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 (Lionnet7). This paper expands on the earlier results and describes the use of a simple mathematical model in analysing the results.

THE CRYSTALLIZATION PROCESS

The controllable factors which affect the crystallization process C-massecuite brix, C-massecuite purity, stirring rate, cooling rate and residence time in the crystallizer.
The controllable factors which affect the crystallization process are C-massecuite purity, stirring rate, cooling rate and residence time in the crystallizer.

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, Graham4 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 Relf14 who concluded that irrespective of the rate of cooling in his pilot-crystallizer the exhaustion achieved was the same after about 30 hours.

Jullienne6 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.

Smythe16 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 data 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 Melet10) The formula is as follows:

\[ P^* = 39.9 - 19.6 \log \frac{RS}{A} \]  \hspace{1cm} (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 (Mullin12). 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:

\[ \text{rate} = \frac{k_a}{d} (C - C_i)^n \]  \hspace{1cm} (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:

\[ \text{rate} = k_b (C_i - C_s)^m \]  \hspace{1cm} (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 (Smythe16, Wright and White18). 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:

\[ \text{rate} = \frac{C - C_s}{d/k_a + 1/k_b} \]  \hspace{1cm} (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:

\[ \text{rate} = \frac{k_a}{d} (C - C_s) \]  \hspace{1cm} (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 450°C (Van Hook\textsuperscript{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.

$$\text{rate} = k A (C - C_s)$$

(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:

$$KA = k_1 \exp (-E_A/RT)$$

(7)

where $E_A$ is the activation 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

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

(8)

where $C_{s,p}$ is the solubility of sucrose in pure solution, and $SC$ is the solubility coefficient. An equation is available for $C_{s,p}$ (Wright and White\textsuperscript{18}) but conflicting information is published on how $SC$ is affected by purity, reducing sugar/ash ratio and temperature (Meade and Chen\textsuperscript{11}, Wright and White\textsuperscript{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.
Although the experiment concerned only the selected factors it was realised that the system partially satisfied the criteria of the experiments.

The mixture was continuously stirred at 4 ω by means of a four-bladed impeller. The impeller speeds used were 90 rpm. The stirring speed was found to have two opposing adverse effects:

<table>
<thead>
<tr>
<th>Stirring speed</th>
<th>Surface area/volume ratio</th>
<th>Working capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 rpm</td>
<td>15 m²/m³</td>
<td>35%</td>
</tr>
</tbody>
</table>

The stirring speed was changed by varying the torque on the impeller, and the impeller speed was measured by changing the voltage on the motor.

A greater number of trials was obtained with the following speeds:

<table>
<thead>
<tr>
<th>Stirring speed</th>
<th>Surface area/volume ratio</th>
<th>Working capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 rpm</td>
<td>15 m²/m³</td>
<td>35%</td>
</tr>
</tbody>
</table>

The experiments were used for the investigation of selected factors was

**Experimental Procedure**

Errors between model and data which is minimum.

A non-linear regression routine was used to fit the model to the data. This is

The central factor measured are used and these is no need for a tolerance.

In practice both measured particle and uncertainties are applied to the model.

The equations in Appendix I were programmed using the ICL SLAM.
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. 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. 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 temperature 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**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Massecuite total solids</td>
<td>90.0</td>
<td>98.0</td>
</tr>
<tr>
<td>Massecuite true purity</td>
<td>50.0</td>
<td>66.0</td>
</tr>
<tr>
<td>Massecuite non-Sucrose/water ratio</td>
<td>3.8</td>
<td>8.6</td>
</tr>
<tr>
<td>Stirring rate (r.p.m.)</td>
<td>1/80</td>
<td>2.0</td>
</tr>
<tr>
<td>Retention time (hours)</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>Initial cooling rate (°C/hr)</td>
<td>1.7</td>
<td>4.2</td>
</tr>
<tr>
<td>Final temperature (°C)</td>
<td>34</td>
<td>40</td>
</tr>
</tbody>
</table>

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\textsuperscript{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:

\[
\frac{\text{NS/W}}{100} = \frac{TSMC (1 - \text{PMC}/100)}{100 - TSMC}
\]  

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

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

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

...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:

\[
PM = 44.17 - 1.21 \text{ NS/W} \\
PM = 113.54 - 0.82 \text{ TSMC}
\]

(10) (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.
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:

\[
\text{target purity difference} = 80.60 \text{TSMC} 0.87
\]  \hspace{1cm} (12)

The correlation coefficient in this case is 0.61.

*Viscosity*

Masscuite 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:

\[
\text{nutsch molasses viscosity} (\times 10^6 \text{ cP}) = 5.94 - 2.86 \text{NS/M} + .383(\text{NS/W})^2
\]  \hspace{1cm} (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 viscosity as a function of non-sucrose/water ratio.
regression equation was derived:

\[
\text{massecuite viscosity (x10}^\text{6 cP)} = 10.0 + 2.1 \text{ NS/W} + 0.08 \text{ crystal content (14)}
\]

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 permissible 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\textsuperscript{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.**

<table>
<thead>
<tr>
<th>Maximum value</th>
<th>Minimum value</th>
<th>Mean</th>
<th>Std. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1(10^9)$</td>
<td>33.0</td>
<td>6.17</td>
<td>7.22</td>
</tr>
<tr>
<td>$k_{50}$</td>
<td>4.89</td>
<td>0.06</td>
<td>0.69</td>
</tr>
<tr>
<td>SC</td>
<td>1.62</td>
<td>0.86</td>
<td>0.19</td>
</tr>
<tr>
<td>$E_A$</td>
<td>71094</td>
<td>49090</td>
<td>61492</td>
</tr>
<tr>
<td>NS/W</td>
<td>7.28</td>
<td>3.31</td>
<td>0.90</td>
</tr>
<tr>
<td>RS/A</td>
<td>1.58</td>
<td>0.64</td>
<td>0.22</td>
</tr>
<tr>
<td>Total solids</td>
<td>94.7</td>
<td>90.0</td>
<td>1.32</td>
</tr>
<tr>
<td>True purity</td>
<td>67.4</td>
<td>51.5</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Regression analysis was carried out to see whether the model parameters were significantly dependent on 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 establish 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 $k_A$ 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 $k_A$ as low values of both $k_1$ and $E_A$.

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

<table>
<thead>
<tr>
<th>Stirring rate (r.p.m.)</th>
<th>2.0</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value of $k_1$</td>
<td>$4.72 \times 10^9$</td>
<td>$2.24 \times 10^9$</td>
</tr>
<tr>
<td>Std. deviation</td>
<td>$2.14 \times 10^9$</td>
<td>$1.39 \times 10^9$</td>
</tr>
<tr>
<td>No. of data points</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Calculated t value</td>
<td>2.63</td>
<td></td>
</tr>
<tr>
<td>t ($11$, 0.05)</td>
<td>2.20</td>
<td></td>
</tr>
</tbody>
</table>
In order to overcome this, values of $k_A$ 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 Arrhenius 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/mole. Values have been reported in the literature covering a wide range of 20,000 to 100,000. However a review by Smythe 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 obtained lie well within this range, but are closer on average to the lattice incorporation controlling values.

Australian work (Wright and White) reports 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 lie in well with expected values, but no conclusions on the mechanism can be drawn from this comparison.

**Values of the Solubility Coefficient $S_C$**

A very strong dependence of $S_C$ 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.

\[ SC = 0.742 + 0.182 \text{ NS/W} - 0.346 \text{ RS/A} \]  

(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, Meade and Chen, Wright and White) 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) 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](image-url)  

**Figure 4.** Fit of the molasses to experimental data. Solid lines represent the best fit in each case to the data.
The equation for SC enables us to calculate equilibrium 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 5. Predicted equilibrium purities as a function of reducing sugar/ash and non-sucrose water ratios at 40°C.

Figure 6. Effect of temperature on predicted equilibrium 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 $1.1$ 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.

![Graph showing predicted equilibrium purity at 40°C (NS/W = 5)](image)

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

<table>
<thead>
<tr>
<th>Initial cooling rate</th>
<th>(°C/hr)</th>
<th>Final Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>1.67</td>
<td>38.4</td>
</tr>
<tr>
<td>Slow cool</td>
<td>0.6</td>
<td>39.3</td>
</tr>
<tr>
<td>Rapid cool</td>
<td>3.0</td>
<td>37.8</td>
</tr>
<tr>
<td>Very rapid</td>
<td>15.0</td>
<td>37.6</td>
</tr>
</tbody>
</table>

Nutsh 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 molasses 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 equilibrium 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 (g/100 g H$_2$O)
- **C$_0$**: Initial sucrose concentration (g/100 g H$_2$O)
- **C$_i$**: Sucrose concentration of crystal interface (g/100 g H$_2$O)
- **C$_s$**: Saturated sucrose concentration (g/100 g H$_2$O)
- **C$_{sp}$**: Saturated sucrose concentration for pure sucrose solution (g/100 g H$_2$O)
- **d**: Diffusion film thickness (m)
- **E$_A$**: Activation energy (J/g mole)
- **k**: Crystallization rate constant (kg/hr m$^2$)
- **K$_0$**: Pre-exponential factor (kg/hr m$^2$)
- **K$_1$**: $K_0$A (kg/hr m$^3$)
- **k$_a$**: Rate constant for diffusion controlled crystallization
- **k$_b$**: Rate constant for lattice incorporation controlled crystallization
- **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$_{so}$**: 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)
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 crystallizer, 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:
      \[
      \frac{d m_s}{dt} = -k A V (C_s - C_p)
      \]  \hspace{1cm} (1.1)
   b) For solid sucrose:
      \[
      \frac{d m_c}{dt} = k A V (C - C_p)
      \]  \hspace{1cm} (1.2)

3. Crystallization rate constant
   - Assume an Arrhenius type dependence of k on temperature
   \[
   i.e. k = k_0 \exp (-E_A/RT)
   \]  \hspace{1cm} (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

$$kA = k_0 A \exp\left(-\frac{E_A}{RT}\right) = k_1 \exp\left(-\frac{E_A}{RT}\right)$$

(1.4)

4. Solubility relationship

Use is made of the equation of Charles\(^{18}\) to calculate the solubility of sucrose in pure solutions,

$$i.e. \quad S_{SP} = 64.407 + 0.07251T + 0.002057T^2 - 9.035 \times 10^{-6}T^3$$

(1.5)

where \(S_{SP}\) is in units of \% sucrose.

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

$$C_{s,p} = \frac{100 S_{SP}}{(100 \cdot S{SP})}$$

(1.6)

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

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

(1.7)

5. Miscellaneous calculations

Volume of massecuite \(V = \frac{m}{p}\)

(1.8)

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

(1.9)

Mass of water \(m_w = m \times (100 \cdot \frac{TSMC}{100})\)

(1.10)

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

(1.11)

Purity of molasses \(PM = \frac{m_s}{m_s + m_1}\)

(1.12)

6. Initial conditions

At time = zero, the concentration of sucrose in molasses (mother liquor) \(C_0\) must be specified

$$C_0 = 100 \frac{m_{so}}{m_w}$$

(1.13)

$$m_s = m_1 \times \frac{PM_0}{(100 - PM_0)}$$

(1.14)
APPENDIX 2

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

\[ C_s = SC \times C_{s,p} \]

From equations (1.5) and (1.6):

<table>
<thead>
<tr>
<th>T°C</th>
<th>C_{s,p}(g/100g H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>223.6</td>
</tr>
<tr>
<td>40</td>
<td>233.6</td>
</tr>
<tr>
<td>45</td>
<td>245.0</td>
</tr>
</tbody>
</table>

\[ SC = 0.742 + 0.1820 \text{NS/W} - 0.3461 \text{RS/A} \]

Calculation Procedure

\[ C_s = SC \times C_{s,p} = \frac{m_s \times 100}{m_w} \]

\[ \frac{m_s + m_w + m_1}{m_w} = 1 \]

\[ \frac{m_s + m_1}{m_w} = \frac{1 - m_w}{m_w} \]

Equilibrium Purity

\[ P_{eq} = \frac{100}{1 - m_w} \left( \frac{m_s}{m_w} \right) = \frac{100 \times m_s}{m_w} \frac{1 - m_w}{m_w} \]

\[ = \frac{100 m_s}{m_w} \frac{m_s + m_1}{m_w} \]

\[ = \frac{SC \times C_{s,p}}{SC \times C_{s,p} + \text{NS/W}} \]
REFERENCES


ESTUDIOS EN PLANTA PILOTO SOBRE AGOTAMIENTO
DE MASACOCIDAS DE BAJO GRADO

R.E. Lionnet y P.W. Rein

RESUMEN

En este trabajo se presentan los resultados de una investigación a escala de planta piloto sobre los factores que afectan la cristalización de masacocidas de 3ª. Se usa un modelo matemático en el análisis de los resultados para separar la información sobre solubilidad y velocidad de cristalización. Se hace especial énfasis en la importancia de la relación no sacarosa/agua en lo que respecta a las características de las masacocidas y a los coeficientes de solubilidad.