GIDA (1989) 14 (6) 343 - 346

Kinetics Of Nonenzymatic Browning in Apple Juice Concentrate

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ABSTRACT

Kinetics of nonenzymatic browning in apple juice concentrate was investigated by following absorbance at 420 nm between the temperatures 338 - 358 K. The soluble solids content ranged from 55 to 69°Brix. Brown color formation was found to increase with both temperature and soluble solids content. A zero - order kinetics was observed after an initial lag period and temperature dependence was described by the Arrhenius relationship with activation energies ranging from 47.5 to 29.6 kJ.mol^{-1} for concentrates from 55 to 69°Brix.

ÖZET

ELMA SUYU KONSANTRESİNİN ENZİMSİZ KARARMA KİNETİĞİ

Elma suyu konsantresinin enzimsiz kararma kinetiği 338 - 358 K arasında 420 nm deki soğurma ölçümlerinin izlenmesiyle incelendi. Çözünebilir katı miktarı 55°Briks'ten 69°Briks'e kadar değiştirildi. Kararmanın oluşumunun hem sıcaklık hem de çözünebilir katı miktarı ile arttığı anlaşıldı. Bir başlangıç reaksiyon gecikmesinden sonra sıfır dereceli reaksiyon kinetiği gözlendi ve sıcaklığa bağlılığın Arrhenius ilgisi ile tarifi sonucu aktivasyon enerjilerinin 55°Briks'ten 69°Briks'e kadar olan konsantrelerde 47.5 ile 29.6 kJ.mol^{-1} arasında değiştiği bulundu.

INTRODUCTION

Accumulation of brown color in fruit juice concentrates during storage is largely due to the occurrence of nonenzymatic browning reactions (1.2). These reactions in citrus fruit juice concentrates involve to a great extent the products of ascorbic acid oxidation (3.4). However, in juice concentrates of fruits such as apples and pears. Maillard type browning, which occurs between the reducing sugars and α - amino groups of amino acids or proteins, is the main cause of darkening during storage (4-8).

Maillard reaction rate depends on several factors including temperature, water activity. pH, and reactant concentration (9-11). The kinetics of brown color formation is generally followed by measuring the absorbance af 420 nm which is a simple and rapid method of analysis. Previous studies have shown that Maillard browning reaction follows a zero order kinetics (12) and occurs at a higher rate at alkaline pH values (13).

The objective of this study was to examine the effect of soluble solids content on the rate of nonenzymatic browning in apple juice concentrate between the temperatures 338 - 358 K.

MATERIALS AND METHODS

Apple juice concentrate was obtained from Güneysu Ltd., Dörtyol, as a 69°Brix syrup. Soluble solids content was determined using an Abbe type refractometer. The pH of the concentrate was 3.93. Other concentrates; 62. 59 and 55°Brix, were prepared by diluting the original concentrate with double distilled water. These concentrates were placed in 1 - L glass bottles with no head space, covered with aluminum foil to exclude the effect of light and stored in refrigerator until use. Selected study temperatures were 338. 343, 348, 353 and 358 K. The thermostat used in experiments was mainly a cylindrical copper container (radius: 25 cm, height: 26.5 cm), which was jacketed with another cylindrical copper container (radius: 27.5 cm. height: 31 cm). The space between the two containers was filled with glass wool, and a thick foam plate was used to cover the top of thermostat. Temperature control was achieved by a Heidolph model temperature controller to ± 0.1°C.

Measurement of nonenzymatic browning procedure. Apple juice concentrate at a selected soluble solids content was filled into a 250 - mL volumetric flask and placed in the thermostat which was adjusted to a selected temperature. In a separate experiment, the time required for 250-mL concentrate to come into thermal equilibrium with the water in thermostat was determined. Therefore the sample taken from the concentrate after this extent of time was named as the sample at zero time. 10-mL sample was withdrawn from the flask in about 10 min. intervals during a total reaction time of about 120 min. The sample was quickly cooled with tap water, diluted when necessary and the absorbance was measured at 420 nm with a Beckman Model 24 UV-spectrophotometer using double distilled water as the reference.

RESULTS AND DISCUSSION

Absorbance measurements showed that brown color formation at each different concentrate was intensified as the temperature was increased from 338 to 358 K. Also, browning was found to increase with increasing soluble solids content of concentrate at each temperature. Another observation at each reaction condition was the occurrence of an initial lag period of about 30 min. This initial lag period most probably involves the production of colorless intermediates in reaction. Such lag periods were also observed previously by some workers as Warmbier et. al. (17) in a solid intermediate moisture model food system. Reyes et. al. (18) in sugar-glycine systems, and Singh et. al. (8), in intermediate moisture apples. Beveridge and Harrison (5), on the other hand, reported no lag period during the nonenzymatic browning of pear juice concentrate. The processing conditions of fruit juice concentrates must be effective and thus, browning could have been initiated during pasteurization and concentration steps. In this case, of course, no initial lag period will be observed.

Occurrence of nonenzymatic browning measured as absorbance at 420 nm versus time at 358 K is shown in Figure 1. Similar plots were obtained at other temperatures. Rate constants of the reaction were calculated from absorbance-time plots assuming a zero order kinetics depending on the observation of linear absorbance-time relationships at each temperature and soluble solids content conditions. They are given in Table 1.

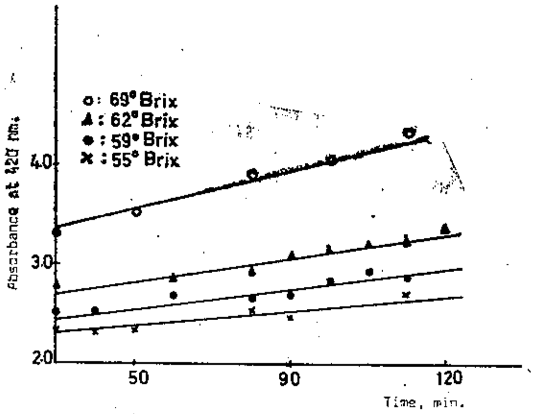

Figure 1. Nonenzymatik browning of apple juice concentrate at 358 K

Table1. Rate constants for nonenzymatic browning in apple juice concentrate.

T (K)	Rate constant (A_{420} . min^{-1}) 55°Brix	59°Brix	62°Brix	69°Brix
338	0.0015	0.0022	0.0023	0.0042
343	0.0020	0.0029	0.0036	0.0043
348	0.0030	0.0033	0.0042	0.0057
353	0.0034	0.0040	0.0056	0.0060
358	0.0045	0.0056	0.0064	0.0075

Activation energies over the temperature range 338-358 K were calculated from the slopes of the Arrhenius plots shown in Figure 2. Tablo 2 represents the values of activation energies for the nonenzymatic browning of each concentrate. Correlation coefficient, r, for each Arrhenius plot is also included in the same table.

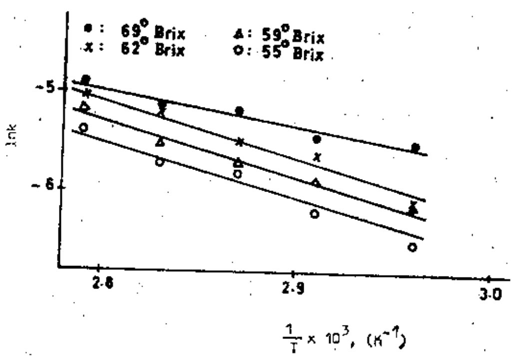

Figure 2. Arrhenius plots for nonenzymatic browning apple juice concentrates

Tablo 2. Activation energies for nonenzymatic browning in apple juice concentrate.

Soluble solids content (°Brix)	Activation energy ($kJ.mol^{-1}$)	r
55	47.8	0.992
59	49.8	0.988
62	57.3	0.984
69	29.7	0.969

Activation energies for 55, 59 and 62°Brix concentrates are rather close to each other. However, 69°Brix concentrate has a lower activation energy which indicates a lower sensitivity of reaction rate to temperature changes compared to the reactions in other concentrates. Literature reports for this kinetic parameter are larger than the values of it obtained in this study. In a related work in this laboratory, activation energies for the nonenzymatic browning reaction of lysine with fructose, glucose and lactose were determined to be 116.6, 153.1 and 162.5 $kJ.mol^{-1}$ respec tively (14), and those results were in agreement with other literature reports (15, 16) which deal with aqueous model food systems. Nonenzymatic browning reactions occur by lower activation energies in foods compared to those in model food systems. Toribio and Lozano (7) indicated that at lower temperatures, an activation energy of 80.8 $kJ.mol^{-1}$ was observed for the brown color formation in 65°Brix apple juice concentrate. The value of the activation energy was found to decrease to 65.8 $kJ.mol^{-1}$ when 75°Brix apple juice concentrate was used in experiments. Deveridge and Harrison (5) reported 91.6 $kJ.mol^{-1}$ as the average activation energy for nonenzymatic browning in pear juice concentrates ranging between 45.2 and 72.5°Brix over the temperatures 323 and 353 K. It is evident that, the rate of nonenzymatic browning in fruit juice concentrate is affected by the kind and chemical composition of fruit, temperature range of study, soluble solids content of concentrates and the processing conditions during juice preparation.

The variation of zero-order rate constants with the soluble solids content of concentrates of this study af five different temperatures is presented in Figure 3.

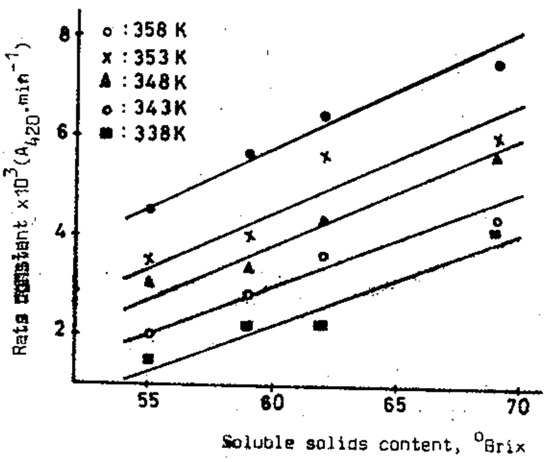

Figure 3. Variation of zero-order nonenzymatic browning rate constants with the soluble solids content of apple juice concentrate.

A close examination of data points in Figure 3 might seem to indicate an exponential relationship between the rate constants and soluble solids content especially at temperatures 343 K and 358 K. However, similar relationship is not present at other temperatures. Eichner and Karel (19) in their study of Maillard reaction at low temperatures in a liquid model system of glycine-glucose which contained the humectant glycerol, had observed an exponential relationship between the browning rate and water activity. They had reported that the maximum browning occured at a water activity of 0.4 Similar observation was also noted by Warmbier and his friends

(17). Beveridge and Harrison (5). however, found that the rate of browning increased linearly with water activity at high temperatures. When the date of the present work at all temperatures are treated by the method of linear least squares, correlation coefficients of 0.973, 0.975, 0.984, 0.925 and 0.988 were obtained for the data at 338, 343, 348, 353 and 358 K, respectively. Therefore, it seems best to assume that the rate of nonenzymatic browning reaction in apple juice concentrate increases linearly with the soluble solids content of concentrate at all temperatures studied.

It can be seen from Figure 3 that temperature and soluble solids content operate in the same direction on rate constant. That is, the rate constant increases with temperature at a constant soluble solids content and with soluble solids content at a constant temperature. Hence, it is very difficult to say which factor is more important on the rate constant. However, it can definitely be stated that if apple juice concentrates are to be stored for a long time, they should be diluted to lower °Brix values and should be maintained at low temperatures.

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The authors thank the Güneysu Ltd. for providing the apple juice concentrate used in this study.

KEYWORDS : Nonenzymatic browning. Maillard reaction, Apple juice.