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Kinetics of non-enzymatic colour development in glucose syrups during storage

A. Bostan & D. Boyacıoğlu

Food Engineering Department, Istanbul Technical University, 80626 Istanbul, Turkey

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Kinetics of non-enzymatic colour development in glucose syrups after 13 weeks storage at 25, 35, 45 and 55°C were studied and the shelf lives of syrups under study were estimated. Syrups with two different dextrose equivalents (38 and 59 DE) at three different pH values (4.0, 4.5 and 5.0) were examined. Syrups stored at 25 and 35°C were not taken into consideration due to minor changes observed during 13 weeks of storage. The longest acceptable shelf life at 55°C was about 13.9 weeks at pH 4.0 and the shortest, 11.5 weeks at pH 5.0. For syrups stored at 45°C, the longest shelf life was observed to be 26.2 weeks at pH 4.0 and the shortest 17.3 weeks at pH 5.0. A practical application of these results could be to use the data to estimate the shelf life of glucose syrups with the same composition under any storage temperature. © 1997 Elsevier Science Ltd

INTRODUCTION

Many foods undergo browning due to enzymatic or non-enzymatic reactions that occur during processing or storage. Such reactions have a direct impact on the food quality, and therefore they are of great importance to the food manufacturer (Sapers, 1993). The goal in handling food is to inhibit undesirable browning reactions as much as possible and to control desirable browning reactions (Penfield & Campbell, 1990).

Maillard reactions, important types of non-enzymatic browning, occur between reducing sugars and amino acids or proteins (Sapers, 1993; Danehy, 1986). Reactive intermediates are formed by a variety of pathways yielding volatile flavour components and brown nitrogenous compounds of higher molecular weight (Balies, 1982) called melanoidin pigments (Wong, 1989).

Glucose syrups are added to a very wide variety of food products which utilize their properties to a greater or lesser extent (Kearsley, 1978). The water white nature of glucose syrups is a temporary factor as, either when stored or processed, the non-enzymatic Maillard browning reactions cause development of first yellow, then brown coloration (Jackson, 1990). Although the formation of these compounds is desirable in the thermal processing of many products such as meat, coffee and bread, their occurrence during storage is undesirable and leads to a reduction in quality (Balies, 1982). In the case of glucose syrup production, the formation of colours and odours determines the sensorial properties such as appearance and flavour and also provides an index of purity. It has been shown previously that Maillard reactions occurring in glucose syrups may contribute to syrup discoloration (Ramchander & Feather, 1975). Discoloration of the glucose syrup during the manufacture of high boiled candies can be a serious problem for the confectionery industry as it may lead to the loss of acceptable colour and to the development of off-flavours (Lees, 1976; Kearsley & Birch, 1985).

It is known that factors affecting colour development in glucose syrups during storage are: time of storage; temperature; dextrose equivalent; pH and sulfur dioxide (Sapers, 1993). However, there is a lack of information on the kinetics of non-enzymatic browning in glucose syrups during their storage. The objectives of this study were to determine the kinetics of brown colour development in syrups and to estimate the shelf life of the product.

MATERIALS AND METHODS

Materials

Glucose syrups containing 10 ppm SO_2 with 38 and 59 DE (Dextrose Equivalent) at pH = 3 – 3.5 were donated by Cargill Vaniköy Co., Corn Products Division, Istanbul, Turkey. Each syrup was adjusted to pH values of 4.0, 4.5 and 5.0 by adding appropriate volumes of NaOH at 8 Baume degrees. The syrups were then

homogenized and portions of approximately 250 ml were put into glass jars and were capped to avoid evaporation. Samples were stored in thermostatic ovens at temperatures of 25, 35, 45 and 55°C.

Physical and chemical analysis

Soluble solids were measured in degrees of Brix with an Abbe refractometer at 25°C according to the method of ISO 1743 (1982*a*). The Brix data were related to the Baume and the total solids content of the syrup using the Critical Data Tables prepared for syrups with known DE values. A temperature correction was also made (Junk & Pancoast, 1973).

The initial pH was measured with a pH-meter according to the method of the Corn Refiners Association CRA E48 (1985).

Colour was determined as absorbance (A_{420}) at 420 nm in samples diluted to 50% solids with an equal volume of distilled water by ICUMSA colour measurement method (ICUMSA, Method 2). Absorbance was determined against distilled water in a Phillips UV/VIS PU 8625 spectrophotometer using 1-cm glass cells.

The DE of syrups was measured according to the method of ISO 5377 (1981) and the ash contents according to the method of ISO 5809 (1982*b*).

The SO_2 levels of samples were determined by using the Corn Refiners Association CRA E67 method (1988).

The protein contents were determined by an MCI Model TN O2 Total Nitrogen Analyzer Instrument according to the ISO 3188 method (1978).

The carbohydrate profiles were determined by a Hewlett Packard 1050 High Pressure Liquid Chromatography (HPLC) instrument integrated with an HP 1047 model differential refractive index detector, an HP 3396 model integrator and an aminex HPX-87C column. The solvent system was distilled water, the column temperature was 85°C and the flow rate, 0.6 ml min^{-1}.

RESULTS AND DISCUSSION

The chemical and physical characteristics of the analysed glucose syrup samples are presented in Table 1. The increases in absorbance capacity of the samples during 13 weeks were used to determine the browning rate. The absorbance values obtained were converted into ICUMSA units and were evaluated to determine the browning reaction kinetics and shelf lives of samples, the end of shelf life being accepted as 200 ICUMSA units based on the formation of an unacceptable dark yellow colour.

First-order kinetics were used to evaluate the data, since the regression analysis of the logarithm of ICUMSA colour values and time gave a linear relationship (Table 2; Figs 1–3). According to Labuza and Riboh (1982), most quality-related reaction rates are either zero or first-order reactions and statistical differences between the two types may be insignificant. Labuza (1979) also stated that the error in the value of the reaction rate constant (k) due to the order of the reaction chosen is less than 5% since the calculated statistical difference between zero- and first- order is small.

The equation representing this relation is

$$A = A_o\, e^{-kt} \tag{1}$$

where A is the ICUMSA unit at time t ; A_0 is the initial value and k is the reaction rate constant. From the slope of each line that represents the increased colour development (browning), the reaction rate constants (k) were obtained using linear regression for each syrup. Because of minor changes that occurred when the syrups were stored at 25 and 35°C, the kinetic parameters and shelf lives of samples were not calculated under these conditions.

The Arrhenius model, namely:

$$k = k_o e^{\frac{-E_a}{RT}} \tag{2}$$

was used to calculate the activation energies (E_a); where k_0 is the frequency factor, R is the gas constant (1.987 cal mol^{-1} K) and T is the absolute temperature in K. Plotting the logarithm (ln) and negative logarithm (-ln) of the rate constants (k) vs reciprocal of absolute temperature, the slope and intercept values were obtained by using least-squares linear regression. The slope values, E_a/R were used to calculate the activation energies for the first-order reactions. The intercepts, however, gave the frequency factors (k_o).

To show the influence of temperature on reaction rates, the Q_{10} values were calculated according to the relationship:

$$\ln Q_{10} = \frac{10E_a}{RT(T+10)} \tag{3}$$

The shelf lives of samples were calculated according to the relationship

$$\theta_s = \frac{\ln A_e - \ln A_o}{k} \tag{4}$$

where θ_s is the shelf life of sample in weeks and A_e is 200 ICUMSA units (Robertson, 1993).

For the comparison of the reaction rate constants (k) of syrups with the same DE and pH degree, but stored at different temperatures, the increases in ICUMSA colour values of syrups were evaluated. The reactions in all of the syrups with the same properties stored at 55°C occur faster than in those stored at 45°C (Figs 1–3). Syrups with different DE at the same pH degree when compared, the reaction occurs faster in 59 DE than in 38 DE excluding the syrup at pH 4.0 (Table 2). The presence

Table 1. Chemical and physical characteristics of glucose syrups

Characteristics	38 DE Glucose syrup	59 DE Glucose syrup
DE	37.5	58.9
pH	3.35	3.46
Sulfur dioxide	40 ppm	40 ppm
Soluable solids	81.5%	81.7%
Protein	0.055%	0.044%
Ash	0.20%	0.37%
HPLC profile*		
DP1	17%	32%
DP2	13%	37%
DP3	11%	1%
DP4	10%	3%
> DP5	49%	27%

*DP = Degree of polymerization, DP 1 = monosaccharides, DP 2 = disaccharides, DP 3 = trisaccharides, DP 4 = tetrasaccharides, DP 5 = penta- and oligosaccharides

Table 2. Effect of temperature and pH on the reaction rate, Arrhenius coefficients, Q_{10} and θ_s on borrowing of glucose syrups

	k[a]		Arrhenius coefficients				
	45°C	55°C	E_a (kcal mol^{-1})	K_o	Q_{10}	θ_s[b] (45°C)	θ_s(55°C)
38DE glucose syrup							
pH = 4.0	0.147(0.9766)[c]	0.232(0.9516)	10.0	$1.1*10^6$	1.6	21.0	13.7
pH = 4.5	0.126(0.9703)	0.209(0.9678)	12.2	$2.8*10^7$	1.8	24.8	12.9
pH = 5.0	0.167(0.9722)	0.252(0.9522)	9.36	$4.4*10^5$	1.6	18.4	12.0
59DE glucose syrup							
pH = 4.0	0.122(0.8151)	0.283(0.9847)	19.2	$1.8*10^{12}$	2.5	26.2	13.9
pH = 4.5	0.219(0.9689)	0.301(0.9672)	7.00	$1.4*10^4$	1.4	19.5	12.5
pH = 5.0	0.203(0.9705)	0.318(0.9673)	7.17	$1.9*10^4$	1.4	17.3	11.5

[a]Reaction rate constant week^{-1}.
[b]Shelf life in weeks.
[c]Numbers in brackets represent the correlation coefficients.

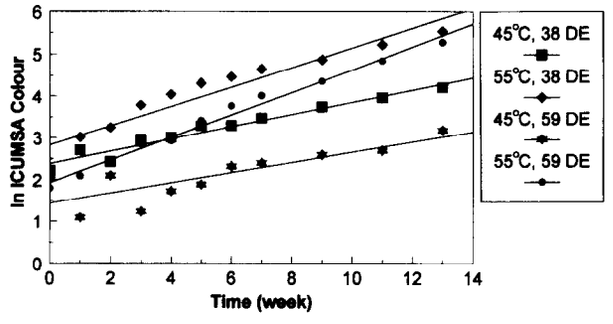

Fig. 1. Colour changes in glucose syrups of 38 DE and 59 DE at pH 4·0 stored at 45 and 55°C.

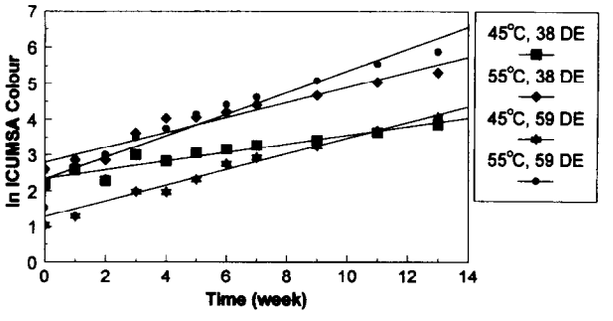

Fig. 2. Colour changes in glucose syrups of 38 DE and 59 DE at pH 4·5 stored at 45 and 55°C.

and concentration of reducing sugars in the food system are important factors affecting browning rate (Warmbier *et al.*, 1976). No colour formation has been observed in model systems containing only the sugar (Reyes *et al.*, 1982). The rate or extent of browning also increases with increasing pH and temperature during processing or storage of foods (Warmbier *et al.*, 1976). The reaction, however, proceeds also at lower temperatures, especially during storage (Balies, 1982).

The activation energies were calculated for 45 and 55°C by using the slopes of the lines representing the increase in colour development with time (Figs 4 and 5). The slopes or the activation energies of the syrups, of 38 DE are close at pH 4.0 and 5.0 and the highest value is at pH 4.5. Those for 59 DE rank from the highest at pH 4.0 and decrease with increasing pH. An overlap was observed between pH 4.5 and 5.0 (Table 2). Since the monosaccharide content was higher in 59 DE syrups (32%) than in 38 DE syrups (Table 1), the rate of the browning reactions is expected to be higher and, correspondingly, the activation energies are lower in 59 DE syrups compared to those of 38 DE.

The effect of pH may be attributed to two facts: (1) increasing the pH increases the reactivity of amino acids due to the acid-base equilibrium, and (2) enolization of glucose to fructose at higher pH may also increase the

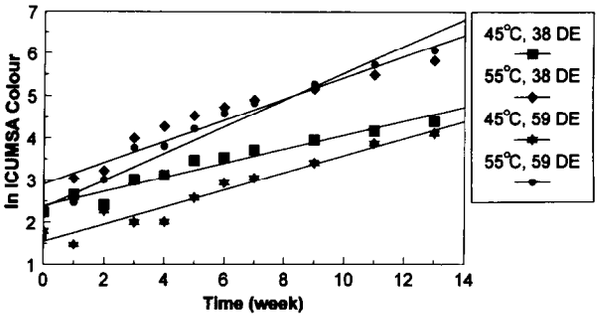

Fig. 3. Colour changes in glucose syrups of 38 DE and 59 DE at pH 5·0 stored at 45 and 55°C.

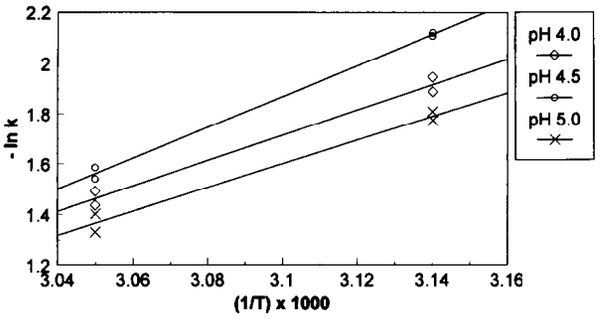

Fig. 4. Arrhenius plot for glucose syrups of 38 DE stored at 45 and 55°C.

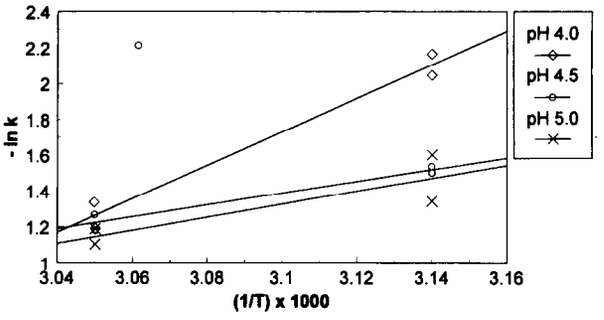

Fig. 5. Arrhenius plot for glucose syrups of 59 DE stored at 45 and 55°C.

rate of non-enzymatic browning (Cerrutti *et al.*, 1985). In apple juice concentrate and in simulating model systems, however, an exceptional darkening occurs as the pH is reduced due to different reactivities of sugars (O'Beirne, 1986). The activation energies of the reactions in this study rank between 7.00 and 19.21 kcal mol^{-1} which corresponds to 29.26 and 80.30 kJ mol^{-1} (Table 2). The typical activation energy range observed for non-enzymatic browning reactions is reported to be between 105 and 210 kJ mol^{-1} (Robertson, 1993). The activation energies reported for all systems compared are relatively close, but it is to be noted that, since foods are complex systems, this comparison is not rigorous in all cases compared. In addition, the variance of activation energy in each case is not always known and it could be expected that the activation energy might somewhat depend on the chemical identity of the browning reactants (Petriella *et al.*, 1985).

The effect of monosaccharides is partially observed as the lowest activation energies are calculated for 59 DE syrups at pH of 4.5 and 5.0, the most alkaline conditions under this study. The highest activation energy is with 59 DE at pH 4.0, however. This may be due to the medium being far from the pH optimum as it is known that the Maillard reaction takes place in alkaline medium, at an optimum pH of 7.8 – 9.2 (Penfield & Campbell, 1990). For 38 DE syrup, the activation energies are similar to those of 59 DE at pH 4.5 and 5.0. This similarity may be related to the higher protein content of 38 DE syrup compared with 59 DE (Table 1). The effect of proteins on browning is being investigated, the development of colour was rapidly accelerated when the amino compound concentration was increased (Wolfrom *et al.*,1974). Cornwell and Wrolstad (1981) also proposed the use of cation-exchange resins for the removal of amino acids from the medium in order to improve colour and flavour stability in pear juice concentrate.

The Q_{10} value is a quotient indicating how much more rapidly the reaction proceeds at a particular temperature than at a temperature 10°C lower, thus reflecting the change in rate for a 10°C rise in temperature (Robertson, 1993). Increasing temperature results in a rapidly increasing rate of browning. In model systems, the rate of browning increases 2 to 3 times for each 10 °C rise in temperature. In foods containing fructose, the increase may be 5 to 10 times for each 10°C rise. At higher sugar contents, the rate may be even more rapid (DeMan, 1990; Eskin, 1990). According to Hanover (1982), the rate of browning reactions in foods is temperature-dependent ($Q_{10}=2-3$). This conclusion is also validated by our results as a 1.4 – 2.5-fold increase is observed for increases of 10°C (45 – 55°C) for the first-order reactions (Table 2). The highest Q_{10} value among different pH values of 59 DE syrup is at pH = 4.0, perhaps indicating the combined effects of pH and temperature in acceleration of the browning reaction.

It is well known that the Maillard reactions occur faster as the temperature is raised (Balies, 1982) leading to deterioration of colour (Petriella *et al.*, 1985) and the shelf life shortens. The shelf lives of samples at 55°C were observed to be the shortest at pH 5.0 for both DEs due to the browning. The longest shelf lives, however, were observed at pH 4.0, with the most acidic syrups. At 45°C, the shortest shelf lives with both syrups were at pH 5.0 as expected. The longest storage time was experienced with 59 DE at pH 4.0. There is an obvious decreasing trend in shelf lives of syrups with decreasing acidity, with a deviation from the general principle at pH 4.5 in 38 DE syrup stored at 45°C.

CONCLUSION

There was no increase of absorbance in the model system solutions containing only the sugar (Reyes *et al.*, 1982), and models containing only glucose as reactant developed practically no colour (Petriella *et al.*, 1985). This indicates that Maillard reactions are the main causes of brown pigment formation in glucose syrups and that the contribution of caramelization may be neglected.

The longest acceptable shelf lives of the syrups studied are about 13.9 weeks at pH 4.0 and the shortest 11.5 weeks at pH 5.0 for syrups of 59 DE when stored at 55°C. For samples stored at 45°C, the longest shelf life is 26.2 weeks for syrups of 59 DE at pH 4.0, and the shortest 17.3 weeks at pH 5.0.

A practical application of these results could be use of the data to estimate the shelf life of glucose syrups with the same composition under any storage temperature.

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