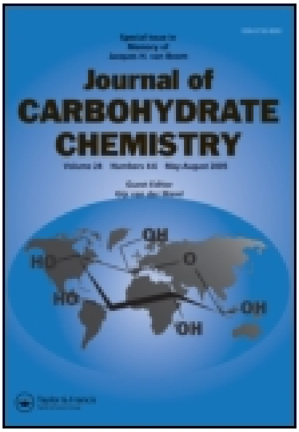

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DEGRADATION OF SUCROSE, GLUCOSE AND FRUCTOSE IN CONCENTRATED AQUEOUS SOLUTIONS UNDER CONSTANT pH CONDITIONS AT ELEVATED TEMPERATURE

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ABSTRACT

The degradation of sucrose can decrease sucrose yield, reduce the efficiency of sugar factory and refinery processes, and affect end product quality. Characterization of sucrose degradation under modeled industrial processing conditions will underpin further technological improvements. Effects of constant reaction pH on sucrose degradation were investigated using simulated industrial model systems (100 °C; 65 °Brix [% dissolved solids]; N_2; 0.05-3 mol NaOH titrant; 8 h), with the use of an autotitrator. Reaction pH values ranged from 4.40 to 10.45. Polarimetry and ion chromatography with integrated pulsed amperometric detection (IC-IPAD) were used to quantify sucrose degradation and first-order reaction constants were calculated. Minimum sucrose degradation occurred between pH 6.45 - 8.50, with minimum color formation between pH's 4.40 - 7.00. Polarimetry, often used in U.S. sugar factories and refineries to monitor chemical sucrose losses, was shown not to be viable to measure sucrose degradation under alkaline conditions, because of the formation of fructose degradation products with an overall positive optical rotation. For comparison, fructose and glucose (80 °C; 65 °Brix; N_2; 3 mol NaOH; 2 h) were also degraded at constant pH 8.3 conditions. For sucrose, fructose, and glucose, formation of organic acids on degradation was concomitant with color formation, indicating they are probably produced from similar reaction pathways. For the glucose and fructose degradation reactions, color and organic acid formation also were highly correlated (R^2>0.966) with changes in optical rotation values, confirming that these compounds are formed from similar reaction pathways.

INTRODUCTION

The degradation of sucrose at high industrial processing temperatures, and the formation of colored and non-colored products, is of considerable importance to the sugar industry; not only from the standpoint of valuable sugar losses, but from the reduction in unit process efficiencies and end product quality. Consequently, the degradation of sugars in aqueous acid and alkaline solutions has been widely studied and has been the subject of several comprehensive reviews,[1,2,3] with the latest review[3] relating the current understanding of the mechanisms of sucrose degradation to product loss. Despite prior and continued interest in sucrose degradation, comparison of literature data is difficult. Most investigators have chosen to study sucrose degradation under various reaction conditions which were too far removed from the conditions in the factory or refinery. For example, much work has been accomplished on dilute solutions, and extrapolation to concentrated solutions is questionable. However, there has not been a systematic screening of the influence of reaction variables on the course of sucrose thermal degradation under industrial processing conditions, particularly on high °Brix (% w/w dissolved solids) solutions of low water activity which are commonly found in the sugar industry.

The rate and course of the acid and alkaline degradation of sucrose can be influenced by several reaction parameters, such as the H^+ and OH^- concentration of the aqueous solution respectively, reaction temperature, presence of salts, concentration of sucrose and monosaccharides therein, and nature and pressure of the gas applied. The role of each parameter still requires further elucidation. For example, pH is known to be critical, but reaction pH naturally decreases with time[4] and, therefore, a full knowledge of constant pH effects has not been ascertained. To overcome this problem, some researchers[5,6] have studied sucrose degradation in buffered solutions. However, this introduces another variable of multiple salt cations which unequivocally have been shown[7,8,9] to catalyze degradation in 65 °Brix sucrose solutions.

The aim of this study was, therefore, to undertake model degradation reactions of concentrated aqueous sucrose solutions (~65 °Brix), under a wide range of constant pH conditions to further elucidate the role of pH in industrial processes. Model reactions were kept at constant pH using an autotitrator with sodium hydroxide as the titrant, rather than a buffer, to minimize interfering multiple ion effects.

RESULTS AND DISCUSSION

Constant pH Model Systems - Autotitration Conditions.

For each individual constant pH reaction, it was necessary to undertake preliminary experiments to optimize the system for autotitration. This involved optimizing the correct titrant concentration and minimum dosing rate (see Table 1); both parameters being critical in preventing pH overshoot problems, and ensuring adequate titration rates. pH overshoot problems are particularly problematic with high °Brix sucrose solutions because of low titrant diffusability.

It was impossible to initially adjust and maintain a pH>9.25, without decreasing the reaction °Brix by dilution. This is due to the high dissociation of water and sucrose at 100 °C. [For example, a simple titration of 65 °Brix sucrose at 100 °C, showed that 28 mL of 3 mol NaOH were required to obtain a pH of 10.55]. An increase in titrant concentration above 3 mol was not possible due to increased viscosity effects impeding the auto-titrator operation. Consequently, to undertake a reaction at constant pH 10.1, a 65 °Brix sucrose solution had to be first dissolved in 500 mmol NaOH, rather than water. On pre-reaction equilibration at 100 °C the pH of the solution was 10.1, hence the reaction pH. To achieve a reaction pH>10.1, a 70 °Brix sucrose solution had to be dissolved in water at room temperature (>70 °Brix sucrose solutions will not fully dissolve at room temperature and increased temperatures would only induce premature degradation; furthermore, dissolving a 65 °Brix solution in >500 mmol NaOH induced alkaline degradation at room temperatures). The 70 °Brix solution was allowed to equilibrate at 100 °C and the initial pH adjusted by adding sufficient concentrated (50% w/w) NaOH to adjust the pH to 10.45; this caused the °Brix to decrease to a value of 63.7 ± 1.8 (Table 1). Within the parameters of the experimental design and titrator capability, a pH>10.45 was not achievable.

Sucrose Degradation Kinetics.

Sucrose degradation was monitored using two techniques: polarimetry and IC-IPAD with a NaOH gradient method (see EXPERIMENTAL section). IC-IPAD is considered to

Table 1. Autotitrator parameters for sucrose degradation reactions under constant pH conditions at 100 °C for 8 h.

Target Reaction pH	Actual Reaction pH	NaOH Titrant Concentration (molar)	Minimum Dosing Rate (μL/min)	Titrant Addition Rates[a] (μL/min)		Actual Reaction Brix[b]
				initial	late	
4.4	4.4 ± 0.08	0.05	6	0.184	0.035	66.92 ± 1.2
5.45	5.45 ± 0.26	0.1	2	0.0058	0.136	66.25 ± 0.8
6.45	6.45 ± 0.33	0.2	2	0.44	0.835	64.9 ± 1.6
7.5	7.5 ± 0.18	0.6	6	1.21	2.42	66.2 ± 0.7
8.3	8.3 ± 0.15	3	2	4.31	4.82	64.8 ± 0.3
8.5	8.5 ± 0.04	3	2	7.54	9.36	65.0 ± 0.1
9.25	9.25 ± 0.16	3	2	12.9	26.3	64.5 ± 0.2
10.1	10.1 ± 0.03	3	25	86.6	70.4	65.0 ± 1.3
10.45	10.45 ± 0.04	3	200	580	141	63.7 ± 1.8

a. Measured as titration curve tangents
b. Target reaction °Brix for all model reactions was 65.0

be a more accurate measure of sucrose concentration because it measures sucrose directly. In comparison, polarimetry is less accurate because the measurement of OR (optical rotation or pol [pol is the sugar industry term for OR]) is the arithmetic sum of all optically active components in the matrix, rather than just sucrose. However, OR would be considered to have greater precision than IC-IPAD.

Since plots of the log of [sucrose] remaining against time were linear, first-order kinetic constants were calculated from the OR and IC-IPAD data, as shown in Table 2.

The IC-IPAD kinetic constants indicate that similar rates and, therefore, extents of sucrose degradation occurred at both extremes of pH studied, even though much higher color formation occurred at the extreme alkaline conditions (see Figure 1). This suggests that color

Table 2. Degradation of concentrated solutions of sucrose under constant pH conditions: first-order kinetics

First-order kinetic constants at 100 °C[a]				
	IC-IPAD		Polarimetry	
Constant Reaction pH	**$k_1 \times 10^{-6}$ (s^{-1})**	**std. error x 10^{-6}**	**$k_1 \times 10^{-6}$ (s^{-1})**	**std. error x 10^{-6}**
4.4	9.8	2.7	12.0	0.38
5.45	9.9	2.8	1.4	0.23
6.45	2.1	0.64	n/d[b]	n/d[b]
8.3	2.3	0.42	n/d[b]	n/d[b]
8.5	2.6	0.7	n/d[b]	n/d[b]
9.25	5.2	0.6	n/d[b]	n/d[b]
10.1	7.4	0.1	n/d[b]	n/d[b]
10.45	9.3	1.7	2.2	0.57

a. The time range over which the initial kinetic constant was measured varied from sample to sample

b. n/d = not determined (see text)

formation under alkaline conditions is a result of subsequent degradation reactions of initial sucrose degradation products and/or degradation of trace amounts of monosaccharides present in the analytical sucrose used. Within experimental error, between pH 6.45 to 10.1, OR generally did not decline across reaction time even though color formed and degradation occurred (an example is shown in Figure 2). Formation of alkaline degradation products of fructose (fructose degrades at a faster rate than glucose) with an overall positive OR will have suppressed the change in OR. Therefore, polarimetry is not a viable technique for measuring sucrose degradation / losses at the levels that occur in factory and refinery unit processes, where pH is alkaline, e.g., in lime clarification. Under acid degradation conditions (pH's 4.4-6.45) pol decreased and calculation of kinetic rates was possible (see Table 2) but they were still generally lower than rates calculated from the IC-IPAD data. This confirms similar results observed with salt induced acid degradation of sucrose.[7,8,9]

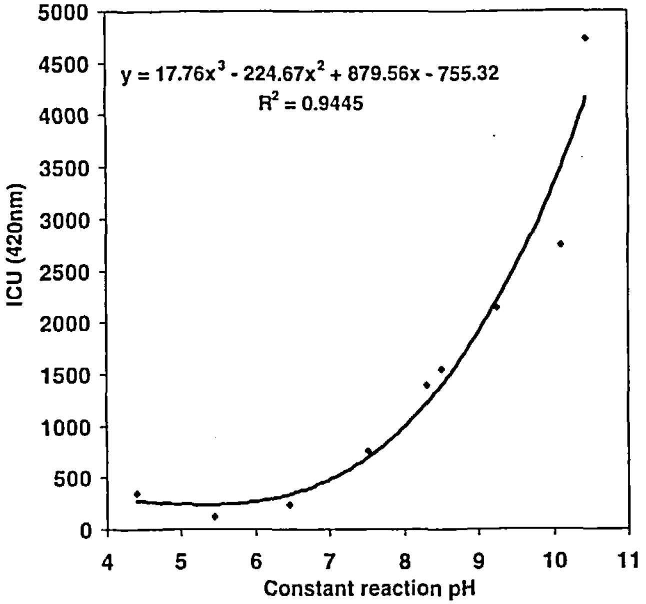

Fig. 1. Effect of constant reaction pH on color formation after 8h sucrose (65 °Brix; 100 °C) degradation

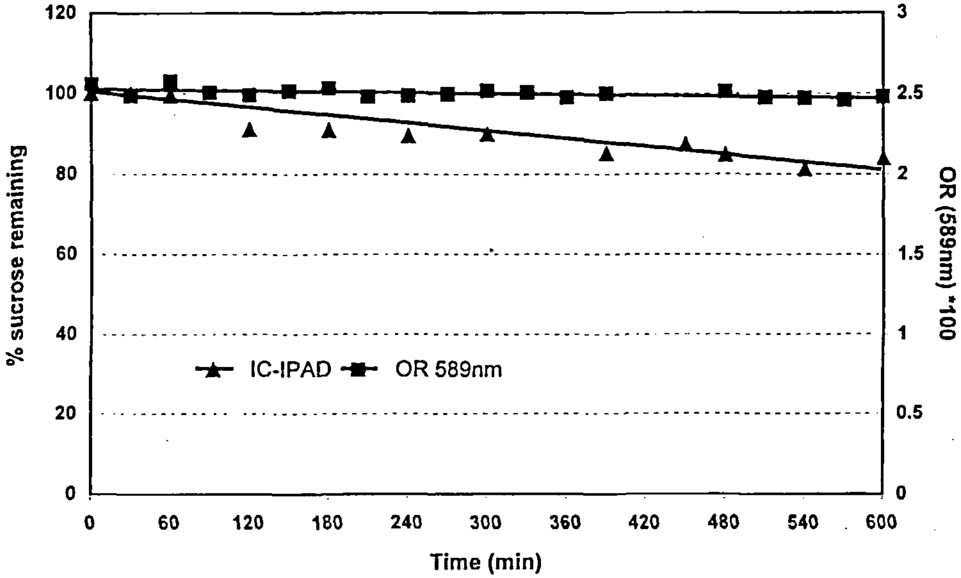

Fig. 2. IC-IPAD versus polarimetry to monitor sucrose (65 °Brix; 100 °C) degradation under constant pH 9.25 conditions

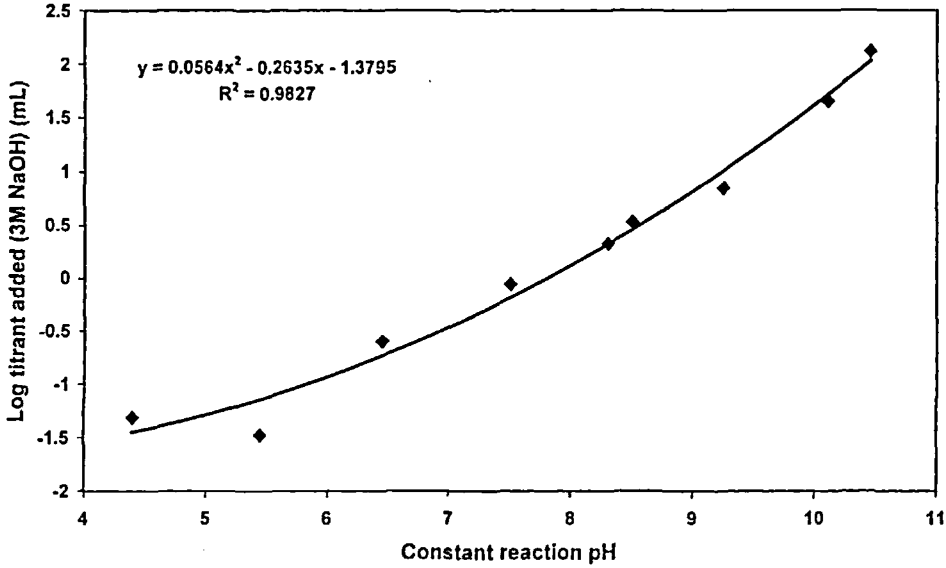

Fig. 3. Effect of constant reaction pH on titrant added after 8h sucrose (65 °Brix; 100 °C) degradation

Color and Organic Acid Formation

A plot of IU_{420nm} color after 8 h reaction time against constant reaction pH is illustrated in Figure 1 and gave an excellent third order polynomial fit (R^2=.945). Minimum color formation occurred at pH 5.45. The more highly acidic conditions at pH 4.4 induced slightly higher color formation. Color formed from alkaline degradation reactions became predominant at pH >~7.5. A similar curve (second order polynomial) fit was observed when titrant added was plotted against constant reaction pH (see Figure 3). This strongly suggests that color formation is concomitant with organic acid formation, as titrant added is an indirect measurement of total formation of organic acid degradation products. De Bruijn[11] earlier observed a direct relationship between color formation from the alkaline degradation of monosaccharides and >C6 organic acid formation, which was more pronounced in more concentrated initial monosaccharide solutions. Furthermore, Yang and Montgomery[12] observed that in 50-100 % w/w glucose solutions degraded in aqueous calcium hydroxide at 100 °C, formation of C6 acids (e.g., hexametasaccharinic acid) was favored over <C6 acids, although color formation was not monitored in this study. In this work presented herein, a

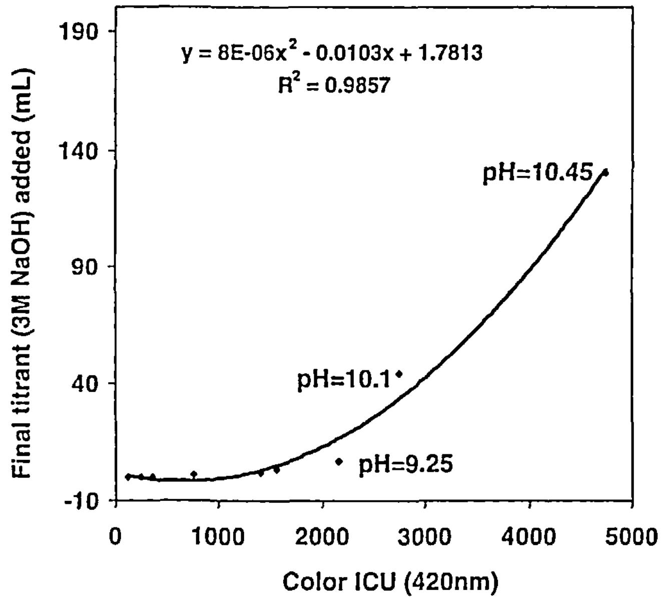

Fig. 4. Effect of titrant added after 8h on color formation from sucrose degradation (65 °Brix; 100 °C) under constant pH conditions

further plot of titrant versus color formation (Figure 4) illustrates that at pH>9.25 there was a marked increase in color and organic acid formation, reflecting the strong influence of the OH^- concentration.

Fructose and Glucose Degradation

Even though the invert sugars, glucose and fructose, usually occur at much lower concentrations than sucrose in sugarcane and sugarbeet factory/refinery juices, their degradation, especially under alkaline conditions, has great consequences for the sugar industry mostly because of unwanted color formation. For example, both fructose and glucose degrade on the addition of lime at high temperatures during juice clarification[13] and in subsequent evaporation,[14] with concomitant formation of unwanted colored products. To generate model solutions for comparison purposes, the degradations of fructose and glucose were also examined at high concentrations (65 °Brix) under constant pH 8.3 conditions, a pH commonly found in sugar processing and at which sucrose is the most stable.[10] Although glucose and fructose are not often found in such high concentrations in the sugar industry,

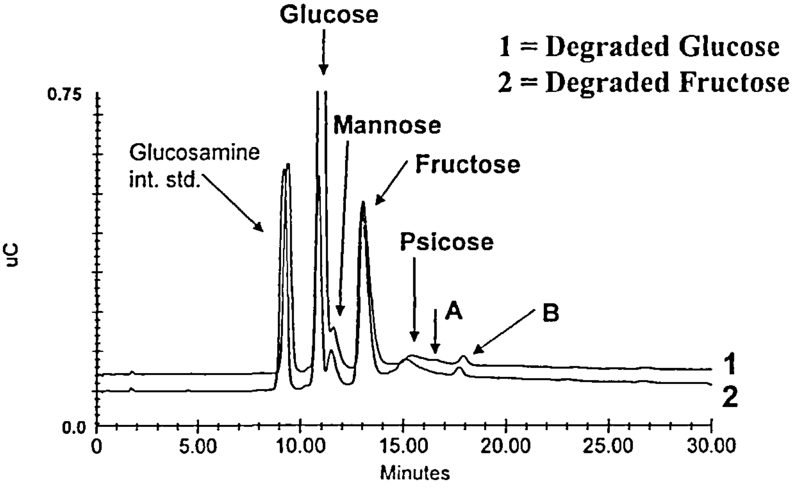

Fig. 5. IC-IPAD Chromatograms of fructose and glucose degraded at pH 8.3 (65°Brix; 80°C)

they are still found in sucrose mixtures of similar concentrations, where the water activity would also be lower than in dilute solutions. Since rates of degradation and color formation in glucose and fructose were markedly higher than for sucrose, the model reactions were undertaken at 80 °C and for only 2 h, which allowed for more accurate measurements. Irrespective of the starting monosaccharide, the final IC-IPAD chromatograms were virtually identical (Figure 5). In the initial stages of alkaline degradation of monosaccharides, glucose, fructose, mannose and, to a much lesser degree psicose,[11] are in equilibrium via the same 1,2- and 2,3- enediol anion species. This is the well known Lobry de Brujn-Alberda van Ekenstein rearrangement.[15] The enediol intermediate subsequently undergoes further non-reversible degradation reactions, including β-elimination, benzylic-acid rearrangements and aldol condensation reactions,[11] with subsequent color formation. Changing levels of glucose, fructose, mannose, and psicose in the degraded glucose sample are shown in Figure 6, as well as two other unidentified peaks (see Figure 5).

As expected, the rate of fructose degradation, as monitored by IC-IPAD (k_1= 100 x 10^{-6} s^{-1} ± SD 18 x 10^{-6} s^{-1}) was higher than for glucose degradation (k_1=53 x 10^{-6} s^{-1} ± SD 1.7 x 10^{-6} s^{-1}). Other workers (Ramaiah and Kumar,[16] De Brujn,[11] De Wit,[17]) have observed similar relative rates for dilute solutions, using other analytical techniques including HPLC.

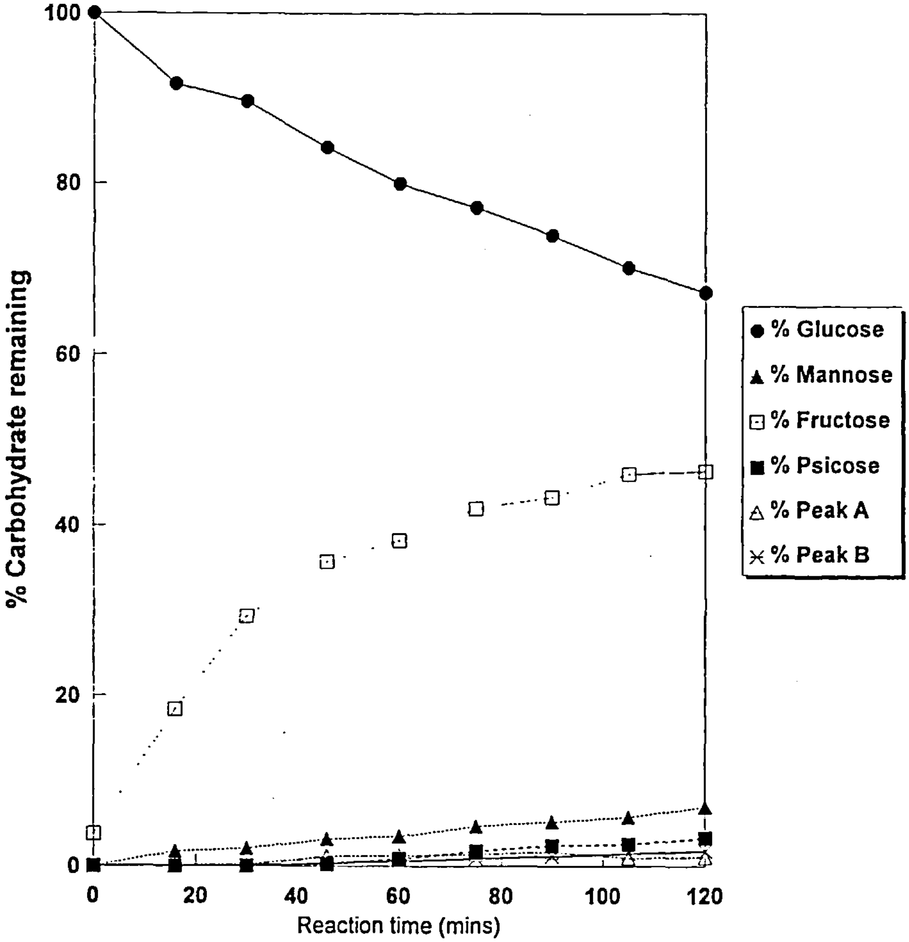

Fig. 6. Carbohydrate Changes in Glucose Degradation, Monitored by IC-IPAD

The initial faster isomerization of fructose with respect to glucose can be attributed to the higher enolization rate of fructose,[17] because of its more favorable configuration to form the enediol-anion species.[17] The alkaline isomerization of both glucose and fructose resulted in the formation of substantial amounts of mannose and psicose after 2h (3.28 and 6.46% of psicose for glucose and fructose degradations, respectively).

Color was approximately three fold higher in the degraded fructose solution (IU_{420nm}=32,884) than for glucose (IU_{420nm}=10,631) after 2 h, with the fructose and glucose

Table 3. Autotitrator parameters for glucose and fructose degradation reactions under constant pH conditions at 80 °C for 2 h.

Sample	Actual Reaction pH	NaOH Titrant Concentration (molar)	Minimum Dosing Rate (μL/min)	Titrant Addition Rates[a] (μL/min)		Actual Reaction Brix[b]
				initial	late	
Fructose	8.3 ± 0.03	3	150	113	525	62.3 ± 1.6
Glucose	8.3 ± 0.04	3	25	31	372	66.0 ± 1.0

a. Measured as titration curve tangents

b. Target reaction Brix for the model reactions was 65.0

solutions characteristic red/brown and orange/brown colors, respectively. Color formation and titrant addition occurred at markedly faster rates for fructose (see Table 3), which further reflects its higher rate of enolization and degradation.

Fructose has a negative OR. On alkaline degradation of fructose over 2h, OR values changed markedly from -3.287 to -0.844, indicating the overall OR of fructose degradation products were positive. Glucose has a positive OR and the OR values, in comparison to fructose, changed from 1.996 to 0.194 over 2h, indicating the overall OR of glucose degradation products were negative. These differences are expected, as isomerization is the major alkaline degradation reaction, and the major isomerization product for fructose is glucose, and for glucose it is fructose (see Figures 5 and 6). Excellent correlations existed between OR (at 589 and 880nm) and color or titrant added for both fructose (R^2 =0.996) and glucose (R^2 =0.966). This further strongly indicates that colored compounds and organic acids are formed from similar reaction pathways and contribute to the optical properties of the degraded solutions, but the actual mechanisms remain to be elucidated. These results are highly significant for the sugar industry, as it confirms that the alkaline degradation of glucose and fructose, especially the more rapid reaction of fructose, affect OR or pol values in industrial process streams, which often causes under-estimations of sucrose losses in the factory or refinery, because of the overall positive OR values of the fructose degradation products formed.

CONCLUSIONS

Color formation in the sucrose degradation reactions was least between pH ~4.4-7.0, and minimum sucrose degradation occurred between pH~6.45-8.5, under constant pH conditions at 100 °C and 65 °Brix solutions. Organic acid formation is concomitant with color formation, suggesting similar reaction pathways for their formation; this is especially true for glucose and fructose degradation in concentrated solutions. Polarimetry is not viable for measuring kinetic rates of sucrose degradation under alkaline conditions in the factory or refinery, because of the formation of fructose degradation products with an overall positive OR. Colored compounds and organic acids formed from the alkaline degradation of glucose and fructose directly affected OR values, suggesting these compounds are formed from similar reaction pathways.

This work is part of an ongoing USDA project. A major aim of this project is to identify stable marker compounds in industrial processes to accurately and easily determine actual chemical sucrose loss. Further studies to separate and identify degradation products formed in the model systems are currently in progress, and are being compared with compounds found in industrial samples.

EXPERIMENTAL

Materials. All carbohydrates were analytical grade. Sucrose[7] and fructose were from Baker, glucose and psicose were from Sigma and mannose from Aldrich. NaOH was Fischer HPLC grade.

Constant pH Model Systems. Constant pH reactions were undertaken in a 1 L jacketed reaction vessel equipped with an Ingold™ combination pH electrode connected to a Metrohm 716 DMS Titrino autotitrator, a magnetic stirrer, a sampling syringe, pure nitrogen gas inlet and outlets and a dosing tube for adding titrant (molar NaOH). The autotitrator was calibrated with two different dilute pH (7 and 10) buffers at the reaction temperature. Sample solutions (65 °Brix [equivalent to ~5.43 molar sucrose]; 800 mL) were first dissolved at room temperature and then allowed to equilibrate at the reaction temperature before the initial pH was adjusted to the reaction pH and the auto-titrator started. Reaction samples (~5 mL) were removed every 30 min and allowed to cool before weight dilutions were undertaken for analyses.

Brix. °Brix was measured using an Abbe™ Refractometer.

Polarimetry. Samples were diluted by weight of water and their optical rotation (pol) at 589 and 880 nm in a 20 cm cell, measured using a Rudolph™ Autopol 880 Polarimeter, calibrated in International Sugar Scale (Z scale - 26.0 g sucrose in 100 mL = 100 °Z) at 20 °C.

Color. Color was measured as the absorbance at 420 nm and calculated according to the official ICUMSA (International Commission for Uniform Methods of Sugar Analysis) method (GS1-7).

Ion Chromatography. Sucrose, glucose and fructose were separated on a Dionex™ CarboPac PA guard (25 x 4 mm) and PA-1 analytical (250 x 4 mm) anion exchange columns at room temperature. See Eggleston et al.[7] for full method.

Kinetic analyses. Kinetic raw data obtained from polarimetry and IC-IPAD, were °Brix adjusted, and used to calculate first-order rate constants by use of a linear, least squares computing method.

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