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Effect of storage on nonenzymatic browning of apple juice concentrates

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Abstract

Kinetics of nonenzymatic browning in Golden Delicious and Amasya apple juice concentrates during 4 months are investigated. Apple juice concentrates were at 65, 70, 75°Bx of Golden Delicious variety, stored at 5, 20, 37 °C and Amasya variety, stored at 37, 50, 65 °C. Colour development was measured by browning index (A_{420}) and the CIE-Lab colour system. Browning level of all apple juice concentrates increased according to a zero-order reaction kinetic. Activation energies for 65–75°Bx of Golden Delicious and Amasya apple concentrates ranged from 21.4 to 21.0 kcal/mol and 33.7 to 32.5 kcal/mol, respectively. Influence of soluble solids content on browning was negligible. HMF concentration, in Golden Delicious apple juice concentrates, was between 0.52 and 963 mg/kg, and between 0.52 and 190 mg/kg in Amasya apple juice concentrates.

Keywords: Nonenzymatic browning; Apple juice concentrate; Storage; 5-HMF

1. Introduction

It is known that many products darken during thermal processing and storage. In apple juice concentrate, accumulation of brown colour during thermal processing is due to enzymatic browning. However, during storage, it is attributed mainly to nonenzymatic reactions (Babsky, Toribio, & Lozano, 1986; Ibarz, Gonzales, Esplugas, & Miguelsanz, 1990). These reactions involve caramelization, ascorbic acid degradation and Maillard reaction. While caramelization occurs on heat treatment of sugars at high temperatures, ascorbic acid degradation occurs by an oxidative path in citrus juices (Clegg, 1964). The Maillard reaction, taking place between α-amino groups and reducing sugars, is the most important cause of browning in apple juice (Toribio & Lozano, 1984). Maillard browning may be desirable during food processing, as in the manufacture of coffee, tea, beer and in the toasting and baking of bread. This reaction improves desirable sensory characteristics of these foods e.g. colour, aroma and flavour (Arnoldi, Arnoldi, Baldi, & Griffini, 1988; Eskin, 1990; Ninomiya, Matsuzaki, & Shigmatsu, 1992; Umano, Hagi, Nakahara, Shyoji, & Shilbamoto, 1995). However, it may be undesirable, as in concentrated, intermediate moisture and dried foods, since maximum rate of Maillard reaction occurs at water activities of 0.6–0.7 (Eskin, 1990). In addition, the Maillard reaction causes losses in nutritional value of foods (Daniel & Whistler, 1985; O'brien, 1996; Martins, Jongen, & Van Boekel, 2001). Studies have also revealed that Maillard reaction products have antimicrobial (Einarsson, 1987) and antioxidative (Lingnert & Hall, 1986; Lingnert & Waller, 1983; Pokorny, 1991; Shaker, Ghazy, & Shibanoto, 1995) activities. It is also reported that some products produced by Maillard reactions have mutagenic effects (Friedman & Molnar-Perl, 1990; Gazzani, Vagnarelli, Cuzzoni, & Mazza, 1987; Nakama, Kim, Shinohara, & Omura, 1993; Shinohara, Kim, & Omura, 1986; Wakabayashi, Takahashi, Nagao, Sato, Kinae, Tomita et al., 1986). Maillard reactions can also cause accumulation of 5-HMF and this indicates severity of heating applied to fruit juices during processing (Lee & Nagy, 1988b). HMF forms by enolization of reducing sugars reacting with aminoacids after Amadori rearrangement (Yaylayan, 1990) and then condenses with nitrogenous compounds and polymerizes

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to give brown pigments (Resnik & Chirife, 1979). HMF is also a breakdown product during dehydration of glucose or fructose in an acid medium (Lee & Nagy, 1988b).

Since quality is supremely important in food, deterioration has to be controlled during storage. In concentrated juices, one of the main causes of deterioration is nonenzymatic browning, since enzymatic browning is eliminated by heat treatment during processing (Ibarz et al., 1990). So, kinetic modelling of nonenzymic reactions is very important for fruit juice storage. By measuring rate and temperature-dependence of these reactions, it is possible to determine the period of storage at a given temperature without quality deterioration.

In Turkey, three apple varieties (Golden Delicious, Amasya and Starking) have been mainly used for apple juice production. There have been studies related to enzymatic browning of these apple juices; however, the number of studies of nonenzymatic browning in these juices have been limited. Since Amasya is indigenous in Turkey and Golden Delicious grows widely in the world, these two varieties were selected as research materials.

The objective of this study was to determine kinetics of nonenzymatic browning in Golden Delicious and Amasya apple juice concentrates during storage and to observe 5-HMF formation.

2. Materials and methods

2.1. Materials

Amasya apple variety was obtained from fruit juice producers in Turkey (Tokat and Mersin), while Golden Delicious variety was supplied by the Experimental Orchards of the Ankara University in Ankara.

Apple juice concentrates were manufactured from Golden Delicious (GAJC) and Amasya varieties (AAJC) using the flowchart shown in Fig. 1. After washing and sorting, the apples were ground and pressed. The enzymatic treatment (Pectinex 3X-L, 0.03 g/l) was performed for 1 h following the heating, up to 90 °C. Clarifying was carried out at 50 °C by using bentonite (0.45 g/l), kiselsol (15%, 0.45 mL/l) and gelatin (5%, 0.05 g/l). At first, 4-folded cheesecloth was used for pre-filtration of apple juice. Then it was vacuum filtered through filter sheet (Carlson filtration Ltd., Barnoldswick, England) in a Buchner funnel and concentrated with a rotary evaporator at 50 °C, 110 mbar. The apple juice concentrates were diluted to 65, 70 and 75°Bx by using a NO.501-Du Abbe Refractometer at 21°C±0.5. All the apple juice concentrates were stored in 300 g glass jars, at 5, 20, 37 °C, during 4 months. Colour development was measured every week and 5-HMF was investigated every month. In addition to this, 50 and 65 °C were also chosen for a 6 week storage to observe the temperature dependence of the nonenzymatic browning reaction in Amasya concentrates, since the reaction could not be observed at 5 and 20 °C for this variety.

2.2. Colour measurement

Browning development was determined by using two colour measurement methods.

2.2.1. Determination of soluble brown pigments

Samples were diluted to 11.2 °Bx with distilled water. The absorbance was determined on a Unicam UV-VIS (UV 2) spectrophotometer in 10 mm cells against water at 420 nm (Ashoor & Zent, 1984; Baxter, 1995; Toribio & Lozano, 1984).

2.2.2. CIE-Lab colour system

The CIE L^*, a^* and b^* values were measured using Minolta CR-300 (0saka, Japan) colourimeter.

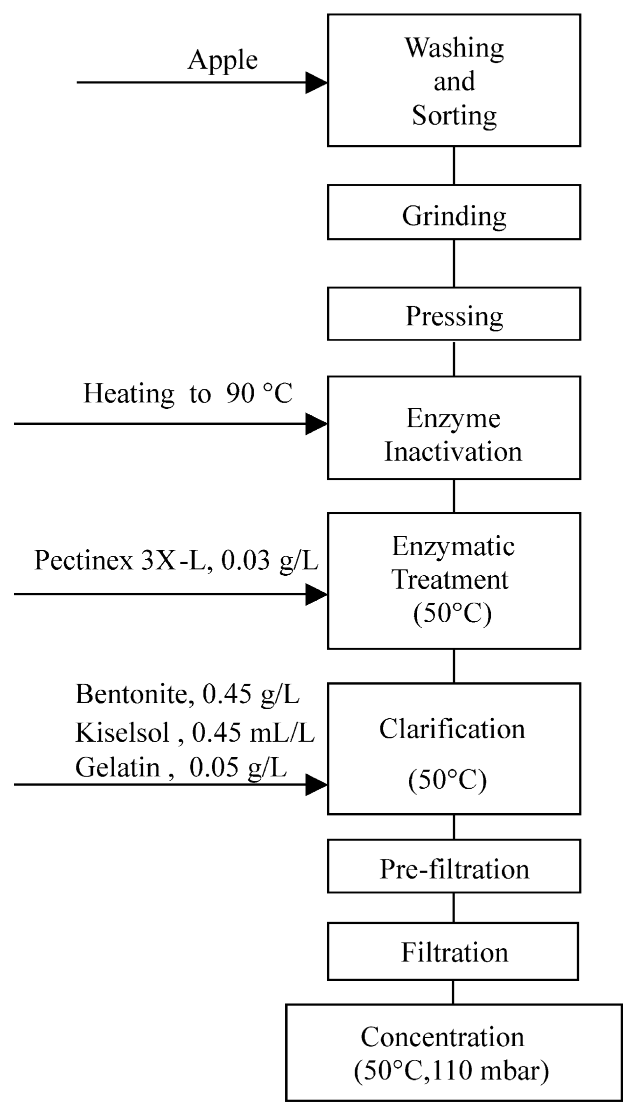

Fig. 1. Flowchart of Golden Delicious and Amasya apple juice concentrate production.

2.3. Determination of 5-HMF

In this method, HMF reacts with *p*-toluidine and barbituric acid and forms red pigments. The intensity of red colour is dependent on the amount of 5-HMF (Anonymous, 1984).

2.4. Statistical analysis

An analysis of variance (ANOVA) and correlation coefficients were obtained by the MINITAB (Version of Release,13) statistical computer programme. Tukey's multiple range taste was used to obtain comparisons among sample means. Evaluations were based on the $P < 0.05$ significance level.

3. Results and discussion

3.1. General

Absorbance values of apple juice concentrates at 420 nm (A_{420}) are shown in Table 1. Optic densities of GAJC increased by increasing storage time and temperature. When these values were plotted versus storage time, it was observed that the curve of nonenzymatic browning reaction followed a zero-order reaction. The zero-order nonenzymatic reaction occured also in AAJC stored at 37, 50 and 65 °C. On the other hand, the kinetics of nonenzymatic browning could not be determined in AAJC stored at 5 and 20 °C. As a matter of fact, regression coefficients showed that no specific colour development occured in these samples (Table 2).

The browning changes of GAJC were also observed by using the CIE colour system. Lightness values decreased by increasing storage time and temperature (Table 3). Decreasing of these values indicates that colours of samples change from orange into brown. However, when lightness values were plotted versus storage time, no fitting kinetic model can be found for nonenzymatic browning. In AAJC, stored at 5 and 20 °C, the first and the last lightness values were found to be almost the same (Table 3). Thus, the CIE colour system also showed that no colour development occurred in these samples. On the other hand, lightness values of Amasya samples, stored at 37 °C during four months, were reduced to 16.6 and 18.9% of those determined at the beginning of storage. Moreover, the variation of lightness in AAJC stored at 50° and 65 °C can be easily seen in Table 3.

Table 1
Browning index (A_{420})[a] at 65, 70 and 75°Bx of Golden Delicious and Amasya apple juice concentrates

Cultivar	°Bx	°C	Storage (week)																
			0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Golden Delicious	65	5	0.278	0.281	0.286	0.290	0.287	0.298	0.294	0.295	0.299	0.303	0.314	0.316	0.310	0.320	0.314	0.317	0.321
		20	0.295	0.294	0.299	0.328	0.333	0.362	0.356	0.369	0.374	0.361	0.380	0.389	0.392	0.412	0.411	0.418	0.420
		37	0.327	0.421	0.484	0.560	0.684	0.863	0.949	1.13	1.3	1.39	1.56	1.73	1.87	2.09	2.15	2.39	2.55
	70	5	0.242	0.247	0.248	0.270	0.265	0.274	0.271	0.262	0.276	0.278	0.281	0.280	0.282	0.291	0.290	0.290	0.292
		20	0.278	0.284	0.272	0.288	0.310	0.302	0.347	0.327	0.329	0.355	0.361	0.364	0.394	0.393	0.399	0.400	0.414
		37	0.306	0.383	0.527	0.577	0.699	0.827	0.966	1.16	1.32	1.49	1.66	1.75	1.89	2.18	2.3	2.49	2.91
	75	5	0.245	0.251	0.247	0.260	0.267	0.270	0.274	0.269	0.271	0.278	0.287	0.288	0.290	0.293	0.294	0.292	0.295
		20	0.298	0.314	0.329	0.332	0.355	0.341	0.356	0.369	0.363	0.366	0.388	0.391	0.386	0.384	0.384	0.412	0.431
		37	0.316	0.403	0.558	0.623	0.762	0.818	1.06	1.18	1.40	1.58	1.59	1.90	1.96	2.22	2.4	2.57	2.86
Amasaya	65	5	0.479	0.482	0.480	0.473	0.452	0.471	0.475	0.464	0.462	0.493	0.490	0.482	0.480	0.470	0.473	0.474	0.481
		20	0.440	0.444	0.459	0.468	0.466	0.471	0.461	0.472	0.463	0.473	0.491	0.492	0.487	0.459	0.455	0.467	0.472
		37	0.343	0.455	0.468	0.479	0.596	0.608	0.642	0.634	0.607	0.690	0.764	0.773	0.810	0.912	0.917	0.935	1.046
		50[b]	0.478	0.711	0.872	1.094	1.339	1.574	1.840										
		65[b]	0.478	1.52	3.7	6.82	11.6	17.9	21.5										
	70	5	0.490	0.517	0.525	0.538	0.546	0.508	0.511	0.509	0.499	0.495	0.492	0.512	0.509	0.501	0.504	0.514	0.524
		20	0.483	0.487	0.510	0.511	0.484	0.481	0.498	0.487	0.489	0.513	0.514	0.510	0.493	0.494	0.516	0.517	0.510
		37	0.497	0.497	0.545	0.597	0.603	0.685	0.749	0.690	0.725	0.801	0.854	0.857	0.954	0.960	1.025	1.096	1.077
		50[b]	0.525	0.679	0.869	1.08	1.38	1.611	1.811										
		65[b]	0.525	1.49	3.59	6.94	9.85	16.5	19.2										
	75	5	0.458	0.467	0.489	0.473	0.463	0.478	0.472	0.462	0.492	0.482	0.470	0.493	0.480	0.482	0.479	0.513	0.516
		20	0.476	0.464	0.503	0.477	0.476	0.512	0.478	0.480	0.523	0.503	0.511	0.512	0.512	0.508	0.490	0.497	0.513
		37	0.370	0.496	0.479	0.569	0.59	0.640	0.675	0.707	0.739	0.818	0.899	0.909	0.935	1.02	1.05	1.11	1.19
		50[b]	0.523	0.712	1.074	1.24	1.587	2.03	2.26										
		65[b]	0.523	1.84	4.96	8.77	14.2	18.0	23.3										

[a] $A_{420} > 2.000$ values were determined after dilution.
[b] Since colour change of Amasya apple juice concentrates stored at 5 and 20 °C could not be observed after a 4-month storage, 50 and 65 °C were also choosen to determine colour development in these samples for 6 weeks.

Temperature dependence of the Maillard reaction was modelled with the Arrhenius equation:

$$k = k_{0.}\ \mathrm{e}^{-E_a/RT}$$

where $k=$ rate constant; $k_0=$ pre-exponential factor; $E_a=$ activation energy (kcal/mol); $R=$ gas constant (1.987 cal/ mol K); $T=$ temperature in °K.

Activation energies over the temperature range 5–37 °C for Golden Delicious samples and 37–65 °C for Amasya samples were calculated from the slopes of Arrhenius plots shown in Fig. 2. Activation energies of GAJC and AAJC at 65, 70 and 75°Bx were found to be 21.3, 21.4 and 21.0 kcal/mol, and 33.7, 32.7 and 32.5 kcal/mol, respectively. The values within the same variety are rather close to each other; thus the influence of soluble solids content on nonenzymatic browning is not important at the applied concentrations. Lower activation energies for GAJC indicated that nonenzymatic browning reactions are favoured in these samples. The

Table 2
Regression coefficients (R^2) and rate constants (k) of zero-order Maillard reactions occuring in Golden Delicious and Amasya apple juice concentrates

Variety	Storage temperature (°C)	R^2			k		
		65°Bx	70°Bx	75°Bx	65°Bx	70°Bx	75°Bx
Amasya	5	0.0174	0.0404	0.465	0.0003	−0.0006	0.0022
	20	0.231	0.27	0.340	0.0014	0.0014	0.0021
	37	0.962	0.977	1.00	0.0380	0.0386	0.0473
	50	0.996	0.99	0.988	0.224	0.222	0.2980
	65	0.952	0.95	0.97	3.70	3.30	3.93
Golden Delicious	5	0.931	0.864	0.932	0.0027	0.0029	0.0032
	20	0.944	0.954	0.914	0.0081	0.0092	0.0066
	37	0.991	0.98	0.9870	0.142	0.156	0.1569

Table 3
Lightness (L*) values at 65, 70 and 75°Bx, of Golden Delicious and Amasya apple juice concentrates

Cultivar	°Bx	°C	Storage (week)																
			0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Golden Delicious	65	5	23.36	23.32	22.70	22.67	22.59	21.42	21.17	21.81	22.22	21.63	21.35	21.03	21.96	21.63	21.47	21.40	20.83
		20	23.36	22.08	21.45	21.69	22.37	21.05	21.68	20.90	21.84	21.34	21.32	21.67	20.42	20.48	22.01	21.44	20.17
		37	23.36	21.71	20.95	20.49	20.06	19.44	18.36	18.61	18.50	18.35	18.06	17.78	17.83	17.57	17.61	17.70	17.63
	70	5	23.30	23.60	21.95	22.14	21.91	22.32	21.69	22.33	22.69	21.46	21.88	22.60	22.40	21.59	22.32	21.90	21.57
		20	23.30	22.29	22.68	21.76	22.21	21.22	21.55	21.34	21.73	21.10	21.50	20.74	20.92	20.11	21.72	20.73	20.40
		37	23.30	21.98	21.24	19.80	19.87	19.09	18.71	18.55	18.15	18.09	18.10	17.82	17.68	17.56	17.63	17.71	17.60
	75	5	22.51	23.01	21.49	21.18	21.11	21.30	21.02	21.21	21.37	21.60	21.06	21.13	21.88	20.87	21.36	21.30	21.02
		20	22.51	21.60	20.74	21.29	21.60	20.54	21.92	20.98	21.30	21.67	21.33	21.89	20.52	20.74	21.79	20.67	19.97
		37	22.50	21.30	20.40	19.60	19.20	18.60	18.30	18.30	18.20	18.00	18.00	17.70	17.80	17.60	17.60	17.70	17.60
Amasya	65	5	22.91	22.88	23.36	22.67	23.35	23.34	22.47	23.21	22.86	22.98	22.32	22.84	23.35	22.46	22.95	22.45	22.51
		20	22.91	23.57	22.70	22.60	23.66	21.67	21.98	21.68	21.92	22.16	21.61	22.53	22.13	22.13	20.76	21.65	22.01
		37	22.91	23.15	23.26	21.91	22.40	21.10	21.08	20.62	20.68	19.94	19.69	19.73	19.08	18.90	18.82	18.50	18.56
		50[a]	22.38	21.19	19.56	18.77	18.22	17.98	17.83										
		65[a]	22.38	18.21	18.02	17.38	17.70	17.65	17.58										
	70	5	21.88	22.32	22.64	21.60	22.31	21.78	22.10	21.79	21.98	21.72	22.54	22.15	22.67	21.74	22.60	22.07	22.17
		20	21.88	22.27	21.87	21.71	22.47	21.17	21.98	21.43	22.03	21.81	22.11	21.95	21.49	22.01	20.89	21.44	21.56
		37	21.88	22.51	21.83	21.41	21.40	20.93	20.69	20.32	20.05	19.74	19.21	19.54	18.40	18.33	18.45	18.21	18.26
		50[a]	21.60	20.52	18.94	18.32	18.41	17.71	17.73										
		65[a]	21.60	18.19	17.50	17.46	17.47	17.55	17.84										
	75	5	21.87	21.34	21.83	21.76	22.91	21.91	21.37	21.66	21.97	21.17	21.56	22.21	22.50	21.64	23.04	21.70	21.89
		20	21.87	21.80	21.37	21.95	21.79	21.84	21.75	21.83	22.09	21.79	21.54	22.48	21.37	21.39	20.74	21.62	21.58
		37	21.87	22.67	22.00	21.20	20.58	20.09	19.90	19.41	19.06	18.88	18.85	18.45	18.23	18.25	18.23	18.08	18.23
		50[a]	22.26	19.43	18.46	17.92	17.78	17.68	17.66										
		65[a]	22.26	17.86	17.54	17.49	17.62	17.51	17.58										

[a] Since colour change of Amasya apple juice concentrates stored at 5 and 20 °C could not be observed after a 4-month storage, 50 and 65 °C were also chosen to determine colour development in these samples for 6 weeks.

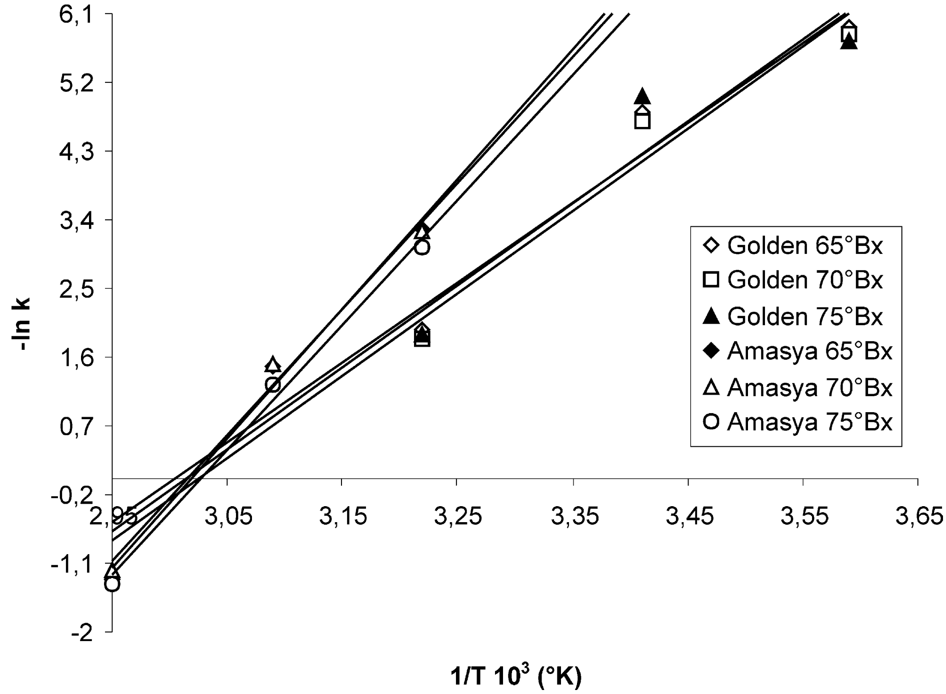

Fig. 2. Arrhenius plots of Golden Delicious and Amasya concentrates at different concentrations and temperatures.

reason why no nonenzymatic browning kinetic was observed in AAJC stored at 5 and 20 °C is the high activation energy for this reaction in the Amasya variety. The activation energies determined in this study are in agreement with other studies. Activation energies for apple juice with heat treatment at 5–37 °C and 37–130 °C have been found to be 19.3 and 27 kcal/mol, respectively (Petriella, Resnik, Lozano, & Chirife, 1985).

In this study, nonenzymatic browning was considered as the Maillard reaction, since it is the most important cause of browning in apple juice (Toribio & Lozano, 1984). Previous studies of the Maillard reaction mechanism have revealed that this reaction fits zero-order, first-order and parabolic kinetic models. In model systems, Peterson, Tong, Ho, and Welt (1994) and Stamp and Labuza (1983) reported that Maillard browning follows a zero-order reaction. On the other hand, a first-order Maillard reaction in a glucose-lysine model system was reported by Cerrutti, Resnik, Seldes, and Fontan (1985). Also, Toribio and Lozano (1984) have revealed that this reaction follows a first-order reaction in apple juice concentrates during storage. A parobolic kinetic model of Maillard reaction of peach juice concentrate was also determined by Buedo, Elustondo, and Urbicain (2001).

The mechanism of browning in AAJC stored at 5° and 20 °C, could not be determined. Therefore, it is suggested that the Maillard reaction occurs preferably in GAJC. As a matter of fact, Table 2 shows that the rate of this reaction in Golden Delicious samples is faster than in Amasya samples. The difference in browning of samples might be attributed to the differences of chemical composition of apple juices. Although the Maillard reaction occurs between reducing sugars and aminoacids, the initial rate of this reaction depends on many factors, such as material composition. The reactivity of aldoses is higher than ketoses in browning systems. Moreover, the type of amino acid affects the Maillard reaction browning. Basic aminoacids have more reactivity than acidic types (Namiki, 1988). Thus, reducing sugars and aminoacids in Golden Delicious apple juice might have more reactivity in the Maillard reaction than those in Amasya apple juice. As a matter of fact, the main sugar in Golden Delicious apple juice is glucose (an aldose), while the major reducing sugar in Amasya apple juice is a ketose, fructose (Karadeniz & Ekşi, 2002).

3.2. HMF formation

The amount of 5-HMF did not change significantly in all the concentrates stored at 5 °C during 4-months, except for 70°Bx of Golden Delicious samples (Table 4). This difference might be due to analytical errors. Solomon, Svanberg, and Sahlström (1995) also observed that HMF and furfural contents did not change significantly during 52-day storage of orange juices at 8 °C. At the storage temperature of 20 °C, HMF levels of GAJC

Table 4
HMF variation of Golden Delicious and Amasya samples at different concentrations and different temperatures

Variety	Storage (month)	HMF (mg/kg)								
		5 °C			20 °C			37 °C		
		65°Bx	70°Bx	75°Bx	65°Bx	70°Bx	75°Bx	65°Bx	70°Bx	75°Bx
Golden Delicious	0	0.17	0.18a	0.62	0.17a	0.18a	0.62a	0.17a	0.18a	0.62a
	1	0.17	0.18a	0.62	0.52ac	0.56ac	0.62a	64b	74b	101b
	2	0.52	0.18b	0.62	0.87c	0.93c	1.44a	160c	237c	338c
	3	0.52	0.56ab	1.03	1.56b	2.07b	2.70b	387d	529d	730d
	4	0.52	0.93b	1.03	2.96d	3.96d	4.37c	706e	835e	963e
Amasya	0	0.17	0.56	0.66	0.17a	0.56a	0.66	0.17a	0.56a	0.66a
	1	0.17	0.56	0.66	0.52ac	1.31ac	1.10	14b	15b	25b
	2	0.52	0.93	0.66	0.52ac	1.31ac	1.10	38c	36c	141c
	3	0.52	1.31	1.54	1.21bc	1.68bc	1.98	80d	78d	153d
	4	0.52	1.31	1.54	1.92b	2.07bc	1.98	158e	129e	190e

Means within a column followed by different letters are significantly different ($P < 0.05$).

Table 5
Correlations between browning index (A_{420}), lightness (L) and HMF

	(°C)	°Bx	Correlation coefficients (r)		
			A_{420}-L	A_{420}-HMF	L-HMF
Golden Delicious	5	65	−0.832*	0.873	−0.771
		70	−0.594*	0.757	−0.654
		75	−0.568*	0.864	−0.189
	20	65	−0.630*	0.908*	−0.907*
		70	−0.801*	0.937*	−0.905*
		75	−0.517*	0.901*	−0.926*
	37	65	−0.858*	0.974*	−0.754
		70	−0.824*	0.992*	−0.763
		75	−0.812*	0.985*	−0.783
Amasya	5	65	−0.303	0.369	−0.341
		70	0.091	−0.031	0.526
		75	−0.016	0.631	−0.065
	20	65	−0.291	0.686	−0.542
		70	−0.247	0.853	−0.441
		75	−0.002	0.617	−0.804
	37	65	−0.942*	0.958*	−0.918*
		70	−0.976*	0.982*	−0.936*
		75	−0.919*	0.935*	−0.968*
	50	65	−0.922*		
		70	−0.895*		
		75	−0.784*		
	65	65	−0.540		
		70	−0.490		
		75	−0.526		

* $P < 0.05$.

significantly ($P < 0.05$) increased at the end of storage time and this increase can be especially seen at the third and the fourth months. AAJC at 20 °C also showed significant increases, except 75 °Bx of AAJC. There was a significant increase of HMF at the end of 4-months storage at 37 °C. The increase of HMF between 5 and 37 °C was approximately 1000 times for GAJC, whereas it was only 142 times for AAJC. Similar results have also been reported by Lee and Nagy (1988a). They found that HMF did not increase in canned grapefruit juices stored at 10 °C, while high accumulation HMF occurred when stored at 50 °C. Babsky et al. (1986) also reported that, after 100 days storage, HMF content of apple juice concentrate at 37 °C was 44 mg/100 g. In this study, accumulation of HMF in GAJC was found to be greater than in AAJC due to rapid occurrence of the Maillard reaction in Golden Delicious samples. However, sugar degradation might also occur in the formation of HMF.

The correlation coefficients among browning index, CIE $L^*a^*b^*$ and HMF values are evaluated in Table 5. As can be seen, correlation coefficients between these variables are changeable according to apple variety, storage temperature and degrees Brix. For example, a negative relationship between A_{420} and lightness values was observed in all GAJC. Similar relationships were also found in AAJC stored at 37 and 50 °C, while no correlation was observed in AAJC at 65 °C. In addition to this, accumulation of HMF in GAJC was significantly correlated with A_{420} values except at the lowest storage temperature. Similarly, there is significant correlation found between L and HMF values only in GAJC at 20 °C and AAJC at 37 °C.

References

Anonymous. (1984). International federation of fruit juice producer methods. *Analysen-Analyses. Zug, Switzerland*, *12*(1–2), 1962–1974.

Arnoldi, A., Arnoldi, C., Baldi, O., & Griffini, A. (1988). Flavor components in the Maillard reaction of different aminoacids with fructose in cocoa butter- water. Qualitative and quantitative analysis of pyrazines. *Journal of Agricultural and Food Chemistry*, *36*, 988–992.

Ashoor, S. H., & Zent, J. B. (1984). Maillard browning of common aminoacids and sugars. *Journal of Food Science*, *49*, 1206–1207.

Babsky, N. E., Toribio, J. L., & Lozano, J. E. (1986). Influence of storage on the composition of clarified apple juice concentrate. *Journal of Food Science*, *51*(3), 564–567.

Baxter, J. H. (1995). Free amino acid stability in reducing sugar systems. *Journal of Food Science*, *60*(2), 405–408.

Buedo, A. P., Elustondo, M. P., & Urbicain, M. J. (2001). Non-enzymatic browning of peach juice concentrate during storage. *Innovative Food Science & Emerging Technologies*, *1*, 255–260.

Cerrutti, P., Resnik, S. L., Seldes, A., & Fontan, C. F. (1985). Kinetics of deteriorative reactions in model food systems of high water activity: glucose loss, 5-Hydroxymethylfurfural accumulation and fluorescence development due to nonenzymatic browning. *Journal of Food Science*, *50*, 627–630.

Clegg, K. M. (1964). Non-enzymic browning of lemon juice. *Journal of the Science of Food and Agriculture*, 15, 878–885.

Daniel, J. R., & Whistler, R. L. (1985). Carbohydrates. In O.R. Fennama (Ed.), *Food chemistry* (2nd ed.) (pp. 70–137). New York: Marcel Dekker.

Einarsson, H. (1987). The effect of pH and temperature on the antibacterial effect of Maillard reaction products. *Lebensmittel Wissenschaftliche und Technology*, *20*, 56–58.

Eskin, N. A. M. (1990). Biochemistry of food processing: Browning reactions in foods. In *Biochemistry of foods*, (2nd ed. pp. 240–295). London: Academic Press.

Friedman, M., & Molnar-Perl, I. (1990). Inhibition of browning by sulfur aminoacids. I. heated amino acid-glucose systems. *Journal of Agricultural and Food Chemistry*, *38*, 1642–1647.

Gazzani, G., Vagnarelli, P., Cuzzoni, M. T., & Mazza, P. G. (1987). Mutagenic activity of the Maillard reaction products of ribose with different aminoacids. *Journal of Food Science*, *52*(3), 757–760.

Ibarz, I., Gonzales, C., Esplugas, S., & Miguelsanz, R. (1990). Non-enzymatic browning kinetics of clarified peach juice at different temperatures. *Confructa*, *34*, 152 - 159.

Karadeniz, F., & Ekşi, A. (2002). Sugar composition of apple juices. *European Food Research and Technology 215*(2), 146–149.

Lee, H. S., & Nagy, S. (1988a). Quality changes and nonenzymic browning intermediates in grapefruit juice during storage. *Journal of Food Science*, *53*(1), 168–172.

Lee, H. S., & Nagy, S. (1988b). Relationship of sugar degradation to detrimental changes in citrus juice quality. *Food Technology*, *11*, 91–97.

Lingnert, H., & Waller, G. R. (1983). Antioxidants formed from histidine and glucose by the Maillard reaction. *Journal of Agricultural and Food Chemistry*, *31*, 27–30.

Lingnert, H., & Hall, G. (1986). Formation of antioxidative Maillard reaction products during food processing. In M. Fujimaki, M. Namiki, & H. Kato (Eds.), *Amino-carbonyl reactions in food and biological systems* (pp. 363–371). Amsterdam: Elsevier.

Martins, S. I. F. S., Jongen, W. M. F., & Van Boekel, M. A. J. S. (2001). A review of Maillard reaction in food and implications to kinetic modelling. *Trends in Food Science and Technology*, *11*, 364–373.

Nakama, A., Kim, E., Shinohara, K., & Omura, H. (1993). Formation of furfural derivatives in amino-carbonyl reaction. *Bioscience Biotechnology Biochemistry*, *57*(10), 1757 - 1759.

Namiki, M. (1988). Chemistry of Maillard reactions: Recent studies on the browning reaction mechanism and the development of antioxidants and mutagens. In C. O. Chichester, & B. S. Schweigert (Eds.), *Advances in food research, vol. 32* (pp. 116–184). London: Academic Press.

Ninomiya, M., Matsuzaki, T., & Shigematsu, H. (1992). Formation of reducing substances in the Maillard reaction between D-glucose and γ-aminobutyric acid. *Bioscience Biotechnology Biochemistry*, *56*(5), 806–807.

O'brien, J. (1996). Stability of trehalose, sucrose and glucose to nonenzymatic browning in model systems. *Journal of Food Science*, *61*(4), 679–682.

Peterson, B. I., Tong, C., Ho, C., & Welt, B. A. (1994). Effect of moisture content on Maillard browning kinetics of a model system during microwave heating. *Journal of Agricultural and Food Chemistry*, *42*, 1884–1887.

Petriella, C., Resnik, S. L., Lozano, R. D., & Chirife, J. (1985). Kinetics of deteriorative reactions in model food systems of high water activity: colour changes due to nonenzymatic browning. *Journal of Food Science*, *50*, 622–626.

Pokorny, J. (1991). Natural antioxidants for food use. *Trends in Food Science and Technology*, *2*(9), 223–227.

Resnik, S., & Chirife, J. (1979). Effect of moisture content and temperature on some aspects of nonenzymatic browning in dehydrated apple. *Journal of Food Science*, *44*(2), 601–605.

Shaker, E. S., Ghazy, M. A., & Shibanoto, T. (1995). Antioxidants activity of volatile browning reaction products and related compounds in a hexanol/hexanoic acid system. *Journal of Agricultural and Food Chemistry*, *43*, 1017–1022.

Shinohara, K., Kım, E. H., & Omura, H. (1986). Furans as the mutagens formed by amino-carbonyl reactions. In M. Fujimaki, M. Namiki, & H. Kato (Eds.), *Amino-carbonyl reaction in food and biological systems* (pp. 353–361). Amsterdam: Elsevier.

Solomon, O., Svanberg, U., & Sahlström, A. (1995). Effect of oxygen and flourescent light on the quality of orange juice during storage at 8 °C. *Food Chemistry*, *53*, 363–368.

Stamp, J. A., & Labuza, T. P. (1983). Kinetics of the Maillard reaction between aspartame and glucose in solution at high temperatures. *Journal of Food Science*, *48*, 543–547.

Toribio, J. L., & Lozano, J. E. (1984). Nonenzymatic browning in apple juice concentrate during storage. *Journal of Food Science*, *49*, 889–892.

Umano, K., Hagi, Y., Nakahara, K., Shyoji, A., & Shibamoto, T. (1995). Volatile chemicals formed in the headspace of a heated D-glucose/L-cycteine Maillard model system. *Journal of Agricultural and Food Chemistry*, *43*, 2212–2218.

Wakabayashi, K., Takahashi, M., Nagao, M., Sato, S., Kinae, N., Tomita, I., & Sugimura, T. (1986). Quantification of mutagenic and carcinogenic heterocyclic amines in cooked foods. In M. Fujimaki, M. Namiki, & H. Kato (Eds.), *Amino-carbonyl reactions in food and biological systems* (pp. 363–371). Amsterdam: Elsevier.

Yaylayan, V. (1990). In search of alternative mechanisms for the Maillard reaction. *Trends in Food Science and Technology*, *1*(7), 20–22.