PILOT PLANT STUDIES ON THE EXHAUSTION OF LOW GRADE MASSECUITES

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ABSTRACT

The results of a pilot plant investigation into factors affecting crystallization of C-massecuites are presented. A mathematical model is used in the analysis of the results to separate solubility and crystallization rate information. The importance of the non-sucrose/water ratio as regards massecuite characteristics and solubility coefficients is highlighted.

INTRODUCTION

Some 3 years ago, Huletts Sugar Ltd. embarked on an investigation on a pilot plant scale into factors affecting low purity massecuite exhaustion in crystallizers. Of the many factors affecting the exhaustion of low purity massecuites, some like the type of impurity present, cannot be controlled, while others such as massecuite brix and purity may be readily changed by factory personnel. The approach used in this investigation has been to conduct the experiments in the factory, changing those factors which the operators in the mill are at liberty to influence or control.

The objective of this work was to be able to answer questions about which there has been a great deal of speculation and little in the way of hard facts. In essence it was aimed at providing a means of establishing how crystallizers should be operated for optimum results.

Preliminary results have been reported earlier (Lionnet[7]). This paper expands on the earlier results and describes the use of a simple mathematical model in analysing the results.

THE CRYSTALLIZATION PROCESS

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Two things affect the results obtained in crystallizers, the solubility of sucrose in the mother liquor, and the rate of crystallization. Both of these factors are affected by massecuite properties i.e. brix, purity, viscosity and type of impurities. Temperature, likewise, affects both the solubility and the crystallization rate, while stirring rate will affect only crystallization rate.

A considerable amount of work has been done in Australia (Foster *et al*[2,3]). This shows that the crystallization continues even at low purities, and that the real controlling factor is the high viscosity of the material at low purities.

In South Africa, Graham[4] showed the importance of high massecuite brixes. He discussed the effect of purity on the amount of massecuite to be handled but does not mention its effect on exhaustion as such.

Cooling rates have been studied by Relf[14] who concluded that irrespective of the rate of cooling in his pilot-crystallizer the exhaustion, achieved was the same after about 30 hours.

Julliene[6] using factory data, stressed the importance of C-massecuite purity on exhaustion. Using an approach involving high A-massecuite exhaustion and low C-massecuite purity, he achieved excellent results.

Smythe[16] in his excellent review on crystal growth, dealt on the effect of stirring on crystallization, on a laboratory scale. In pure sucrose solutions, the crystallization rate at constant supersaturation tends symptomatically to a limit (at approximately double the rate without stirring) as stirring increases. Quantitative date for factory scale operation is rather scarce.

In South Africa, a common approach to gauging the efficiency of C-massecuite exhaustion has been to compare molasses purities with the SMRI 'target purity formula', derived from laboratory exhaustion tests (Mathesius and Mellet[10]) The formula is as follows:

$$P^* = 39.9 - 19.6 \log RS/A \qquad (1)$$

This equation takes account of the effect of reducing sugar/ash ratio which affects sucrose solubilities.

In analysing the results of the pilot plant experiments, it is desirable to be able to separate the effects of solubility and crystallization rate. For this reason, a simple crystallization model has been drawn to compare experimental data.

FORMULATION OF THE MODEL

Mechanism of crystallization

There are 2 processes involved in crystallization (Mullin[12]). First, sucrose molecules in solution must be transported by diffusion from the bulk of the mother liquor across a boundary film surrounding the surface of the crystal, and second, once at the crystal surface, the sucrose molecules must be incorporated into the crystal lattice. This can be represented as follows:

$$\text{solution} \xrightarrow{k_a} \text{surface} \xrightarrow{k_b} \text{lattice}$$

The diffusional process may be represented as:

$$\text{rate} = \frac{k_a}{d}(c - C_i)^n \qquad (2)$$

where C and C_i are the concentrations of sucrose in the bulk of the mother liquor and at the interface between crystal and mother liquor, and d is the thickness of the surface layer across which the sucrose has to diffuse. The lattice incorporation step can be written as:

$$\text{rate} = k_b\,(C_i - C_s)^m \qquad (3)$$

where

C_s is the equilibrium concentration.

The values of the exponents n and m are generally close to unity but various workers disagree on what these values should be (Smythe[16], Wright and White[18]). In some cases, it is reported that the exponent depends on the value of the concentration difference.

As a close approximation, we can assume m = n = 1. In this case we can eliminate C_i from equations (2) and (3) to give:

$$\text{rate} = \frac{C - C_s}{d/k_a + 1/k_b} \qquad (4)$$

In general, the rate constants are not equal. If the diffusion process is much slower than the lattice incorporation step, $k_a \ll k_b$. Thus, $1/k_a \gg 1/k_b$ and equation (4) becomes:

$$\text{rate} = k_a/d\,(C - C_s) \qquad (5)$$

In this case the diffusion step is rate controlling.

It is generally conceded that the diffusion step is rate controlling at higher temperatures, but that the situation changes at a temperature of around 45°C (Van Hook[17]) Both k_a and k_b changed with temperature, but to different degrees i.e. they have different activation energies.

Because of the uncertainty regarding the exact mechanism of crystallization, the simplest equation regarding the rate of crystallization was assumed, i.e.

$$\text{rate} = kA\,(C - C_s) \tag{6}$$

This makes no assumption about the mechanism of crystallization, other than that it is dependent on the degree of supersaturation.

The rate constant k and the crystal surface area A are combine into a single parameter, since we do not know the total crystal surface area, let alone the surface area active for crystallization. Incorporating an Arrhenius type temperature dependence leads to:

$$KA = k_1 \exp(-E_A/RT) \tag{7}$$

where

E_A is the activitation energy.

Nomenclature used is listed at the end of the paper and the full set of equations used in the model is shown in Appendix 1.

Solubility of sucrose in impure solution

The solubility of sucrose in an impure solution can be written as

$$C_s = SC \times C_{s,p} \tag{8}$$

where $C_{s,p}$ is the solubility of sucrose in pure solution, and SC is the solubility coeficient. An equation is available for $C_{s,p}$ (Wright and White[18]) but conflicting information is published on how SC is affected by purity, reducing sugar/ash ratio and temperature (Meade and Chen[11], Wright and White[18])

Model parameters

Although various published information is available on crystallization rate k_1, activation energy E_A, and solubility coefficient SC, such information is often conflicting, and does not apply to South African conditions. It was therefore decided that these three quantities should be parameters of the model, which are evaluated by comparing the model with experimental data. By analyzing the values of these parameters, it should be possible to infer how the experimental variables considered affect both crystallization rate and solubility.

Programming procedures

The equations in Appendix 1 were programmed using the ICL SLAM language (Simulation Language for Analogue Modelling). This language allows differential equations to be solved numerically, without having to solve the equations analytically. Although the equations used are fairly simple, they cannot be solved analytically since temperature varies, and C_s and k vary with temperature.

In practice both measured purities and temperatures are input to the model. The actual temperatures measured are used, and there is no need for a heat balance.

A non-linear regression routine was used to fit the model to the data. This it does by systematically varying values of k_1, E_A and SC until the sum of squared errors between model and data reaches a minimum.

EXPERIMENTAL PROCEDURE

The experimental approach used for the investigation of selected factors was given careful consideration. The operational and control flexibility required demanded pilot plant scale, which however is often not representative because of its relativley small size while also presenting scale up problems. The requirements were:

(a) The plant should be of a capacity that would allow relatively by large quantities of massecuite to be treated, enabling samples to be taken throughout the treatment without reducing the level of massecuite significantly.
(b) It should provide stirring and cooling (or reheating) facilities to exceed the range of usual factory operational levels.

A kneader mixer or Z-blade mixer was obtained with the following specifications:

Working capacity	80 liters
Surface area jacketted for water flow	35%
Surface area/volume ratio	15 m^2 / m^3
Stirring rate	Variable 2 - 1/80 rpm

The high stirring levels were found to have two serious adverse effects, namely air entrainment into the massecuite resulting is viscosity increases, and generation which prevented or reduced cooling. Rotational speeds used were therefore usually confined to a 1/4 - 1/80 rpm range.

Further details of the pilot plant are given elsewhere (Lionnet[7])

Although the experiment concerned only the selected factors it was realized

that changes in both type and quantity of impurities in the massecuites would have a very pronounced effect on exhaustion. Since these changes cannot be controlled, it was decided to adopt an experimental approach which would give an indication of, and possibly help reduce, the effects of these changes.

The approach adopted involved factorially designed experiments and has been described by Lionnet and Baker[8]. This approach shows interactive effects between the factors if these effects are present, and therefore allows all factors under study to be optimized as a group rather than individually. Secondly, it requires measurement of the experimental error which includes the effects of changes in massecuite quality.

Massecuites and nutsch molasses were analyzed for brix, total solids by vacuum oven drying, and sucrose. All purities reported here are therefore true purities. Analytical methods used are described in the SASTA Laboratory Manual[15]. Temperatures were recorded on a multipoint temperature recorder.

In the last series of tests, viscosities were measured using a Brookfield HBT viscometer with a no. 7 spindle at the same rotational speed of 2.5 rpm. all at a temprature of 40°C.

A total of about 200 massecuites were treated in the pilot mixer during three seasons.

In all cases, trends established in one series of experiments were confirmed by the other series. Results presented here are therefore grouped together to represent the overall findings.

The overall range and levels of the factors investigated are shown in Table 1.

TABLE 1. Range of factors investigated

	Minimum	Maximum
Massecuite total solids	90.0	96.0
Massecuite true purity	50.0	66.0
Massecuite non-Sucrose/water ratio	3.8	8.6
Stirring rate (r.p.m.)	1/80	2.0
Retention time (hours)	10	24
Initial cooling rate (°C/hr)	1.7	4.2
Final temperature (°C)	34	40

The findings of this investigation obviously apply only over the ranges shown.

RESULTS AND DISCUSSION

Effect of massecuite characteristics

Massecuite total solids and true purity

Evaluation of the factorial tests showed that massecuite total solids was the most important factor, with higher values of total solids leading to lower final nutsch molasses purities.

Massecuite purity on the other hand was shown to have no statistically significant effect.

It has been shown that the non-sucrose/water ratio (NS/W) is an important factor affecting exhaustion (Jesic[5]) and so the results were analyzed in terms of NS/W as well. Regression analyses of the first series of data showed that the NS/W ratio gave a better correlation with nutsch molasses purity than did total solids % massecuite.

Since NS/W is calculated by the equation:

$$NS/W = \frac{TSMC\ (1 - PMC/100)}{100 - TSMC} \qquad (9)$$

it can be seen that both massecuite total solids and purity influence the NS/W ratio, which might explain the better correlation in terms of NS/W. Also it can be calculated from equation (9) that NS/W is influenced more by total solids than purity; a 1 unit change in total solids has the same effect of NS/W as roughly as a 6 unit change in purity.

Following these results, a factorial test was undertaken to investigate the effect of non-sucrose/water ratio. There are two ways of obtaining a high NS/W ratio. These are:

Case 1: By aiming for the highest possible massecuite total solids, but allowing massecuite true purity to rise to improve handling.

Case 2: By aiming for the lowest possible massecuite purity but allowing massecuite total solids to drop to improve handling.

These two approaches were investigated, and the results are summarized in Table 2. This table shows average massecuite conditions and exhaustions calculated at pan drop and after 15 hours in the pilot crystallizer.

It was found to be easier to obtain very high NS/W values through raising

TABLE 2. Summary of results of NS/W ratio investigation

	Case 1	Case 2
Massecuite total solids	94.4	91.6
Massecuite purity	63.2	53.1
NS/W	6.4	5.2
RS/A	1.38	1.32
Viscosity at 40°C (cP)	6.0×10^6	2.5×10^6
Total exhaustion	67.8	44.7
Pan exhaustion	59.3	35.5
Crystallizer exhaustion	8.5	9.2
Final molasses nutsch purity	35.0	39.0

Note: $\text{No. of Exhaustion} = \frac{10000\ (PMC - PM)}{PMC\ (100 - PM)}$

total solids than lowering massecuite purities. The case 1 results with the higher total solids and NS/W values showed very much higher exhaustions, and it is clear that most of this improvement was due to better pan work. Exhaustions in the crystallizer in case 1 were not significantly lower than in case 2 where purities were higher and viscosities lower. This applies to a highly efficient pilot crystallizer, and it is probable that on a factory scale, total exhaustion depends to an even larger degree on pan work.

In this particular series of results, massecuite total solids did in fact correlate better with molasses purity than NS/W ratio. In general lower molasses purities were obtained via the high-brix purity route than the low purity-low brix conditions.

Molasses purity was not found to be significantly correlated with nutsch viscosity. Visual observation of purity vs. massecuite viscosity data suggests a trend, but scatter renders any relationship non-significant.

Overall, NS/W was still more highly correlated with molasses purity, Regression analysis yields the following equation:

$$PM = 44.17 - 1.21\ NS/W \quad (10)$$

$$PM = 113.54 - 082\ TSMC \quad (11)$$

Correlation coefficients of 0.56 and 0.52 respectively with 58 degrees of freedom indicated relationships significant beyond the 0.1% level. The data is compared with these equations in Figs. 1 and 2.

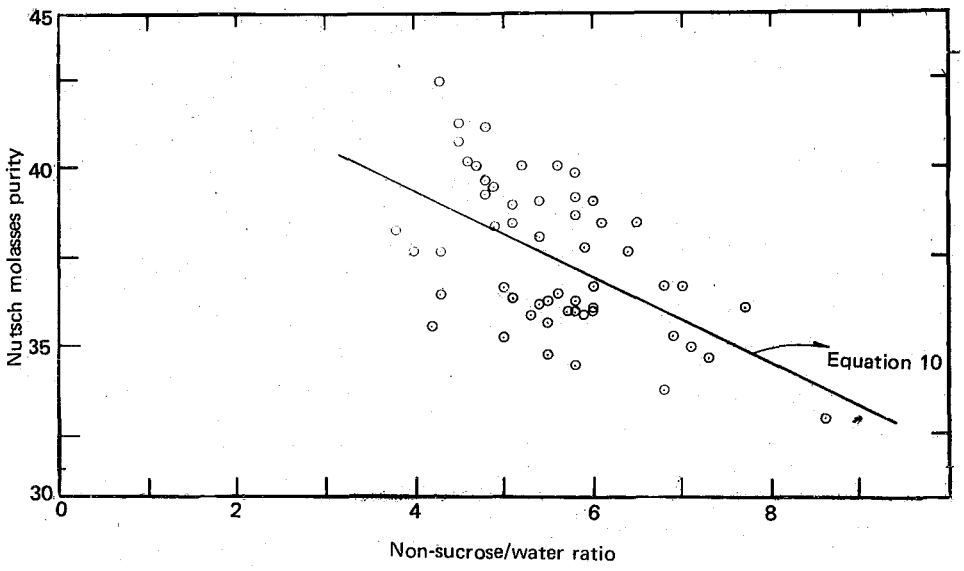

FIGURE 1. Effect of non-sucrose/water ratio on nutsch molasses purity after 15 hours in pilot crystallizer

The scatter is not surprising since the data included the full range of reducing sugar/ash ratios. A slightly better correlation was obtained when the target purity difference was used to account for varying RS/A values, particularly in the case of total solids % massecuite. Using the SMRI formula (equation 1) as the target, the following equation results:

$$\text{target purity difference} = 80.60\ \text{TSMC}\ 0.87 \qquad (12)$$

The correlation coefficient in this case is 0.61

Viscosity

Massecuite characteristics which affect exhaustion are also expected to affect viscosity. It is important that viscosities be considered in exhaustion experiments, particularly to ensure that conditions which limit handle ability are not exceeded. Viscosities were therefore measured in the latter series at 40°C.

It was found that viscosities could best be correlated in terms of NS/W. Fig. 3 shows nutsch molasses viscosities and the correlation equation obtained was:

$$\text{nutsch molasses viscosity}(\times 1^{-6}\ \text{cP}) = 5.94 - 2.86\,\text{NS/W} + .383(\text{NS/W})^2 \qquad (13)$$

The correlation coefficient was 0.99 and Fig. 3 indicates the excellent correlation.

Measurement problems were experienced with massecuite viscosities at high NS/W ratios. The scatter in the data becomes very much greater at values of NS/W 6. Crystal content was also found to influence viscosity and the following

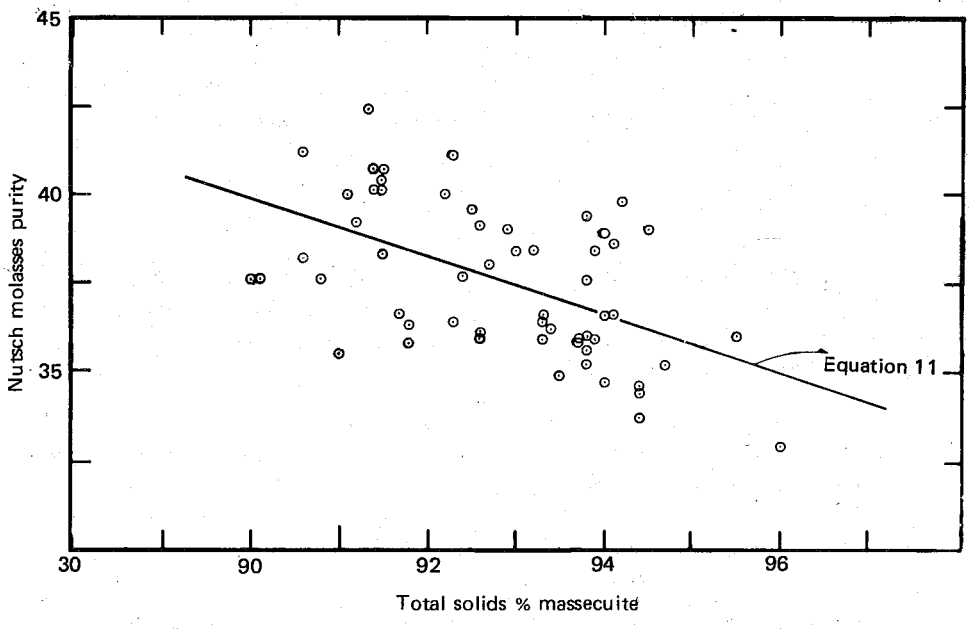

FIGURE 2. Effect of total solids % massecuite on nutsch molasses purity after 15 hours retention in pilot crystallizer.

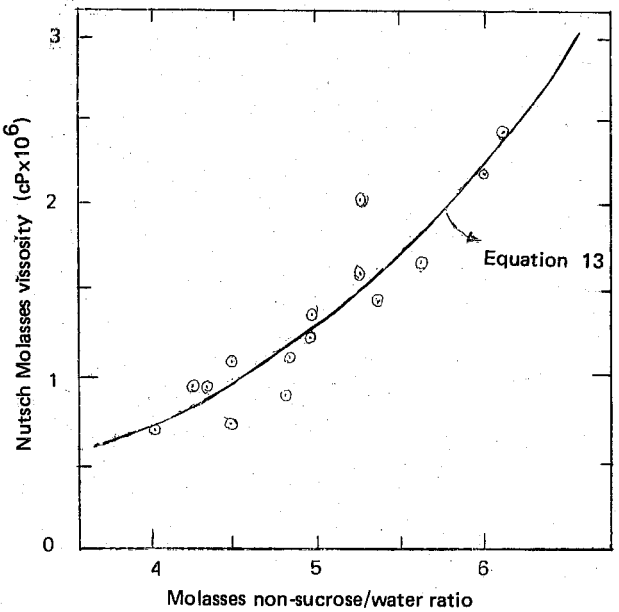

FIGURE 3. Molasses vissosity as a function of non-sucrose/water ratio

regression equation was derived:

$$\text{massecuite viscosity } (\times 10^{-6} \text{ cP}) = 10.0 + 2.1\ \text{NS/W} + 0.08\ \text{crystal content} \quad (14)$$

In this case the correlation coefficient was much lower at 0.76.

If viscosity is the limiting factor in massecuite treatment, these equations will allow an estimate of the NS/W ratio permissable to remain below the limiting viscosity.

Gassing Reactions in Massecuite

The interference of Maillard type reactions in the exhaustion of massecuites was encountered in some of the pilot plant experiments, mainly in cases where massecuite strike temperatures were high. These reactions have a number of undesirable side-effects such as:

(a) carbon dioxide is liberated, which increases massecuite viscosity.
(b) the reactions are exothermic, which interferes with cooling to an extent where temperature increases could occur.
(c) products of the reactions include polymers which also increase viscosity.
(d) glucose is consumed, which lowers the RS/A ratio and hence the exhaustibility of the massecuite is affected.

A recent investigation (Newell[13]) has shown that temperature is the most important factor influencing the reactions, with the rate doubling for a 5°C increase in temperature. Although gas information is most prevalent in C massecuites, it can occur in A and B molasses and syrup at 70°C. Total solids is the second most important variable affecting the reaction, and increasing total solids or NS/W ratio to improved exhaustion may also promote the gas forming reactions.

However, low temperature represent the best means of restricting the extent of these reactions.

Modelling Results

Validity of the model

The suitability of the model can be judge by the fit of the model to the data. Some examples of the type of fit obtained are shown in Fig. 4. The fit was good in most cases, but obviously, cannot follow the sort of changes shown when measured values fluctuated widely (see experimental data 27/6/77 in Fig. 4).

The changes in slope evident in the fitted curves in Fig. 4 are generally due to measured temperatures changing in a non-uniform way.

Values of the model parameters

For each set of experimental data, the best fit of the model yield a set of values of the parameters K^1, SC and E_A.

The values so obtained are listed in Table 3 together with means and standard deviations, as well as the main experimental variables.

TABLE 3. Values of model parameters and main operating variable.

	Maximum value	Minimum value	Mean	Std. deviation
K1 ($X10^9$)	33.0	0.43	6.17	7.22
k_{50}	4.89	0.06	0.69	0.83
SC	1.62	0.86	1.24	0.19
E_A	71094	49090	61492	4365
NS/W	7.28	3.31	5.12	0.90
RS/A	1.58	0.64	1.26	0.22
Total solids	94.7	90.0	92.3	1.32
True purity	67.4	51.5	58.5	3.0

Regression analysis was carried out to see whether the model parameters were significantly dependent or any of the independent variables listed Table 3.

Where no dependence of the parameter on various variables can be proved, it does not necessarily mean that there is no relationship. In some cases the range of variables encountered may be too small to established a relationship.

Values of k_1

Values of k_1 were found to be correlated with E_A. This is not altogether surprising since it can be seen from equation (7) that the same value of the overall crystallization rate kA can be obtained with different combinations of values of k_1 and E_A, i.e. high values of both k_1 and E_A can give the same value of kA as low values of both k_1 and E_A.

TABLE 4. Comparison of values of k_1 at two different stirring rates.

Stirring rate (r.p.m.)	2.0		0.3
Mean value of k_1	4.72×10^9		2.24×10^9
Std. deviation	2.14×10^9		1.39×10^9
No. of data points	6		7
Calculated t value		2.63	
$t_{11, 0, 05}$		2.20	

In order to overcome this, values of kA were calculated form equation (7) at a temperature of 50°C. (k_{50}). The showed a significant correlation at the 5% level with stirring rate only, higher rates of stirring leading to greater crystallization rates.

A factorial experiments was designed to investigate the effect of stirring rate, at 2 levels of 2.0 and 0.3 rpm. The resulting values of k_1 are shown in Table 4.

This shows a significant effect of stirring rate and suggests an increase in rate by a factor of just over 2 in going from the lower to the higher stirring rate.

The fact that stirring rate does affect crystallization rate implies that for part of the crystallization process at least, the diffusion controlled step plays an important part.

Neither k_1 nor k_{50} were found to be dependent on crystal content, although a relationship might be expected since the surface area is related to the crystal content. Temperature was not significant either, since the Arrthenius type of temperature dependence allows for the effect of temperature on crystallization rate.

Although there appeared to be some correlation between k_{50} and NS/W, the correlation coefficient was too low to be significant, (r = -0.235). Total solids and purity did not appear to affect k_1 or k_{50}.

Values of Activation Energy E_A

Stirring rate was found to affect values of E_A, with higher stirring speeds giving lower values of E_A - Although not significant, higher mean temperatures tended to give lower values of E_A, which might imply a closer approach to diffusion controlled crystallization under these conditions.

Values of E_A were found to average 61,500, covering a range of 71,000 to 49,000 J/g mole. Values have been reported in the literature covering a wide range of 20,000 to 100,000. However a review by Smythe[16] suggests that for pure sucrose solution a value of 67,000 J/mole is expected if the lattice incorporation step is controlling, or 29,000 - 38,000 if the diffusion step is controlling. The values obtain lie well within this range, but are closer on average to the lattice incorporation controlling values.

Australian work (Wright and White[18]) eports a value of 62,800 J/mole at 60°C, with a non-sucrose water ratio of 0.5 rising to 63,100 at 45°C and dropping to 62,500 at 75°C. They predict however that higher values are to be expected with higher non-sucrose/water ratios.

Clearly the values obtained from the model tie in well with expected values, but no conclusions on the mechanism can be drawn from this comparison.

Values of the Solubility Coefficient SC

A very strong dependence of SC on non-sucrose/water ratio (NS/W), total solids, purity and reducing sugar/ash ratio (RS/A) was evident. However, when all

of these 4 variables were included as independent variables in a regression analysis, only NS/W and RS/A were significant at the 5% level. A correlation coefficient of 0.85 was obtained for the following equation.

$$SC = 0.742 + 0.182\ NS/W - .346\ RS/A \qquad (15)$$

If only total solids and purity are included, the correlation coefficient drops to 0.75, and if total solids and RS/A are included, the coefficient is 0.71. Again NS/W ratio showed up as being a more significant variable than total solids or purity.

Values of SC averaged 1.23 and covered the range 0.86 to 1.62. Values greater than 1 implied that solubilities of sugar in impure solution were greater than those in pure solution. This conflicts with data of many other workers (De Brujin[1], Meade and Chen[11], Wright and White[18]) who found that in cane syrups values of SC are normally well below 1, implying that the impurities decrease the solubility of sugar. However, the reported information relates to lower NS/W ratios than were found in South African massecuites. Recent work from Australia (Maudarbocus and White[9]) confirms the type of relationship shown in equation 15, and shows that although values of SC less than 1 are obtained in the range they worked in ($2 < NS/W > 4{,}5$), indications are that values greater than 1 will be obtained for $NS/W > 4{,}5$, particularly with low RS/A ratios.

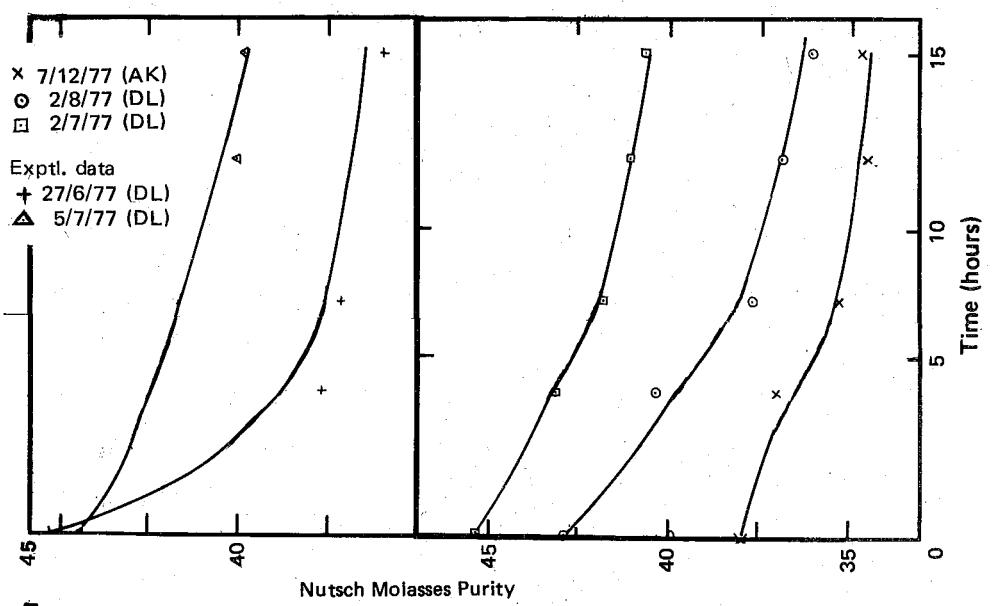

FIGURE 4. Fit of the molasses to experimental data. Solid lines represent the best fit in each case to the data

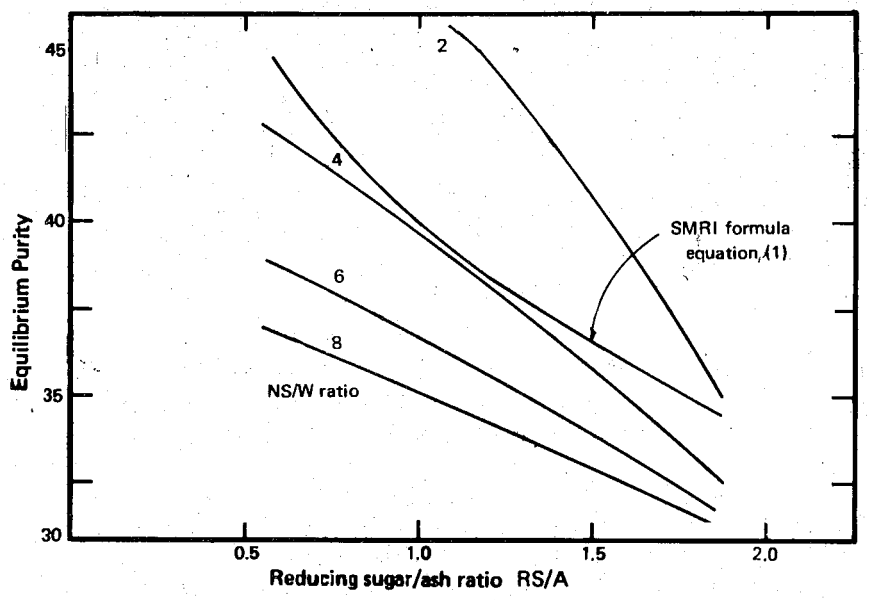

FIGURE 5. Predicted equilibrium purities as a function of reducing sugar/ash and non-sucrose water ratios at 40°C

The equation for SC enables us to calculate equilibruim purities as a function of NS/W and RS/A as shown in Appendix 2.

Equilibrium purities calculated for a temperature of 40°C are shown in Fig.5.

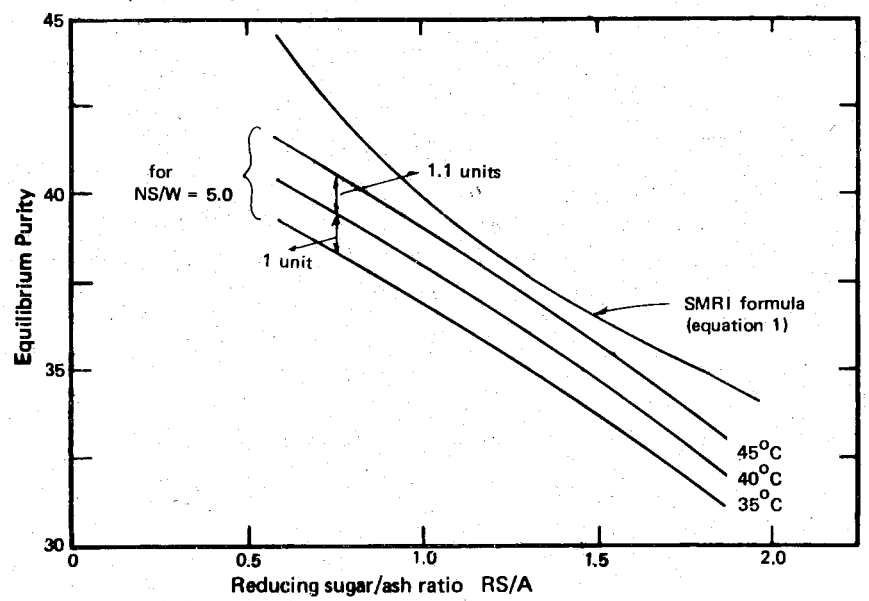

FIGURE 6. Effect of temperature on predicted equilibruim purities

This shows the importance of both RS/A and NS/W ratios. The effect of NS/W is more pronounced at low values of RS/A; this shows that more importance should be attached to obtaining high NS/W ratios when RS/A values low. At values of NS/W ratio commonly obtained, equilibrium purities significantly below the SMRI log formula (equation 1) should be obtained.

Since no dependence of SC on temperature was evident, the same procedure can be used to calculate equilibrium purities at different temperatures. Fig. 6 shows that a change of 5°C leads to a change of ¼1 unit in equilibrium purity.

A comparison of purities from Huletts Research and Development boiling down tests during the 1978/79 season is shown in Fig. 7. The agreement between this data and the predicted equilibrium purity for NS/W = 5.0 is remarkable. The significance of the agreement shown in Fig. 7 is considerable, when it is realized that the predictions were based on pilot plant experiments using mainly Darnall massecuites, while the boiling down test data represents laboratory boilings from 6 different mills in South Africa and one in Rhodesia.

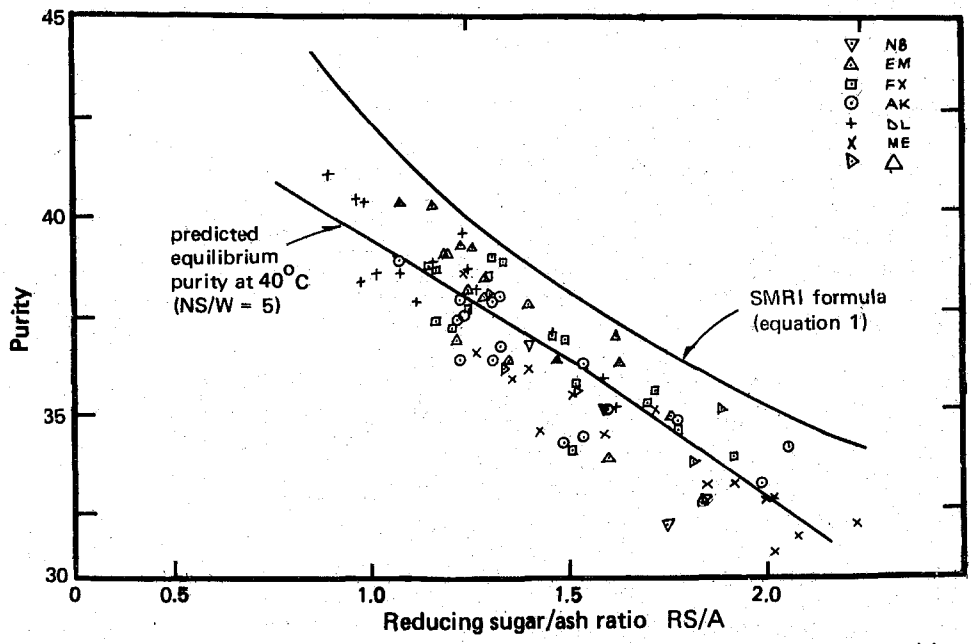

FIGURE 7. Comparison of purities obtained in laboratory exhaustion tests with predicted equilibruim purities

EFFECT OF COOLING RATE

A factorial experiment was undertaken to investigate the effect of cooling rate. Unfortunately the final temperature to which the massecuites were cooled was not constant in each case, so the effect of cooling rate cannot be judged from final

TABLE 5. Effect of cooling rate on final molasses purity

Initial cooling rate	(°X/hr)	Final Purity
Base Case	1,67	38.4
Slow cool	0.6	39,3
Rapid cool	3.0	37,8
Very rapid	15,0	37,6

nutsch purities. However values of the model parameters obtained appeared to be independent of the cooling rate applied. We can therefore use the model to predict what the effect of cooling rate should be. This was done for massecuite of average total solids (9,20) and purity (58,0) during these tests, and assuming average values of the model parameters. The base case assumed a linear temperature drop from 65°C to 40°C over 15 hours (cooling rate 1,67°C/hr) and this was compared with other case where the final temperature is 40°C, but different initial cooling rates over the first 5 hours. The results are shown in Table 5.

Clearly, the more rapid the cooling, the lower is the final purity, Thus, although the actual crystallization rate constant is lower at lower temperature, the net effect of low temperature when the degree of super-saturation is considered, as an increased rate of crystallization. Although these results apply strictly only to the pilot plant crystallizer, it is likely that the same qualitative results will be obtained in practice.

The very high cooling rates shown in Table 5 are obviously hypothetical, as such rapid cooling would lead to false grain formation. In the pilot plant tests, no false grain formation was observed at cooling rates up to 3°C/hr. At 3,2°C/hr, 30% of the tests showed the presence of false grain, under conditions of high NS/W ratio and low stirring rate.

CONCLUSIONS

This investigation has shown clearly the importance of the non-sucrose water ratio as a parameter in crystallization control. High values of non-sucrose water ratio are highly desirable from an exhaustion point of view, because of the effect on the solubility of sucrose and the final equilibruim purities attainable.

However, high values of non-sucrose water ratio also have a significant effect on viscosity. Equations are provided on how non-sucrose/water affects viscosity for South African conditions. Another effect of high non-sucrose/water ratios is the

promotion of Maillard type reactions accompanied by the evolution of gas. Apart from the loss of sugars which this reaction causes, the viscosity of the massecuite rises sharply as a result.

The effect of stirring rate has been investigated. An increase in rotational speed of crystallizer stirring elements results in faster crystallization. Large increases are necessary however to result in significant increases in crystallization rate.

The cooling profile found to be optimum is the fastest one which does not result in false grain formation. The industrial application of this finding will require additional information on the factors which affect false grain formation.

Values of solubility coefficient have been evaluated, and are shown to be strongly dependent on reducing sugar/ash ratio as well as non-sucrose/water ratio. This has enabled the calculation of equilibrium purities, which show good agreement with results obtained from laboratory exhaustion tests.

NOMENCLATURE

A	Crystal surface area (m^2/m^3)
C	Sucrose concentration (9/100 g H_2O)
C_o	Initial sucrose concentration (g/100 H_2O)
C_i	Sucrose concentration of crystal interface (g/100g H_2O)
C_s	Saturated sucrose concentration (g/100g H_2O)
Cs,p	Saturated sucrose concentration for pure sucrose solution (g/100g H_2O)
d	Diffusion film thickness (m)
E_A	Activation energy (J/g mole)
k	Crystallization rate constant (kg/hr m^2)
k_o	Pre-exponential factor (kg/hr m^2)
K_1	K_oA (kg/hr m^3)
k_a	Rate constant for diffusion controlled cyrstallization
k_b	Rate constant for lattice incoporation controlled cyrstallization
NS/W	Non sucrose/water ratio
m	Mass of massecuite (kg)
m_c	Mass of sucrose crystal (kg)
m_I	Mass of impurities (kg)
m_s	Mass of sucrose in solution (kg)
$m_{s,o}$	Initial value of m_s (kg)
m_w	Mass of water, Mass of sucrose, total (kg)
P^*	Target purity (from equation 1)
PMC	Purity of massecuite (%)
PM	Purity of molasses (nutsch molasses)

PM_o	Initial purity of molasses (nutsch molasses)
R	Universal gas constant (J/g mole ^oK)
RS/A	Reducing sugar/ash ratio
SC	Solubility coefficient, defined by equation 8
SS_p	Saturated concentration of sucrose in pure solution (% by weight)
t	Time (hours)
T	Absolute temperature (^oK)
TSMC	Total solids % massecuite
V	Massecuite volume (m^3)
ρ	Density of massecuite (kg/m^3)

APPENDIX 1

MATHEMATICAL MODEL OF A BATCH CRYSTALLIZER

1. Basic assumptions

No evaporation or addition of water
Amount of impurities (non-sucrose) constant
Concentrations expressed as g sucrose/100 g water
Crystal surface area A is constant
Perfect mixing in the cyrstallizer, i.e. uniform conditions of temperature, brix, etc.
Non-nucleating conditions i.e. no false grain formation allowed for

2. Rate Equations

a) For sucrose in solution:

$$\frac{dm_s}{dt} = -k\,A\,V\,(C - C_s) \qquad (1.1)$$

b) For solid sucrose:

$$\frac{dm_c}{dt} = k\,A\,V\,(C - C_s) \qquad (1.2)$$

3. Crystallization rate constant

Assume an Arrhenius type dependence of k on temperature

$$\text{i.e. } k = k_o \exp(-E_A/RT) \qquad (1.3)$$

where E_A is the activation energy and T the absolute temperature

In the simplified case, the surface area A is considered together with the crystallization rate constant k as one entity

then

$$kA = k_o A \exp(-E_A/RT) = k_1 \exp(-E_A/RT) \quad (1.4)$$

4. Solubility relationship

Use is made of the equation of Charles[18] to calculate the solubility of sucrose in pure solutions,

$$\text{i.e. } SS_p = 64.407 + 0.07251T + 0.002057T^2 - 9.035\times10^{-6}T^3 \quad (1.5)$$

where SS_p is in units of % sucrose.

In order to convert to g sucrose/100 g water, the following relationship is used:

$$C_{s,p} = 100\, SS_p/(100 - SSp) \quad (1.6)$$

For impure solutions, the saturation solubility is multiplied by a solubility coefficient, SC

$$\text{i.e. } C_s = SC \times C_{s,p} \quad (1.7)$$

5. Miscellaneous calculations

Volume of massecuite V = m/p (1.8)

Mass of sucrose m_{suc} = $m(PMC/100 \times TSMC/100)$ (1.9)

Mass of water m_w = $m \times (100 - TSMC)/100$ (1.10)

Mass of impurities m_1 = $m(1-m_w - m_{suc})$ (1.11)

Purity of molasses PM = $m_s/(m_s + m_1)$ (1.12)

6. Initial conditions

At time = zero, the concentration of sucrose in molasses (mother liquor) C_o must be specified

$$C_o = 100\, m_{so}/m_w \quad (1.13)$$

$$m_s = m_1 \times PM_o/(100 - PM_o) \quad (1.14)$$

APPENDIX 2

CALCULATION OF EQUILIBRIUM PURITIES AS A FUNCTION OF TEMPERATURE, RS/A AND NS/W

$$C_s = SC \times C_{s,p} \qquad (8)$$

From equations (1.5) and (1.6):

T°C	35	40	45
$C_{s,p}$(g/100g H_2O)	223.6	233.6	245,0

$$SC = 0.742 + 0.1820\ NS/W - 0.3461\ RS/A \qquad (15)$$

Calculation Procedure

$$C_s = SC \times C_{sp} = \frac{m_s \times 100}{m_w}$$

$$NS/W = \frac{m_1}{m_w}$$

$$m_s + m_w + m_1 = 1$$

$$\frac{m_s}{m_w} + \frac{m_1}{m_w} = \frac{1 - m_w}{m_w}$$

Equilibrium Purity

$$Peq = \frac{100\ m_s}{1 - m_w} = \frac{100\ (m_s/m_w)}{\frac{1 - m_w}{m_w}}$$

$$= \frac{\frac{100 m_s}{m_w}}{\frac{m_s}{m_w} + \frac{m_1}{m_w}}$$

$$= \frac{SC \times C_{sp}}{\frac{SC \times C_{sp}}{100} + NS/W}$$

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ESTUDIOS EN PLANTA PILOTO SOBRE AGOTAMIENTO DE MASACOCIDAS DE BAJO GRADO

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RESUMEN

En este trabajo se presentan los resultados de una investigacion a escala de planta piloto sobre los factores que afectan la cristalizacion de masacocidas de 3ª. Se usa un modelo matematico en el analisis de los resultados para separar la informacion sobre solubilidad y velocidad de cristalizacion. Se hace especial enfasis en la importancia de la relacion no sacarosa/agua en lo que respecta a las caracteristicas de las masacocidas y a los coeficientes de solubilidad.