Effects of Influence Parameters on Color Formation in Glucose Syrups during Storage

Ahmadreza Raisi[i]; Abdolreza Aroujalian[ii*]

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ABSTARCT

Effects of pH, temperature, and syrup concentration on color formation in glucose syrups were studied and the shelf life of syrups under various conditions was estimated. Temperatures of 5, 25, and 45 ºC, pH values of 4, 5, and 6 as well as concentrations of 30, 40, 50, 60, 70, and 80 ºBrix were examined. After 26 weeks no significant color changes were observed at 5 ºC. At 45 ºC, color formation rate was highest and after 2 weeks color changes were visible, and at 15th week syrup color was completely brown. At 25 ºC, color formation rate was low and at week 18 color changes were visible. At pH 5, rate of browning was lower than at other pH values. Increasing the syrup concentration up to 70 ºBrix enhanced the color formation rate but higher concentrations decreased the color formation rate. The kinetics of color formation was studied and rate constants and activation energies were calculated.

KEYWORDS

Glucose syrups; Browning; Maillard reaction; Reaction kinetic; Shelf life

1. INTRODUCTION

Non-enzymatic browning reactions (Maillard reactions) between reducing sugars and protein/amino acids occur during processing and storage of many foods. Maillard reactions are one of the most complex reactions involving food components of low molecular weight. Color and colorless components can be produced by Maillard reactions in some foods. Formation of brown color represents only one feature of these diverse reactions. Browning must be controlled to avoid undesirable products, such as in the case of certain canned fruits. In some case this brown color is highly desirable, for example, in the baking of bread where a brown crusty loaf is acceptable, or in the making of toffee [1].

Glucose syrups are refined, concentrated aqueous solutions of D(+)-glucose, maltose, and other polymers of D(+)-glucose obtained by the controlled partial hydrolysis of edible starch [2]. Glucose syrups are added to a very wide variety of food products, which utilize such properties as bodying effect, viscosity, and osmotic pressure of the syrups to a greater or lesser extent [3]. Colorlessness is a temporary property of glucose syrups; soon the Maillard browning reactions cause formation of first yellow, then brown coloration, either when stored or processed. Hydroxymethylfurfural (HMF) and 2-(2-hydroxyacetal)-furan (HAF) are formed in yields, which increase with color formation in glucose syrups. These minor components are more likely formed via an Amadori compound in Maillard reactions rather than by the thermal degradation of sugars [4].

In previous work [5], the influence of modified atmospheric packaging on glucose syrup shelf life was investigated. In this work, the effects of some parameters such as pH, temperature, and syrup concentration on color formation in glucose syrups are studied and the shelf life of syrups under various conditions is estimated.

The rest of the paper is organized as follows. Section II briefly the materials and methods needed in the paper. Section III presents simulation results. Finally section IV concludes the paper.

2. MATERIALS AND METHODS

Glucose syrups with 42 DE, 82.5 ºBrix, and pH 4.78 were supplied by Glucosan Co. (Tehran, Iran). Chloride acid and sodium hydroxide were obtained from Merck (Darmstadt, Germany) and were used for pH adjustment.

The pH was measured using a Jenway pH-meter

i A. Raisi is with the Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran (e-mail: ahmadreza@aut.ac.ir).
ii * Corresponding Author, A. Aroujalian is with the Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran, and Food Process Engineering and Biotechnology Research Center, Amirkabir University of Technology, Tehran, Iran (e-mail: aroujali@aut.ac.ir).

(Dunmow, Essex, UK) which was calibrated with pH 3 and 7 buffers according to the method CRA E48 of the Corn Refiners Association [6].

The soluble solids were measured in degrees Brix with an Abbe refractometer at 25 ºC according to the method 1743 of ISO [7]. The Brix data were related to the total solids content of the syrups using the Critical Data Tables prepared for syrups with known DE values.

Color indices of the syrups were measured by their absorbance at 295 nm on a Perkin-Elmer model 550 UV/VIS double-beam spectrophotometer (Wellesley, USA). The wavelength used was based on the maximum wavelength obtained from spectral scans of aged syrups [8].

The protein contents were determined with a Kjeltec Auto 1030 Analyzer (Foss Tecator AB, Hoganas, Sweden) according to the method of ISI 24-1e [9].

The carbohydrate profiles were determined with a Jasco high-pressure liquid chromatography (HPLC) instrument (Dunmow, Essex, UK) with a carbohydrate analysis column. The solvent system was a mixture of acetonitrile and deionized water (80/20), and the flow rate was 2 ml/min.

The glucose syrups used were produced from acid hydrolysis of corn starch. These syrups had pH of 4.78, 42 DE, and 82.5 ºBrix. The physical and chemical characteristics of these syrups are presented in Table 1. For preparation of samples, the syrups were first diluted and adjusted to pH values of 4, 5, and 6; then they were concentrated to 82.5 °Brix by vacuum evaporation and filled into polyethylene jars and capped. These samples were stored at 5, 25, and 45 °C.

Syrups with lower concentration (30, 40, 50, 60, 70, and 80 °Brix) were prepared by appropriate dilution of the concentrated syrup which was subsequently filled into glass jars, capped, and sterilized. These samples were stored at ambient temperature (25 °C).

TABLE 1

CHEMICAL AND PHYSICAL CHARACTERISTICS OF GLUCOSE SYRUPS

Characteristic	Value
DE	42
pH	4.78
Soluble solids	82.5%
Glucose	24.38%
Maltose	13.87%
Protein	0.033%
Ash	0.20%

3. RESULTS AND DISCUSSION

Browning rates were measured in term of absorbance change intensity at 295 nm as a function of time. During storage of glucose syrups, Maillard reactions cause color pigment formation; and at the end of storage dark brown color was observed. This color corresponded to an absorbance value of 3.72. At an absorbance value of 0.9, syrup color was light yellow color.

The effect of temperature on browning rate of glucose syrups with pH 5 is shown in Fig. 1. As shown, the fastest browning rates occurred in the syrups stored at 45 °C, whereas the syrups stored at 5 °C had the lowest browning rate.

Many researchers have studied influence of temperature on browning rate. Maillard [10] reported an enhancement in the rate of browning with increasing temperature due to the increase in reactivity between sugars and amino groups.

In the investigation of the temperature effects on the browning rate it is more conventional to determine the Q10 value. This is defined as amount of increase or decrease in the reaction rate for every 10 °C change in temperature. The Q10 value is related to the activation energy and varies depending upon which stage the Maillard reaction is being measured and the temperature range looked at. For example, when the initial step has a Q10 of 2, then the formation of flavor intermediates has a value of 4-6, depending on the type of intermediate. The Q10 for brown pigment formation has been determined to be between 3 and 8. Thus, the Maillard reaction has a relatively high Q10 value of 2-8 [11].

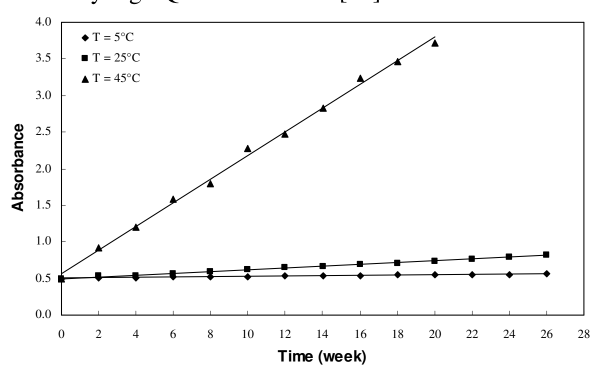

Figure 1: Influence of temperature on browning rate in glucose syrups with pH 5.

Most quality-related reaction rates are either zero-order or first-order, and statistical differences between the two types may be insignificant [12]. At temperatures up to 60 °C, browning rate is normally a zero-order reaction. At higher temperatures, changes may follow a first-order reaction [13]. The error in the value of the reaction rate constant due to the order of the reaction chosen is less than 5% since the calculated statistical difference between zero and first is small [14].

Zero-order reaction kinetics was used to evaluate the data, since the regression analysis of absorbance values and time gave a linear relationship. Thus,

$$-\frac{dC}{dt}=k \quad \text{or} \quad C=C_0-kt \qquad (1)$$

where C is the concentration at time t, C_0 is the concentration at zero time and k is a rate constant.

The temperature-dependence of a reaction rate constant is often described by the well-known Arrhenius equation:

$$k=A.\exp(-E/RT) \qquad (2)$$

where k is the rate constant, A is the so-called frequency factor, E is the activation energy, R is the gas constant (8.314 J/mol.K), and T is the absolute temperature (K).

By plotting the logarithm of rate constant against inverse of absolute temperature (Arrhenius plot), activation energy and frequency factor can be determined. In the Arrhenius plot, the slope and intercept values were obtained using the well-known least-squares linear regression. The intercept yields the frequency factor and the slope, $-\frac{E}{R}$ was used to calculate the activation energy for the zero-order reactions.

Arrhenius plots for syrups with various pH values are shown in Fig. 2 and k, A, E, and shelf life is presented in Table 2 for syrups with different pH and temperature values.

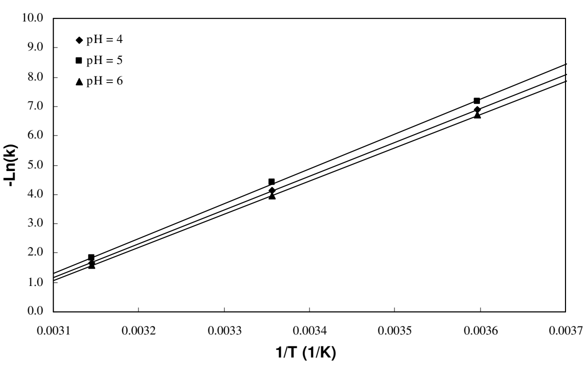

Figure 2: Arrhenius plot for browning reaction in glucose syrups.

The effects of pH on brown color formation in syrups stored at 25 and 45 °C are shown in Fig. 3 and Fig. 4, respectively. As shown in these figures, at both storage temperatures the lowest browning rate was obtained with syrups having pH 5 was whereas the browning rate for syrups with pH 6 was the highest.

The effect of pH on the Maillard reaction in model systems has been studied at various pH ranges, namely pH 4-6 [15], pH 5-7 [16], pH 5.5-7.5 [17], and pH 6-12 [18]. Most of these studies showed enhanced browning rates with increasing pH, however some studies [19] showed different roles for pH in Maillard reactions.

The effect of pH may be attributed to three facts: 1) increasing the pH enhances the reactivity of amino acids and sugars because the open chain form of sugar and the unprotonated form of the amino groups considered to be the reactive forms, are favored at higher pH, 2) formation of HMF, one of the main intermediates in color pigment formation in Maillard reactions, decreases with increasing pH [20], and 3) enolization of glucose to fructose at higher pH may also increase the rate of non-enzymatic browning [21].

The effect of syrup concentration on color formation is shown in Fig. 5, which indicates that the color formation rate has a maximum at a concentration of approximately 70 °Brix. The influence of concentration on browning rate at high concentration can be related to solute mobility and diffusion limitation, whereas at low concentration this effect may be related to dilution effect. As concentration is decreased, dilution effect decreases the browning rate. For concentrations above maximum points, mobility can be limited then the probability of amino acids and reducing sugars to make contact will decrease, thus the color formation rate will decrease.

TABLE 2

EFFECT OF TEMPERATURE AND pH ON THE REACTION RATE, RATE CONSTANT, ACTIVATION ENERGY AND SHELF LIFE OF GLUCOSE SYRUPS

pH	$(mol/cm^3.s)$ k			Time (week) to abs.=0.9		Time (week) to abs.=3.72		(kJ/mol) E	$A*10^{-14}$	R^2
	5 ºC	25 ºC	45 ºC	25 ºC	45 ºC	25 ºC	45 ºC			
4	0.0076	0.0158	0.1871	25.2	1.5	203.7	16.6	95.55	21.82	0.9956
5	0.005	0.0122	0.1616	32. 9	2.1	264.0	19.5	98.57	9.40	0.9821
6	0.0092	0.0191	0.2065	21.5	1.3	169.9	15.0	94.10	2.44	0.9906

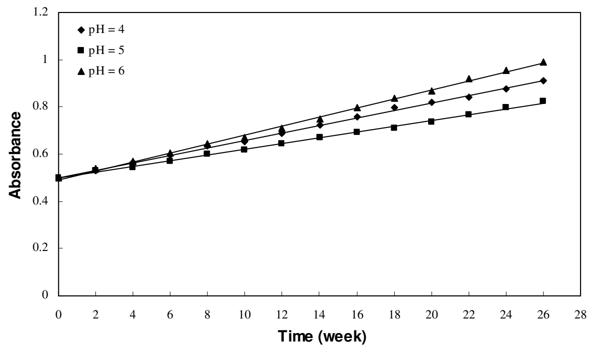

Figure 3: Influence of pH on browning rate in glucose syrups stored at 25 ºC.

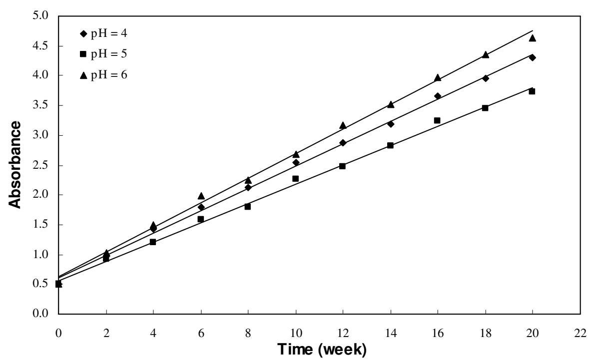

Figure 4: Influence of pH on browning rate in glucose syrups stored at 45 ºC.

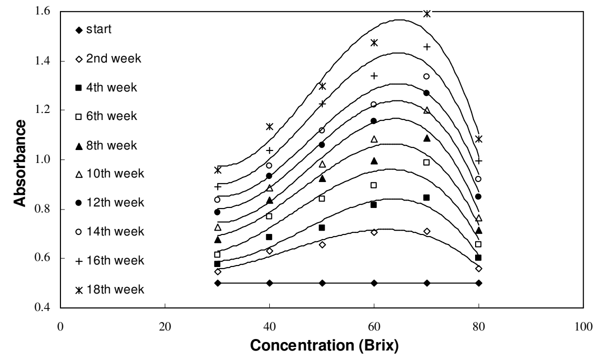

Figure 5: Influence of concentration on browning rate in glucose syrups with pH 5 stored at ambient temperature.

4. Conclusions

Brown color formation in glucose syrups stored under the conditions used in these experiments was found to follow zero-order kinetics. As expected, an increase in temperature enhances the browning rate of glucose syrups. For syrups stored at 25 and 45 ºC, the rates of browning at pH 5 were lower than at other pH values. Thus, the shelf life at this pH was higher than at the other pH values. Therefore, in this work the best temperature and pH for storage of glucose syrups was found to be 25 ºC and 5, respectively. Increasing concentration can reduce the browning rate in glucose syrups during storage, however this has no commercial interest because of difficulty with high viscosity.

A particular application of these results could be to use the data obtained in this work to estimate the shelf life of glucose syrups with the same properties under any storage temperature.

5. Acknowledgment

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