of browning reaction for peach juice. The E_a values for the changes of L , a^* , b^* of peach juice were 13.31, 30.88 and 18.00 kJ/mol (Table 1), respectively, which were higher than those of apple juice (Burdurlu and Karadeniz 2003) and pear puree (Garza et al. 1999), but lower than pineapple juice and pear juice (Rattanathanalerk et al. 2005). The above results implied that browning of peach juice in the present study was easier to happen than pineapple juice and pear juice. This phenomenon could attribute to the different chemical compositions in various fruit juices, such as Vitamin C, sugars, amino acids and phenols (Ahmed et al. 2002). Additionally, the E_a value for the change of L was the lowest, which indicated that the lightness of peach juice was most easily to change due to non-enzymatic browning reaction during the storage.

Degradation of Vitamin C

Vitamin C is a kind of sensitive compound which could be easily oxidized and decomposed during storage. As shown in Fig. 3, Vitamin C content decreased remarkably with the

Table 1 The Kinetic parameters of quality indicator changes during storage

Parameter	T (°C)	Kinetic model	k_0 (day ⁻¹)	k_1 (day ⁻¹)	R^2	E_a (kJ/mol)
$A_{420}/(A_{420})_0$	4	n = 0	0.007 ± 0.001		0.901	
	25		0.016 ± 0.003		0.978	
	37		0.024 ± 0.007		0.993	
$A_{420}/(A_{420})_0$	4	n = 1	0.006 ± 0.001		0.917	
	25		0.013 ± 0.002		0.995	
	37		0.017 ± 0.007		0.990	
$A_{420}/(A_{420})_0$	4	Combined	-0.026 ± 0.001	-0.030 ± 0.000	0.916	
	25		-0.011 ± 0.000	-0.021 ± 0.003	0.997	
	37		0.014 ± 0.002	-0.007 ± 0.001	0.992	
L^*/L_0^*	4	Combined	0.015 ± 0.003	0.018 ± 0.006	0.972	13.31
	25		0.043 ± 0.001	0.048 ± 0.002	0.983	
	37		0.044 ± 0.001	0.055 ± 0.003	0.996	
a^*/a_0^*	4	n = 0	0.003 ± 0.000		0.802	30.88
	25		0.007 ± 0.001		0.958	
	37		0.012 ± 0.003		0.802	
b^*/b_0^*	4	n = 0	0.001 ± 0.000		0.859	18.00
	25		0.001 ± 0.000		0.971	
	37		0.002 ± 0.000		0.909	
$V_c (C/C_0)$	4	n = 0	-0.008 ± 0.000		0.916	
	25		-0.010 ± 0.000		0.880	
	37		-0.012 ± 0.000		0.954	
$V_c (C/C_0)$	4	n = 1	-0.009 ± 0.000		0.926	
	25		-0.013 ± 0.001		0.933	
	37		-0.016 ± 0.002		0.967	
$V_c (C/C_0)$	4	Combined	0.005 ± 0.000	0.015 ± 0.003	0.951	
	25		0.029 ± 0.004	0.052 ± 0.007	0.993	
	37		0.001 ± 0.000	0.017 ± 0.003	0.891	
5-HMF (C/C_0)	4	n = 0	0.062 ± 0.007		0.981	
	25		0.062 ± 0.005		0.786	
	37		0.072 ± 0.003		0.855	
5-HMF (C/C_0)	4	n = 1	0.025 ± 0.001		0.908	
	25		0.020 ± 0.001		0.656	
	37		0.022 ± 0.001		0.740	
5-HMF (C/C_0)	4	Combined	0.106 ± 0.013	0.018 ± 0.004	0.996	
	25		0.284 ± 0.017	0.075 ± 0.008	0.993	
	37		0.267 ± 0.015	0.063 ± 0.005	0.986

Fig. 2 Changes of L^* values (a), a^* values (b) and b^* values (c) of peach juice versus storage time at different temperatures

Fig. 3 Relationship between Vitamin C and storage time at different temperatures for peach juice

extension of storage time. Moreover, storage temperature showed a significant effect on the degradation of Vitamin C ($p < 0.05$). The Vitamin C content decreased by 29.32, 38.66 and 46.68% at the storage temperature of 4, 25 and 37 °C, respectively. One of the oxidative decomposition products of Vitamin C was HMF, which could participate in the Maillard reaction and form the black substances eventually (Polydera et al. 2003). Degradation of Vitamin C content during the storage was well fitted to the combined kinetics ($R^2 > 0.926$) and the kinetic parameters were listed in Table 1. The obtained kinetic models could be used to predict the changes of degradation of Vitamin C content during the storage under different temperature, which could also provide a scientific basis for the quality control of peach juice.

Changes of free amino acids

For fresh peach juice, serine accounted for 69.60% of TAA (data not shown). Serine, aspartic acid, glutamic acid and alanine (accounted for 93.05% of TAA) were found to be the main constituents of the free amino acids. Figure 4 showed the contents of the free amino acids in peach juice after 40 days storage at different temperatures. Serine was lost by 17.14, 12.29 and 3.43% after 40 day storage at 4, 25 and 37 °C, respectively. Contents of glutamic acid and alanine were also lost correspondingly. However, the total free amino acids increased by 6.67 and 3.89% at the storage temperature of 25 and 37 °C for 40 days, respectively, which was attributed to the degradation of asparagine (Buedo et al. 2001).

5-HMF generation

Change in 5-HMF content of in peach juice during storage is plotted in Fig. 5. The content of 5-HMF content for fresh peach juice was 1.75 mg/L, while the value increased to 6.00, 6.63 and 8.06 mg/L after 40 day storage under 4, 25 and 37 °C, respectively. As seen in Table 1, the variation of 5-HMF contents were well fitted to the combined kinetic model ($R^2 > 0.98$), which were consistent with previous study for citrus juice storage (Burdurlu et al. 2006). The high values of kinetic constants were observed in the combined kinetic model for 25 and 37 °C, which indicated that it was easy and fast to generate 5-HMF at 25 and 37 °C during the storage. However, the above result was different from other reports. For instance, the values of 5-HMF contents were well fitted to zero order kinetic model for lemon juice and first order kinetic model for apple juice,

Fig. 4 Change in free amino acids during storage of peach juice

Fig. 5 Relationship between 5-HMF rate and storage time at different temperatures of peach juice

respectively (Robertson and Samaniego 1986; Toribio and Lozano 1984). The difference in browning of fruit juice might be attributed to the differences of chemical composition of fruit juice.

According to the kinetic modeling results of browning degree, color parameters, Vitamin C content and 5-HMF content, the color related indicators showed different regular pattern during storage, demonstrating the changes of color characteristics in different ways.

Relationship between 5-HMF and color parameters

It has been reported that 5-HMF was the most important intermediate product during the Maillard reaction and led to the dark color of peach puree (Buedo et al. 2000). A_{420} and color parameters were usually regarded to be the apparent characteristic indicators of fruit juice. Özhan et al. (2010) found good linear correlation between the formation of HMF and A_{420} value in carob pekmez. In our study, the relationships between 5-HMF content (C_{5-HMF}) and A_{420} value were found to be well fitted to the Quadratic model under different storage temperature. And the correlation coefficient (R^2) were 0.975, 0.875 and 0.999 for the storage temperature of 4, 25 and 37 °C, respectively. Similarly, the content of 5-HMF and a^* value could be well expressed by the Quadratic models. Additionally, the correlation coefficient (R^2) were 0.912, 0.866 and 0.962 for the storage temperature of 4, 25 and 37 °C, respectively. As it can be seen that the 5-HMF formation showed good correlations with A_{420} and a^* value, respectively. The correlation coefficients (R^2) between 5-HMF content and A_{420} value and also between 5-HMF content and a^* value were in the range of 0.866–0.999 ($p < 0.05$). Therefore, the 5-HMF contents could be predicted by the values of A_{420} and a^* . Therefore, color parameters could be used instead of measurements of 5-HMF contents to evaluate the non-enzymatic browning reaction during juice storage.

Conclusion

The changes of non-enzymatic browning of peach juice during storage were characterized in this study. A_{420} , color parameters, Vitamin C content, free amino acids and 5-HMF were measured to evaluate the browning degree of peach juice stored at different temperatures. Vitamin C content decreased by 29.32, 39.65 and 46.68% after 40-day storage under the temperature of 4, 25 and 37 °C, respectively. Serine, alanine, glutamic acid and aspartic acid were the main constituents of the free amino acids in fresh peach juice. After the 40-day storage, serine and glutamic acid were lost greatly, aspartic acid was increased caused by the degradation of asparagine. During the storage period, A_{420} , L^* value and 5-HMF, a^* and b^* values, and Vitamin C content were well fitted to the combine kinetic model, zero-order kinetic model and first-order kinetic model, respectively. The relationship between 5-HMF and A_{420} was satisfactorily expressed by means of Quadratic model, as well as 5-HMF and a^* value. The kinetic models and Arrhenius equation could be used to predict the reaction rate constants and E_a values for non-enzymatic browning during the storage of peach juice.

Acknowledgements This work was supported by the National Key R&D Program of China (2016YFD0400302).

Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

References

- Ahmed J, Shivhare US, Kaur M (2002) Thermal colour degradation kinetics of mango puree. *Int J Food Prop* 5(2):359–366
- AOAC (1980) Official methods of analysis. Association of analytical chemists, Washington, DC
- AOAC (1984) Method 985.26 Vitamin C (Total) in Food Semiautomated Fluorometric Method. official methods of analysis of AOAC international, USA
- Buedo AP, Elustondo MP, Urbicain MJ (2000) Non-enzymatic browning of peach juice concentrate during storage. *Innov Food Sci Emerg Technol* 1(4):255–260
- Buedo AP, Elustondo MP, Urbicain MJ (2001) Amino acid loss in peach juice concentrate during storage. *Innov Food Sci Emerg Technol* 1(4):281–288
- Burdurlu H, Karadeniz F (2003) Effect of storage on nonenzymatic browning of apple juice concentrates. *Food Chem* 80(1):91–97
- Burdurlu HS, Koca N, Karadeniz F (2006) Degradation of Vitamin C in citrus juice concentrates during storage. *J Food Eng* 74(2):211–216
- Chinese National Standard (2014) Determination of free amino acids in plants. GB/T 30987-2014. Standard Press of China, Beijing
- Chutintrasri B, Noomhorm A (2007) Color degradation kinetics of pineapple puree during thermal processing. *LWT Food Sci Technol* 40(2):300–306

- Cornwell CJ, Wrolstad RE (1981) Causes of browning in pear juice concentrate during storage. *J Food Sci* 46(2):515–518
- Damasceno LF, Fernandes FAN, Magalhães M, Brito ES (2008) Non-enzymatic browning in clarified cashew apple juice during thermal treatment: kinetics and process control. *Food Chem* 106(1):172–179
- Garza S, Ibarz A, Pagan J, Giner J (1999) Non-enzymatic browning in peach puree during heating. *Food Res Int* 32(5):335–343
- Koca N, Burdurlu HS, Karadeniz F (2007) Kinetics of colour changes in dehydrated carrots. *J Food Eng* 78(2):449–455
- Labuza TP, Tannenbaum SR (1972) Nutrient losses during drying and storage of dehydrated foods. *Crit Rev Food Sci* 3(2):217–240
- Martins SI, Jongen WM, Van-Boekel MA (2000) A review of Maillard reaction in food and implications to kinetic modelling. *Trends Food Sci Technol* 11(9):364–373
- Özhan B, Karadeniz F, Erge HS (2010) Effect of storage on nonenzymatic browning reactions in carob pekmez. *Int J Food Sci Technol* 45(4):751–757
- Polydera AC, Stoforos NG, Taoukis PS (2003) Comparative shelf life study and Vitamin C loss kinetics in pasteurized and high pressure processed reconstituted orange juice. *J Food Eng* 60(1):21–29
- Quevedo RA, Aguilera JM, Pedreschi F (2010) Color of salmon fillets by computer vision and sensory panel. *Food Bioprocess Technol* 3(5):637–643
- Rattanathanalerk M, Chiewchan N, Srichumpoung W (2005) Effect of thermal processing on the quality loss of pineapple juice. *J Food Eng* 66(2):259–265
- Robertson GL, Samaniego CML (1986) Effect of initial dissolved oxygen levels on the degradation of ascorbic acid and the browning of lemon juice during storage. *J Food Sci* 51(1):184–187
- Roig MG, Bello JF, Rivera ZS, Kennedy JF (1999) Studies on the occurrence of non-enzymatic browning during storage of citrus juice. *Food Res Int* 32(9):609–619
- Saguy I, Kopelman IJ, Mizrahi S (1978) Extent of nonenzymatic browning in grapefruit juice during thermal and concentration processes: kinetics and prediction. *J Food Process Preserv* 2(3):175–184
- Toribio JL, Lozano JE (1984) Nonenzymatic browning in apple juice concentrate during storage. *J Food Sci* 49(3):889–892
- Vaikousi H, Koutsoumanis K, Biliaderis CG (2008) Kinetic modeling of non-enzymatic browning of apple juice concentrates differing in water activity under isothermal and dynamic heating conditions. *Food Chem* 107(2):785–796