ESTIMATION OF pH OF SUGAR CANE JUICES AT HIGH TEMPERATURE

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Abstract

Theoretical estimates of sucrose losses during evaporation are critically dependent on an accurate estimate of pH at operating temperature. The pH values of about 80 juices from several factories were determined at three different temperatures and in all cases a linear drop in pH with increasing temperature was found. Regression analysis of pH and its temperature coefficient produced an excellent second order polynomial relationship. This equation was tested and was found to predict pH at high temperature with a good degree of accuracy. The model has been used extensively during the 1985/86 season to compare theoretical and measured sucrose losses.

Introduction

Sucrose losses during evaporation can be estimated either by measuring changes in the glucose concentration analytically[1] or theoretically from a mathematical model provided pH, temperature, brix and residence time are known.[2,3,4] The latter approach is critically dependent on an accurate estimate of pH at operating temperature. Temperature has a profound effect on pH, and pH values of evaporator juices at ambient temperature are significantly different from those at vessel temperature. Accuracy is necessary due to the logarithmic pH scale (a 0,1 unit error in pH represents a 25 % change in both hydrogen ion concentration and inversion).[5] The pH at high temperature is normally not measured, as it is easier to cool the sample and read its pH at laboratory temperature. A decrease in pH is normally experienced when sugar juices are heated.[6,7] Vignes[6] found that the temperature coefficient of pH (dpH/dT) ranged from −0,006 to −0,013 for clear juice. Molasses produced a lower dpH/dT. However, he inferred that due to a non-linear relationship between pH and dpH/dT, the pH under actual working conditions could not be calculated with any degree of accuracy. Kulkarni[7] studied a wide variety of liquors from both a raw sugar factory and a direct consumption white sugar plant. He concluded that although certain regularities were evident, it was not possible to predict accurately the change in pH with temperature. Culp,[8] after studying the available literature, came to the conclusion that any attempt to establish standardised temperature coefficients or corrections would be futile. Gross[9] reported to ICUMSA that despite quoted discrepancies there are strong indications of regularities, particularly with respect to certain products of similar origin and process history. Although ICUMSA recommended that the influence of both brix and temperature on pH be futher studied no further work appears to have been carried out.[10] Lemaitre[11] reported to ICUMSA that Caceres was developing a method which would enable the analyst to determine in the laboratory the true pH which existed in the factory at any particular temperature. However no further details or references were given in Lemaitre's report. Many of the comparisons cited in the literature covered a very wide range of products (raw cane juice to raw sugar) and included products from different processes and even different countries. It was decided to narrow the range to front-end juices from local raw sugar factories in the hope of obtaining a better relationship between pH and dpH/dT.

Experimental procedure

Sampling and storage

Catch samples of mixed juice (MJ), clear juice (CJ) and syrup from 5 factories (Sezela SZ, Illovo IL, Mount Edgecombe ME, Empangeni EM and Noodsberg NB) were taken twice per shift over a 5-day period. After the samples had been transferred to polythene sachets and heat sealed they were immediately deep-frozen by the Sugar Industry Central Board staff.

Equipment

A Philips digital pH-meter (PW9422) equipped with a Philips high temperature pH-electrode (CH 85D–SD) and platinum 100 thermometer was used in the autocalibrate mode to standardise itself using 2 NBS-buffers (phthalate and borax solutions). The instrument automatically identifies each buffer and uses the current temperature to select the exact buffer value from its look-up table. Temperature compensation for electrode slope changes due to temperature changes was also automatic.

Procedure

Clear juice, syrups and buffer solutions were transferred to large test tubes which in turn were placed in a thermostatically controlled waterbath fitted with a stirrer. The pH and temperature probes were placed in these test tubes loosely stoppered with cotton-wool to prevent evaporation. The meter was calibrated at 3 temperatures (30–35°C, 50–55°C and 80–85°C). The pH and exact temperature of the juices were obtained from the meter's digital readout. Over 80 samples were studied.

Results and discussion

In all cases there was a linear drop of pH as temperature increased. Linear regression of pH and temperature from individual juices resulted in excellent correlations (correlation coefficient for all samples ranged from 0,96 to 1,00). The slopes of the regressions (ie temperature coefficients (dpH/dT)) however varied substantially (see Table 1).

Table 1

Effect of temperature on pH of front-end juices

Juice	pH at 25°C	dpH/dT	pH at 100°C	No. of samples
MJ	5,11	−0,002	—	20
Syrup	6,19	−0,008	—	10
Diff.J	6,56	−0,009	—	7
CJ/EM	7,04	−0,011	6,2	9
CJ/NB	7,11	−0,012	6,2	10
CJ/IL	7,09	−0,013	6,2	22
CJ/SZ	7,39	−0,017	6,1	4

Two important points are immediately obvious from the data in Table 1:-

● There is a greater temperature effect on process liquors with higher pH values than those with lower pH values. This observation is especially important for evaporator juices because they have a fairly high pH (7,0 to 7,4) and they are also subjected to the highest temperatures (100–115°C).

● Pure water dissociates into hydrogen and hydroxyl ions. The product of the concentration of these 2 ions, the dissociation constant is $1,0 \times 10E{-}14$ (pK = 14,00) at 25°C and therefore the neutral point (at 25°C) is at pH 7. On increasing the temperature more and more water dissociates and at 100°C the pK-value climbs to 12,24 and therefore the neutral point shifts to 6,1. It is interesting to note that all 4 CJ streams in Table 1 produced similar mean pH-values (6,1–6,2) at typical evaporator temperatures. Table 2 illustrates the effect of temperature on ionisation and pH of water more comprehensively.

Table 2

Effect of temperature on the dissociation of water

Temperature (°C)	pK	pH
0	14,9	7,5
25	14,0	7,0
50	13,3	6,6
80	12,6	6,3
100	12,2	6,1
110	12,1	6,0
120	12,0	6,0

$$H_2O \rightarrow H+ \; + \; OH-$$

Although other sugar technologists were rather pessimistic concerning the accurate estimation of pH at high temperature using pH data at 25°C we subjected the measured pH values and dpH/dT to regression analysis. Linear regression yielded a reasonable agreement between pH at 25°C and dpH/dT, however a second-order polynomial regression produced a far better fit (correlation coefficient = 0,91). The equation for calculating dpH/dT from pH at 25°C was:-

$$dpH/dT = -0,0339 + 0,015 \times pH - 0,0017 \times pH^2 \ldots (A)$$

The raw data and the polynomial fit are shown in Figure 1. Equation (A) was then rigorously tested by heating a fur-
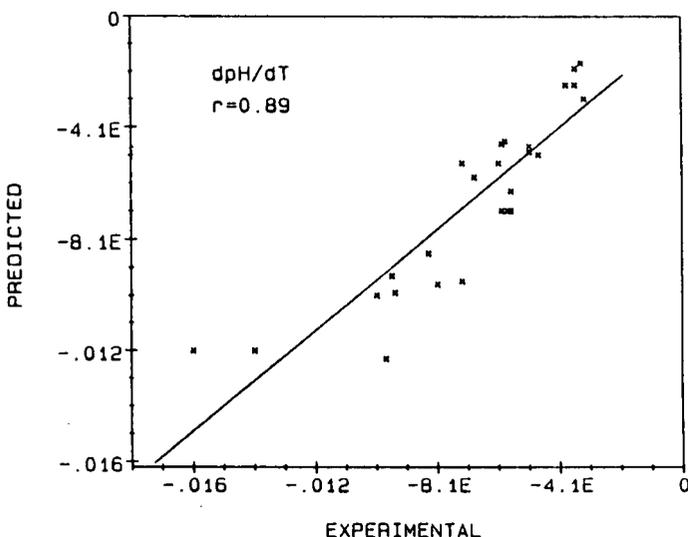
ther 25 samples of MJ, intermediate evaporator juices and syrups from a sixth factory (PG) and determining dpH/dT for each of these samples. These dpH/dT values obtained from experimental results were compared to the predicted values obtained using equation (A). The agreement between the measured and the predicted results was excellent, a linear correlation coefficient of 0,89 was obtained, the raw data and the regression are shown in Figure 2.
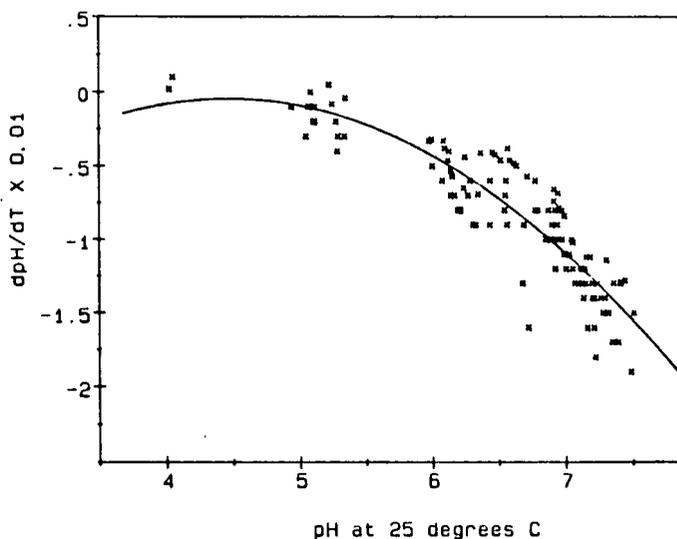

FIGURE 2 Comparison between experimental and derived temperature coefficients. Correlation coefficient of regression = 0,89.

The relationship between pH and dpH/dT was derived using a limited temperature range (25 to 85°C). The validity of equation (A) at higher temperatures was tested by heating 2 clear juices from ambient to 125°C in a heating cell[12]. Temperature and pH were logged continuously using a micro-computer. Temperature coefficients for these juices were found to be −0,009 and −0,012 respectively. Calculated values of dpH/dT using equation (A) were −0,009 and −0,010 respectively. The good agreement (admittedly on only 2 samples) between measured and predicted values tends to suggest that extrapolation of equation (A) to evaporator temperatures is justifiable.

It must be remembered that the good agreement found is probably due to the limited range of factory intermediates studied and also perhaps to the use of modern instrumentation and stable high temperature electrodes. It is not our intention to suggest that equation (A) be used as a correction factor for all juices and sugars from factories irrespective of process history but rather as a useful local tool. Table 3 has been derived from equation (A) and can be used to estimate pH values at working temperature.

Table 3
Estimation of pH at high temperature from pH at 25°C

Temp (°C)	pH						
25	6,2	6,4	6,6	6,8	7,0	7,2	7,4
40	6,1	6,3	6,5	6,6	6,8	7,0	7,2
50	6,0	6,2	6,4	6,5	6,7	6,9	7,0
60	6,0	6,1	6,3	6,4	6,6	6,7	6,8
70	5,9	6,1	6,2	6,3	6,5	6,6	6,7
80	5,9	6,0	6,1	6,2	6,3	6,4	6,5
90	5,8	5,9	6,0	6,1	6,2	6,3	6,4
100	5,7	5,8	5,9	6,0	6,1	6,1	6,2
110	5,7	5,8	5,8	5,9	6,0	6,1	6,0
120	5,6	5,7	5,7	5,8	5,8	5,9	5,9

FIGURE 1 Relationship between pH at 25°C and dpH/dT for 80 juices from 5 South African factories.

Applications

Vacuum versus pressure evaporation

Recently Wittwer[3,4], concerned about thermal efficiency, suggested that higher temperatures could be used in cane sugar evaporators, arguing that although losses were greater at the higher juice temperature they were still very low (0,06%).

However the pH values that he used to estimate losses from Vukov's mathematical model were in fact pH values at laboratory temperature[13]. Vukov's equation requires a pH value at working temperature[14]. Using equation (A) and pH-values measured at 25°C for South African factories we were able to calculate pH at these higher temperatures. The sucrose losses were then recalculated (Appendix 1). If the proposed higher temperatures are used the sucrose losses are no longer insignificant and begin to approach 1% (actual calculated loss = 0.8%).

Undetermined loss project

Investigations of high undetermined losses at Pongola (PG) have been in progress for the past 4 years[15,16]. Theoretical calculations of inversion across the PG evaporator were done using brix, temperature, pH and flow measurements supplied by PG staff. Operating volumes were obtained from engineering drawings. A typical calculation of theoretical losses in the PG evaporator is shown in Appendix 2. Equation (A) was used to calculate pH at operating temperature. A summary of the estimates across the 1985 season suggested a loss of at least 0,5% with most of this occurring in the 1C vessel. As a direct result of these calculations a comparison of losses with and without this vessel in use confirmed that the major part of the evaporator losses were due to the 1C vessel[17]. The implications of thermal efficiency and possible sucrose losses are covered elsewhere[18].

Conclusions

It has been established that there is a good relationship between pH and its temperature coefficient for South African evaporator juices. An equation expressing this relationship has been used extensively for the theoretical calculation of sugar losses during evaporation.

Acknowledgements

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APPENDIX 1

Pressure evaporation and sucrose losses using Wittwer's data

(pH corrected for temperature)

Effects	Time (min.)	pH @ 25	dpH/dT (°C⁻¹)	pH @ T°C	Temp T. (°C)	Bx	log k	% loss
1	5	7,1	−0,013	5,8	125	16	−3,185	0,33
2	7	6,8	−0,011	5,7	118	26	−3,378	0,30
3	8	6,6	−0,009	5,7	109	42	−3,795	0,13
4	10	6,3	−0,007	5,6	96	58	−4,327	0,05
							Total	0,81

APPENDIX 2

Analysis of theoretical losses in the PG Evaporator[16]

Vessel	CJ	Kest	1c	2	3	4	5
Volume (m³)		12,8	19	14	7,2	7,2	7,4
Outlet Bx	13,5	25,6	40	48,5	57	63	70
Density (g cm⁻³)	1,05	1,11	1,17	1,22	1,27	1,3	1,35
Sucrose (g m⁻¹)	0,14	0,28	0,47	0,59	0,72	0,82	0,95
Tons h⁻¹ out	200	106	68	56	47	43	39
Tons vap h⁻¹		94	38	12,5	8,3	4,5	4,4
Vap % total		58	23	7,7	5,2	2,8	2,7
Vol. juice m³h⁻¹	190	96	58	46	37	33	39
Res. time (m in)		4	14,8	18,4	11,5	13,1	15,5
pH @ 22°C	6,7	6,7	6,4	6,0	5,9	5,8	5,6
dpH/dT × 100		−1,00	−0,75	−0,52	−0,44	−0,39	−0,33
Oper. temp (°C)	102	108	112	105	96	86	62
Oper. pH		5,88	5,7	5,6	5,5	5,5	5,5
Inversion							
Calculated log k		−3,93	−3,69	−3,88	−4,26	−4,72	−5,9
rate k × 10⁴ (min⁻¹)		1,16	2,04	1,32	0,55	0,19	0,01
% per hour		0,7	1,23	0,79	0,33	0,11	0,01
% lost/vessel		0,05	0,3	0,24	0,06	0,03	0,00
						TOTAL %	0,68