

POST-HARVEST DETERIORATION OF WHOLE STALK SUGARCANE

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Abstract

The effect of cane deterioration on both the sucrose and impurity contents of clean, whole stalk NCo 376, burnt and trashed, was investigated. At a given temperature the purity drop was found to vary exponentially with time.

Temperature had a very important effect on the rate of the purity drop, a 10°C increase causing the drop to be 3 to 4 times faster. Cane deterioration had little to no effect on the concentrations of colour bodies in clean, healthy cane, but resulted in the production of large quantities of ethanol and lactic acid. It is possible to obtain a good measure of the cut-to-crush delay, on the industrial scale, by analysing cane (DAC) extracts for ethanol.

Introduction

It is generally accepted that cane starts deteriorating immediately after it has been cut or burnt. This deterioration is essentially caused by two types of processes. The first involves the inversion of sucrose by enzymes naturally present in the cane while the second, which predominates in wet, warm weather and can cause rapid and serious sucrose losses, involves the infection of the cane by micro-organisms which secrete sucrose inverting enzymes.

Cane invertases have been studied by Hatch, Galsziou and Sacher¹⁻³ who have identified three different types of invertases. Alexander⁴ shows that the top part of the cane stalk deteriorates faster than the rest of the stalk, probably due to higher concentrations of enzymes in that part of the cane. The post harvest activities of the invertases are affected⁴ by the cane variety, climatic conditions, storage conditions, burning and complex interactions of these factors.

Work done in Australia has shown the importance of micro-organisms in cane deterioration. Micro-organisms are always present in green cane and re-infestation, by insect, rain, wind and direct soil contamination, occurs rapidly after burning. Egan^{5,6} isolated seventeen different organisms on the surface of burnt cane, some as early as ten minutes after the burn. Burning may in fact facilitate infection by causing splitting of the stalk and seepage of juice. Bevan⁷ reports that tests on cane wax indicated that certain of its fractions were somewhat bacteriostatic. The removal of wax by heat may thus allow organisms to grow more freely. Bevan⁷ shows that organisms enter the cut stalk through the vascular bundles and found massive infections up to 15 cm from the cut end after 90 minutes.

The rate at which harvested cane deteriorates is influenced primarily by temperature, humidity, cane variety and the state of the stalk (eg whole/chopped, burnt/trashed). For given cane quality and agricultural practices, temperature is recognised as being a major factor. Many workers, however, either do not quote the temperature at which their tests were done or only give wide ranges showing that temperature was not a controlled variable in their experiments. Furthermore, no attempts seem to have been made to include temperature as a variable in mathematical approaches aimed at describing deterioration.

Wood^{8,11}, in South Africa, has investigated the effects of cane deterioration on sucrose losses. Impurities, including alcohols, acids, polysaccharides, dextran and reducing sugars, have been investigated by Bruijn¹²⁻¹⁴, Ivin^{15,16} and Foster¹⁷ among others. There is, however, very little work done on the effects of deterioration on colour.

A number of workers have investigated the possibility of developing a chemical index for cane deterioration. Yeh¹⁸, in a recent publication proposes a pol deviation index, an index based on starch and a flocculation test using lead nitrate. His approach is considered to be too dependent on cane quality to be of practical value under South African conditions. Fulcher¹⁹ shows that pH is not suitable and that dextran levels can be misleading, while Bruijn¹²⁻¹⁴ discusses the juice titrable acidity and shows that this quantity is not acceptable because of large variations due to the cane itself. Komar²⁰ uses reducing sugar levels to gauge the amount of deterioration but requires that the cane from the supplying areas be sampled and analysed fresh to obtain the base-line, which is not a practical situation here. Horwitz²¹ analyses the bacterial population in maple sap using the dye resazurin. His method permits a rapid estimation of bacterial populations of 1×10^6 per cm³ and higher in maple sap.

Although deterioration has been investigated extensively both here and elsewhere, deterioration rates have not been described mathematically. Furthermore, very little information concerning its possible effects on colour bodies and colour precursors is available. This paper presents some results of investigations into cane deterioration with particular emphasis on a more general mathematical approach and on the production of impurities, particularly colour.

Experimental procedure

Conditions of deterioration

Whole stalk, 18 to 22 month old cane of NCo 376 variety was used for the investigation. All the cane originated from the Mount Edgecombe area and was grown by the Experiment Station of the SA Sugar Association.

Only temperature, time and cane burning/trashing were selected as independent variables. Different levels of temperature were obtained by carrying out three sets of experiments, one in January, one in May and the last in October. The harvested cane was left in a greenhouse. This resulted in higher temperatures being reached, protection from rain and some smoothing out of temperature extremes. A temperature and humidity recorder was placed next to the cane sample.

Each main sample of cane (120 stalks) was cut or burnt and cut immediately on the morning of the first day (day 0) of each set. The cane was then transported, without being cleaned, to the greenhouse. Sub-samples (12 stalks) were randomly selected, on days 0, 1, 2, 3, 4, 7, 8, 9 and 10. These were taken to the laboratory, topped at the natural breaking point and trashed. The clean stalks were then shredded in a Jeffco cutter-grinder and the pulp was mixed well.

Analytical approach

Sub-samples of the cane pulp were analysed by the Direct Analysis of Cane (DAC)²² and by an equilibrium method²³ which is particularly useful for the determination of impurities, such as colour bodies in cane. This method was used to measure the concentrations in cane of the following:

- Lactic acid and ethanol, which are produced by micro-biological activity.
- Total phenols and amino nitrogen, which include plant pigments and colour precursors.
- Optical absorbance in the visible and UV regions of the spectrum, which provides direct indications of colour levels.
- Sucrose by gas chromatography.
- Pol and brix.

Lactic acid and ethanol are reported as ppm on brix in cane.

Total phenols analysed by the Folic-Ciocalteu method is reported as ppm caffeic acid on brix in cane while amino nitrogen, analysed by the ninhydrin method is reported as ppm aspartic acid on brix in cane. Absorbances are reported as absorbance units on brix in cane. The use of brix is aimed at cancelling any drying effect taking place as the cane deteriorates.

Mathematical approach

The deterioration of sugarcane has been treated as a chemical process taking place at a given temperature and represented in a simple way by the equation



where A represents the reactants and B the products.

If the rate of the deterioration is assumed to follow first-order kinetics then

$$\begin{aligned} \text{Rate} &= -d(A)/dt & \dots \dots \dots (1) \\ &= d(B)/dt & \dots \dots \dots (2) \\ &= k_1 \cdot (A) & \dots \dots \dots (3) \end{aligned}$$

The rate may now be determined by using the concentration of a reactant, for example sucrose. From equations (1) and (3)

$$\frac{-d(A)}{(A)} = k_1 \cdot dt$$

which on integration yields

$$A_t = A_0 \cdot e^{-k_1 \cdot t} \dots \dots \dots (4)$$

where A_t and A_0 are the concentrations of sucrose at times t and zero respectively and k_1 is the first order rate constant. A plot of $\log_e(A_t)$ against t then yields a straight line with slope equal to $-k_1$.

The rate may also be determined by using the concentration of a product. Let B_t be the concentration of product B after time t . The initial concentration of product (B_0) is zero. Then

$$\frac{d(B)}{dt} = k_1 \cdot (A_0 - B)$$

which on rearrangement and integration yields

$$\log_e \frac{A_0}{A_0 - B} = k_1 \cdot t \dots \dots \dots (5)$$

Equation 5 shows that a plot of $\log_e \left(\frac{A_0}{A_0 - B} \right)$ against time

yields a straight line with slope k_1 and an intercept equal to zero. This equation has been used for products such as ethanol, for which the initial concentration in fresh cane is close to zero.

Results and Discussion

Deterioration times, temperatures and other key details are given in Table 1.

Table 1
Experimental details of the deterioration runs

Series/Run	Month	Duration (hours)	Ave. Temp. (°C)	Type of Cane
1/1	Jan.	220	34	Trashed
1/2	Jan.	220	31	Burnt
2/1	May	240	19	Trashed
2/2	May	240	19	Burnt
3/1	Sept.	240	19	Trashed cane (diseased)
3/2	Sept.	240	25	Burnt

The cane used in series 3, run 1 was found to be diseased and the run yielded results which did not fit with those of the other runs. The results from this run have therefore not been included with those from the other runs.

Changes in pol and sucrose

Changes in the apparent purity are represented by equation 4.

$$\left(\frac{\text{pol}}{\text{brix}} \right)_t = \left(\frac{\text{pol}}{\text{brix}} \right)_0 \cdot e^{-k_1 t}$$

The results obtained are given in Table 2. Some typical results have been plotted in Figure 1 and it is evident that the fit is good.

Table 2
Changes in the cane apparent purity with deterioration

Series /Run	Temp. (°C)	Equation 4	No. of observations	Corr. coeff.
1/1	34	Ap.pur. = 87,7 · e ^{-0,00148 × hours}	8	- 0,91
1/2	31	Ap.pur. = 91,0 · e ^{-0,000556 × hours}	8	- 0,86
2/1	19	Ap.pur. = 92,6 · e ^{-0,000182 × hours}	10	- 0,97
2/2	19	Ap.pur. = 88,1 · e ^{-0,000249 × hours}	8	- 0,87
3/2	25	Ap.pur. = 91,5 · e ^{-0,000260 × hours}	9	- 0,90

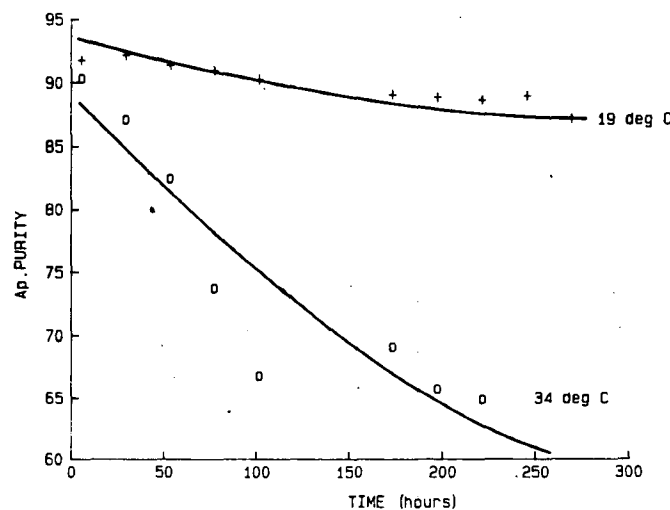


FIGURE 1 The change in apparent purity with deterioration time

Equation 4 was also fitted, whenever possible, to data given in the literature. Typical results are shown in Table 3.

Table 3
The fit of Equation 4 to data from the literature

Temp. (°C)	Material	Equation 4	No. of obs.	Corr. coeff.	Ref.
21	Juice	Ap.pur. = 91,0 · e ^{-0,000341 × hours}	7	-0,95	14
24	Cane	Ap.pur. = 90,9 · e ^{-0,000411 × hours}	6	-0,98	11
31	Juice	Ap.pur. = 87,8 · e ^{-0,000446 × hours}	10	-0,86	24
22	Juice	Ap.pur. = 89,0 · e ^{-0,000133 × hours}	4	-0,99	10
21	Cane	Ap.pur. = 92,3 · e ^{-0,000666 × hours}	6	-0,99	8
20	Cane	Ap.pur. = 91,4 · e ^{-0,000195 × hours}	4	-0,86	9

Again excellent fits are obtained confirming the validity of the approach used. It is therefore concluded that, at a given temperature, purity drops exponentially with time.

It is expected that temperature will have a significant effect on the rate of the purity drop, k₁. The effect of temperature was obtained by using the Arrhenius equation

$$\log_e k_1 = -\frac{E_a}{RT} + \log_e A$$

where E_a is the activation energy, R the gas constant, T the absolute temperature and A the pre-exponential factor. This equation shows that a plot of log_e k₁ versus 1/T should be a straight line with slope E_a/R.

The regression:

$$\log_e k_1 = -\frac{11801}{T} + 31,6 \quad \dots \dots \dots (6)$$

(n = 10; r = 0,93)

was obtained from the data of this work and yields a value of 98 kJ mol⁻¹ for the activation energy.

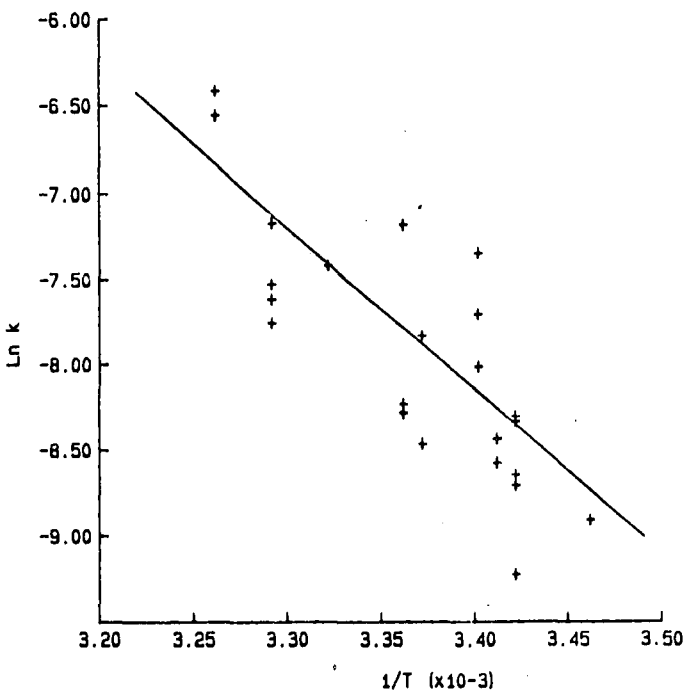


FIGURE 2 The effect of temperature on the rate of change of purity.

The complete data set, namely the data from this work and from the literature, gave

$$\log_e k_1 = -\frac{9498}{T} + 24,1 \quad \dots \dots \dots (7)$$

(n = 23; r = 0,81)

with an activation energy of 79 kJ mol⁻¹. This has been plotted in Figure 2.

The scatter is large but, considering that these tests were done in different countries, with different cane varieties and other experimental conditions, the agreement is surprisingly good.

An activation energy of 79–98 kJ mol⁻¹ means that the rate of purity drop at 30°C will be 3 to 4 times faster than at 20°C. This highlights the overriding influence of temperature on the rate of deterioration of cane.

As the cane deteriorates and purity drops, pol becomes less and less accurate as an estimator of sucrose content. Some typical results are given in Table 4.

Table 4
Pol and Sucrose (by GC) in extracts from deteriorated cane

Deterioration time (hours)	Pol/sucrose	Ap. pur.	True pur.
4	1,02	92,4	90,9
28	1,04	88,6	85,4
52	0,99	83,6	84,8
76	0,96	76,8	79,8
100	0,94	67,0	71,5
172	0,96	66,8	69,2
196	0,96	65,6	68,3
220	0,97	64,3	66,2

Pol underestimates sucrose at the lower purities and inflates the rate of deterioration.

Changes in colour impurities

The levels of total phenols on brix were not affected by cane deterioration and remained unchanged at about 5 700 ppm on brix.

This was not the case, however, for the diseased cane of run 3/1 which showed a lower initial level of total phenols, viz. 3 100 ppm instead of 5 700, and also showed a statistically significant increase with deterioration.

There was no change in the amino nitrogen content of cane with deterioration, the average value being 360 ppm on brix. Again, this was not the case for the diseased cane which showed an initial value of 780 ppm and a highly significant increase with time as the cane deteriorated, given by equation 8:

$$\text{Amino nitrogen/brix} = 783 \cdot e^{0,00144 \times \text{hours}} \quad \dots \dots \dots (8)$$

(n = 9; r = 0,91)

This has been plotted in Figure 3.

Absorbance, in the visible and UV regions, on brix in cane, showed a small increase with deterioration, given by equations 9 and 10:-

$$\text{Abs. units (visible)/brix} = 25,1 \cdot e^{0,000711 \times \text{hours}} \quad \dots \dots (9)$$

(n = 8; r = 0,76)

$$\text{Abs. units (UV)/brix} = 182 \cdot e^{0,000481 \times \text{hours}} \quad \dots \dots (10)$$

(n = 8; r = 0,69)

Temperature effects, if any, could not be obtained due probably to the lack of precision in the analytical determi-

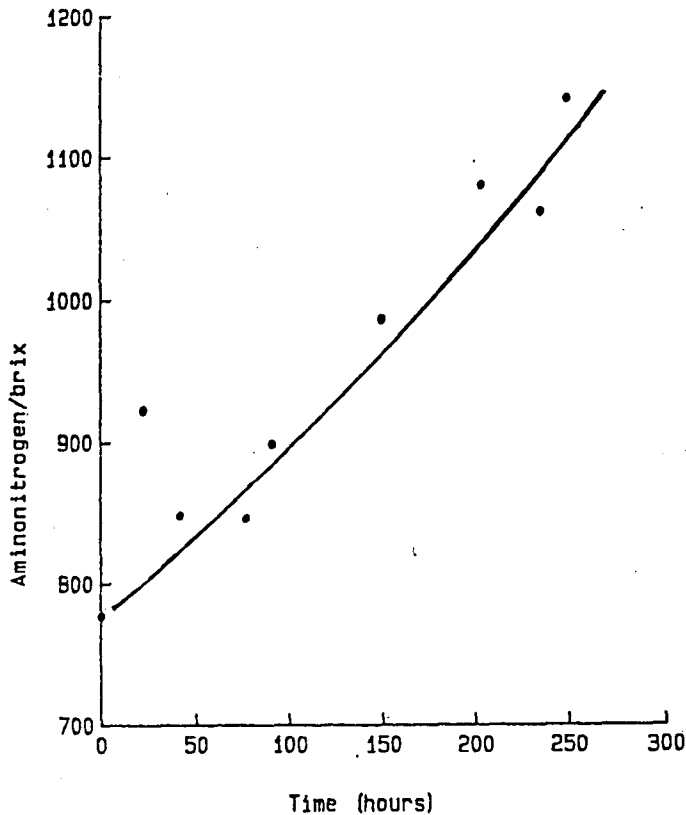


FIGURE 3 Amino nitrogen/brix versus time during the deterioration of diseased cane

nation of absorbance. The absorbances obtained with the diseased cane were not different from those of the other runs.

Indicator values (IV), given by the ratio of the absorbance at pH 9, 420 nm, to the absorbance at pH 4, 420 nm, have been used^{16,25} to differentiate between plant pigments (IV of 7-13) and colour formed enzymatically (IV of 3-5). The IV values obtained were all well within the 7-13 range and did not change as deterioration progressed.

Ethanol and lactic acid

Equation 5 is used to model the production of these two components during deterioration. A typical result is shown by equation 11:-

$$\log_e \left[\frac{(\text{Pol \% brix})_0}{(\text{Pol \% brix})_0 - \text{EtOH \% brix}} \right] = 0,626 \times 10^{-6} \cdot (\text{Time}) - 16,4 \times 10^{-6} \dots \dots \dots (11)$$

(n = 8; r = 0,98)

This result and that from a burnt cane sample are shown graphically in Figure 4.

The fits are reasonably good showing that the model used is satisfactory.

These results show that both temperature and burning have significant effects on the production of ethanol during deterioration. Both effects were modelled by using multilinear regressions to correlate $\log_e k_1$ versus $1/T$ and a dummy variable, B, representing burning or trashing. Thus B = 1 for burnt cane and B = 0 for trashed cane. The result obtained for ethanol is shown by equation 12:6

$$\log_e k_1 = - 10355/T + 1,7 B + 19,2 \dots \dots \dots (12)$$

(n = 5; r = 0,96)

where T is the absolute temperature. Although the number

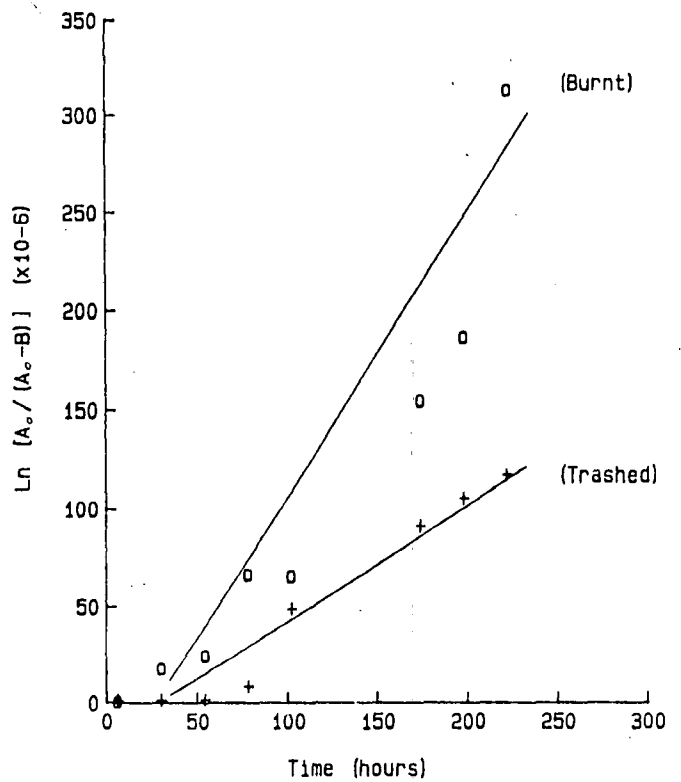


FIGURE 4 Production of ethanol during deterioration

of observations is small, it would appear that equation 12 could be used to model these effects.

The results obtained for lactic acid generally followed trends similar to those found with ethanol, with two important differences. Firstly, fresh cane showed significant levels of lactic acid in 3 of the 5 runs and secondly, the rate of formation of lactic acid is very much lower than that of ethanol causing its range of concentrations to be much narrower.

These results show clearly that ethanol is much more suitable as an indicator of deterioration than lactic acid. No lactic acid or ethanol was produced by the deterioration of the diseased cane of run 3/1, although the apparent purity dropped from 88 to 79. This confirms the abnormal deterioration process caused by disease.

Deterioration index

Industrial cane delays are usually measured by a tagging system which involves entering dates and times on a tag attached to each bundle or consignment. Although the methods gives delays directly, it is costly and labour intensive and tag recovery can be poor. A chemical deterioration index would therefore be useful.

Since the Illovo sugar mill tags its miller-cum-planter cane, a project was carried out in co-operation with the IL process and SICB staff, to collect data from the tags and the corresponding DAC extracts. Sub-samples of the relevant DAC extracts were frozen in sachets and kept at - 10°C. The data available consisted of delay times, cane varieties, field location and DAC analytical results. In addition daily maximum and minimum temperatures and daily rainfall figures were obtained from two meteorological stations in the area. All the cane was burnt.

Twenty-six DAC samples and their corresponding sets of data were obtained with time delays ranging from 22 to 331

hours. The samples were analysed at the SMRI to investigate the suitability of a number of chemical indices.

The use of ethanol/brix ratios gave the best indication of cane delays. Equation 12 yielded the best fit:-

$$\log_e(\text{delay time}) = 11,0 + 3,62 \times 10^{-3} \cdot (\text{Ethanol/brix}) - 3,20 \times 10^{-1} \cdot (\text{Ave. Temp.}) - 1,79 \times 10^{-1} V_1 - 2,79 \times 10^{-1} V_2 \dots \dots \dots (12)$$

(n = 26; r = 0,92)

where the temperature is in degrees centigrade and represents the average temperature over the 5-10 days prior to crushing; the delay time is in hours; V_1 and V_2 are dummy variables describing cane varieties, with $V_1 = 1$, $V_2 = 1$ representing NCo 376, $V_1 = 1$, $V_2 = 0$ representing NCo 293, while other varieties have $V_1 = 0$ and $V_2 = 0$.

Although the correlation coefficient is high, scatter is still present. This is illustrated in Figure 5.

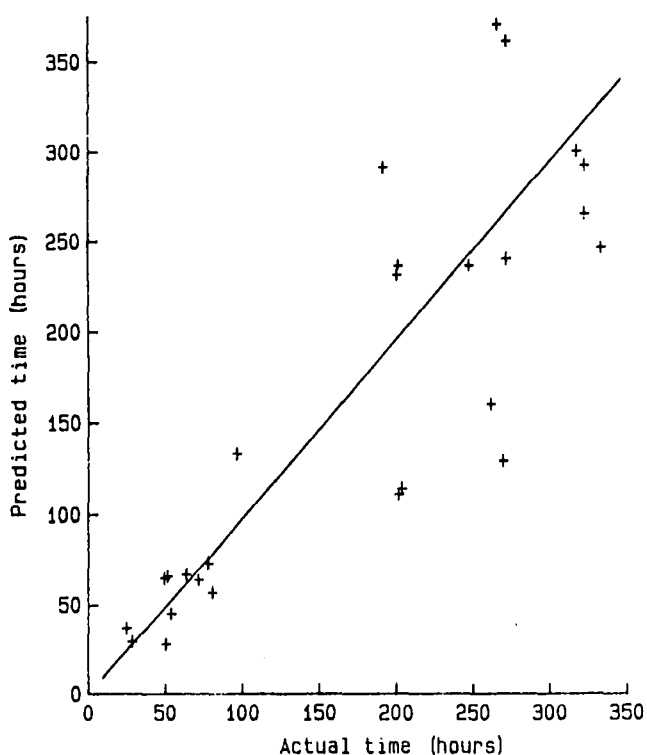


FIGURE 5 Predicted versus actual delays. Equivalence line shown

It can be calculated that the value predicted by equation 12 will be on average within ± 30 hours of the actual delay time. It is thus evident that some uncertainty will have to be tolerated if a chemical index method is used.

Conclusion

This investigation has shown that it is possible to quantify the effect of cane deterioration on both the sucrose and impurity contents of cane by the use of mathematical approaches.

The factors that influence the deterioration rate of clean, whole stalk cane are the temperature, burning/trashing and cane variety. Of these temperature is by far the most important.

Deterioration results in serious sucrose losses and significant increases in the lactic acid and ethanol contents of cane, but has little to no effect on the concentration of colour bodies in cane. There is evidence, however, that the deterioration of diseased cane can result in large increases in amino nitrogen concentrations. This requires further investigation.

It has also been shown that it is possible to use the ethanol content of DAC extracts in conjunction with temperature and cane variety, to calculate the cut-to-crush delay. Further work is needed, however, for the method to be applied more generally.

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REFERENCES

1. Hatch MD, Sacher JA and Glasziou KT (1963). Sugar accumulation cycle in sugarcane. Studies on enzymes of the cycle. *Plant Phys.* 38: 338-343.
2. Hatch MD and Glasziou KT (1963). Sugar accumulation cycle in sugarcane. Relationship of invertase activity to sugar content and growth rate of storage tissue of plant grown in controlled environment. *Plant Phys.* 38: 344-348.
3. Sacher JA, Hatch MD and Glasziou KT (1963). Sugar accumulation cycle in sugarcane. Physical and metabolic aspects of cycle in immature storage tissue. *Plant Phys.* 38: 348-354.
4. Alexander AG (1973). *Sugarcane physiology*. Elsevier: 574-609.
5. Egan BT (1967). A sour storage of mechanically harvested chopped-up sugar cane. *Int Soc Sug Cane Technol* 12: 1199-1205.
6. Egan BT (1966). Investigation into the sour storage rot problem. *Queensland Soc Sug Cane Technol* 31: 15-26.
7. Bevan D and Bond J (1971). Micro-organisms in field and mill - a preliminary survey. *Queensland Soc Sug Cane Technol* 38: 137-143.
8. Wood RA (1976). Cane deterioration as affected by billet size, delay in milling and other factors. *S Afr Sug Technol Ass* 50: 12-17.
9. Wood RA (1973). Varietal differences in rate of deterioration of whole stalk sugar cane. *S Afr Sug Technol Ass* 47: 133-139.
10. Wood RA, Du Toit JL and Bruijn J (1972). Deterioration of whole stalk sugar cane. *S Afr Sug Technol Ass* 46: 151-157.
11. Wood RA (1973). Deterioration losses: burnt cut versus burnt standing cane. *S Afr Sug Technol Ass* 47: 160-163.
12. Bruijn J (1966). Deterioration of sugarcane after harvesting. *Int Sug J* 68: 331-334.
13. Bruijn J (1970). Deterioration of sugarcane after harvesting. *Int Sug J* 72: 195-198.
14. Bruijn J (1973). Changes in the chemical composition of sugarcane during storage. Ph.D. Thesis. University of Natal.
15. Ivin PC and Bevan D (1973). Further measurements of chopped cane deterioration. *Queensland Soc Sug Cane Technol* 40: 31-38.
16. Ivin PC (1972). The effect of billet size on the rate of cane deterioration. *Queensland Soc Sug Cane Technol* 39: 279-280.
17. Foster DH (1969). Deterioration of chopped cane. *Queensland Soc Sug Cane Technol* 36: 21-28.
18. Yeh CS (1984). Development of rapid assessment on cane deterioration. *Taiwan Sugar*. 31: 11-13.
19. Fulcher RP and Inkerman AA (1978). Further studies on the deterioration of cane and cane juices. *Queensland Soc Sug Cane Technol* 41: 161-169.
20. Kumar A, Sachdeva P and Gupta AP (1984). Parameter to evaluate staleness of harvested cane, reducing sugar. *Sug Tech Ass of India*. 48: 78-84.
21. Horwitz W (1980). Bacterial population in maple sap. Official methods of analysis of the AOAC. 13th edition: 531.
22. Anon. (1977). *Laboratory Manual for South African Sugar Factories*. South African Sugar Technologists' Association.

23. Lionnet GRE (1985). Preliminary study on the extraction of some impurities from cane during diffusion. *S Afr Sug Technol Ass* 59: 92-95.
24. Hermia GR, Lourdes MA, Escarilla T and Gregorio JV (1982). Preliminary study on the rate of deterioration of mechanically harvested cane. *Philippine Sug Tech Ass* 29: 369-370.
25. Anon (1979). *Varietal and seasonal deterioration of burnt cane*. Report 7500/1/2. Rhodesia Sugar Association Experiment Station.
26. Smith P, Paton NH, Delaney HR and Ames R (1981). Colour studies in milling. *Aust Soc Sug Cane Technol* 71-80.
27. Smith P and Gregory PE (1971). Analytical techniques for colour studies. *Int Soc Sug Cane Technol* 15: 1115-1625.