SOLUBILITY—CRYSTALLIZATION CHARACTERISTICS OF QUEENSLAND MOLASSES

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ABSTRACT

Molasses from five different cane growing areas along the Queensland coast have been studied in the laboratory to characterize the dependence of sucrose solubility, viscosity and crystal growth rate on impurity composition and concentration. A statistical analysis of the results was also conducted.

Over defined ranges, the values of the solubility coefficient of the molasses have been correlated with the impurity/water ratio, the reducing sugar/ash ratio and the molasses temperature with an expression involving a root mean square error of 0.017 in its fit to the data. Crystal growth rate, measured in a modified version of the apparatus of Smythe, decreased linearly with the exponential of the impurity/water ratio and also showed a strong dependence on molasses viscosity under the growth conditions, indicating a strongly diffusion limited growth regime. Crystal growth rates were measured at two different rates of shear. Molasses viscosity measurements have been correlated with molasses solids concentration, temperature, molasses purity and viscometer shear rate with a standard error of 27%.

INTRODUCTION

Increased understanding of the solubility of molasses, particularly in low purity solutions would encourage better factory performance towards improved molasses exhaustion. This is one reason which has prompted this investigation. Also, the continuing search for greater efficiency in pan stage operations through microprocessor control on batch pans, continuous pan installations, etc. has required tighter design calculations. To achieve these goals, more precise knowledge of the crystallization behavior and flow properties of the molasses is necessary.

The study was undertaken to determine the solubility crystallization characteristics of molasses samples obtained from different geographical cane-growing areas of Queensland. Properties measured included the solubility coefficient, the growth rate and molasses viscosity. In particular, the influence of impurity composition on these properties is of primary interest.
EXPERIMENTAL PROCEDURE

Equilibration Method

Composites of final molasses samples collected from individual mills in five specific cane-growing regions were obtained. A subsample of approximately one liter from each composite was concentrated under a vacuum of -86 kPag in a rotary film evaporator until the saturation temperature, as measured on the Sugar Research Institute automated saturation temperature apparatus (Wright\textsuperscript{7}), was in the range of 47-49°\textordmasculine. Approximately 700 ml of molasses was transferred to a container and 150 g of sieved high pol sugar (size range 0.4-1.0 mm) was added. The container was sealed and tumbled in a temperature-controlled water bath held at 50°C for approximately 20 hours. This apparatus has been described in detail by Miller and Wright\textsuperscript{15}.

An additional equilibrium trial was conducted for each molasses in a second water bath apparatus held at 65°C. The molasses in this test had previously been concentrated to a saturation temperature of approximately 62-64°C.

A sample of each equilibrated molasses was obtained subsequently by pressure filtration. The remaining crystals were observed under a microscope to check if the edges had been rounded confirming that saturation had been reached from an initial undersaturated condition. The photometric method for determining saturation temperature greatly assisted the experimental procedure as a similar degree of undersaturation prior to the equilibration step could be achieved quite readily.

The above procedure was repeated for higher purity molasses obtained by dissolving refined sugar in the original composite final molasses. The additional samples were approximately 50, 55, 62, 70 and 80 true purity.

Growth Rate Measurement

The average rate of crystallization on all faces of a sugar crystal was estimated by measuring the individual increase in mass on four crystals suspended in a growth apparatus similar to that employed by Symthe\textsuperscript{19}.

The apparatus consisted of a 200 ml beaker which was immersed in a temperature-controlled water bath. Four pairs of sharpened tongs made on stainless steel spring wire were spaced equally about the circumference of an assembly which sealed the beaker. These tongs secured the sugar crystals at a position about 1 cm from the periphery of a two-blade impeller and directly in the radial discharge from the blades. A photograph of this assembly in readiness for a period of crystal growth is shown in Fig. 1.

The sugar crystals were prepared previously, by growing them in a low supersaturation syrup and these were then washed, dried and stored for the tests.

The rate of crystallization was determined at a temperature of 50°C for each molasses sample which have been saturated at 65°C. The procedure adopted in carrying out the measurements was as follows:

1. Four crystals were wiped clean with tissue paper and weighed separately on a Beckman microbalance (Wright and White\textsuperscript{25}). These were then secured
FIGURE 1. Apparatus per crystal growth rate measurements.

firmly between the needle points of the tongs.

2. The test molasses were heated to about 75°C to ensure no crystal fragments or fine grain were present and the temperature then reduced to 50°C for the growth tests. The crystals were submerged into the molasses and the stirrer speed adjusted to 2000 rpm.

3. The run was continued for approximately two hours and the crystals removed,
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4. The crystals were re-clamped in the tongs and the procedure repeated for a run at 400 rpm.

The average linear growth rate, expressed as the rate of change of equivalent spherical diameter, was determined for each crystal from the measured increase in mass of the crystal by the formula:

\[ G = \frac{1}{t} \left[ \frac{6M_F^{1/3}}{\pi p} - \frac{6M_I^{1/3}}{\pi p} \right] \]

where \( t \) = time for crystal growth
\( M_I, M_F \) = initial and final crystal mass
\( p \) = density of crystal (1582 kg/m³)

This becomes:

\[ G (\mu m/h) = \frac{6.39 \times 10^4}{t (mins)} (M_F^{1/3} - M_I^{1/3}) \]

where crystal mass is expressed in mg.

Frequently, crystal growth rate data are quoted in terms of the dimensions according to the shape factor of Kucharenko. The conversion to these growth rates can be determined by the relationships:

\[ G \text{ (equiv. spherical diameter, } \mu m/h) = 1.17G \text{ (Kucharenko length, } \mu m/h) \]

\[ = \frac{\text{Area deposition rate (mg m}^{-2} \text{ min}^{-1})}{11.399} \]

Viscosity Measurements

The viscosity of each equilibrated molasses was measured using a Brookfield RVT series viscometer with a small sample adaptor and a SC4-27/13 spindle. Measurements at different shear rates (available range 0.2-34 s⁻¹) were made at temperatures of 40, 50 and 60°C.

Chemical Analysis

The methods of analysis for reducing sugars, sucrose, dry substance and ash as recommended in the Laboratory Manual for Queensland Sugar Mills were used for the chemical analysis of all samples.
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<th>Mill Area</th>
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<th>Sludge % Mol. Solids</th>
<th>Sample</th>
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<th>Ash*</th>
<th>Ca*</th>
<th>Mg*</th>
<th>K*</th>
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*Quantities expressed as mass % solids.
De-sludged molasses samples were obtained by diluting original molasses samples to 70 D.S. and centrifuging at 5000 times gravity for 30 minutes. The sludge was washed 5 times with a minimum quantity of cold water. Both the de-sludge molasses and dried sludge were analyzed by atomic absorption spectrophotometry for Ca, Mg, K and Na using a slight variation of the method of Sang et al.\textsuperscript{18}

Table 1 presents the results of analyses on the de-sludged molasses and sludge for the live mill areas. Constituent quantities are expressed as a percentage on solids.

**DISCUSSION**

**Solubility of sucrose in molasses**

By definition, the solubility coefficient (SC) relates the effect of non-sucrose material on the sucrose solubility in impure sucrose solutions, Meade and Chen,\textsuperscript{13}, viz.

\[
SC = \frac{(S/W) \text{ impure sucrose solution saturated at temperature } T}{(S/W) \text{ pure sucrose solution saturated at temperature } T}
\]

where $S/W = \text{ mass ratio of sucrose to water.}$

An impurity compound which reduces the solubility coefficient of sucrose not only reduces the solution viscosity by virtue of the reduction in sucrose concentration of the saturated solution, but also tends to reduce the amount of sugar dissolved in the 'exhausted' molasses.

Generally, it is considered that reducing sugars lower the solubility of sucrose and most inorganic salts increase the solubility.

Because of this general pattern the solubility of sucrose in impure solutions is related often to the relative proportion of the reducing sugars to inorganic substances. However, while Kelly\textsuperscript{7} agreed with this view, he pointed out that several inorganic salts, particularly those which form stable hydrates e.g. calcium chloride, magnesium sulphate, decrease the solubility of sucrose. It is therefore necessary to consider the nature of the inorganic salts in the molasses in addition to their total concentration.

The effect of temperature on the solubility coefficient is also of importance. In general the solubility coefficient increases with temperature although this effect depends to some extent on the composition and amount of impurities (Kelly\textsuperscript{6}).

Considerable research work into the variables affecting SC viz. impurity concentration (I/W ratio), composition of the impurity substances, and temperature have been undertaken in the sugar beet industry and this has contributed greatly to the technology employed in beet molasses exhaustion. Wiklund\textsuperscript{24} found that for any given molasses at I/W concentrations above 1.5, the SC increases linearly with increasing impurity concentration. Simple laboratory procedures (Wagne-
rowski et al. are conducted regularly in many beet factories to establish changes in the solubility.

The effect of impurities on the solubility of sucrose in cane molasses has attracted lesser attention. Generally, it has been regarded that within the range of conditions encountered in normal factory crystallization, the solubility reduced at higher impurity concentration levels due to the predominating influence of the reducing sugars present in cane molasses. Recently, however, Maudarbocus and White proposed a correlation for SC in terms of the I/W and reducing sugar/ash ratio (RS/ash) from data previously available on Queensland molasses. Here, at I/W ratios above 2, the solubility coefficient increased at higher total impurity concentrations. This same observation was reported by Jesic for Hawaiian molasses. He attributed the increase in sucrose solubility to the formation of salt-sucrose molecular-type compounds at higher non-sucrose concentrations thus allowing additional sucrose to be dissolved in the available water.

However, in both these investigations, saturation temperatures were measured for molasses at different concentrations using the saturascope apparatus and the determination of the solubility coefficients was made over a range of temperature e.g. 26-58°C for the Hawaiian study. It was assumed that the effect of temperature on the values of SC was not sufficient to influence the results, although the findings in this present study indicate this is incorrect. This is discussed further in the section to follow.

Results of Solubility Coefficient Measurements

Sucrose and dry substance analyses were undertaken on the pressure-filtered saturated molasses and the values of SC determined using the solubility data of Charles for pure sucrose. These measurements were made for the molasses taken from mill areas A-D (see Table 1). The values of SC determined for each molasses at the two temperatures of 50 and 65°C are plotted in Fig. 2 as a function of I/W ratio.

It is evident that the general pattern obtained was that of reduced solubility at higher total impurity concentration levels. No evidence of increased solubility at high I/W values was observed. It did appear, however, that a change in molecular arrangement occurred at I/W values in the range 1.5-2.5 resulting in a slight localized increase in sucrose solubility. However, there is insufficient data in this study to conclude if such a change positively exists. For each molasses higher values of SC were measured at the higher saturation temperature. No correlation was observed between sucrose solubility and the concentration of specific impurity components of the molasses though, in general, the value of SC was lower in molasses of higher RS/ash.

The values of SC have been correlated with the variables I/W, RS/ash and temperature (T) and an optimization search on the parameters has indicated the expression
The predicted values of SC according to expression (5) have been plotted in Fig. 2.

It is important to note that curves similar to those of the legend in Fig. 3 and 4 were obtained for a given molality, through a range of concentrations with SC being determined at the measured saturation temperature. The magnitude of the increase in saturation temperature at higher non-sucrose water ratios is sufficient to ensure that SC values increase.

Growth rate measurements

Sucrose crystal growth is controlled by the mass transfer of molecules of sucrose from the bulk of the solution to sites on the growing crystal surface, by a surface incorporation process, or by a combination of both. Under usual industrial boiling conditions, neither of these steps is exclusively rate-controlling and the overall crystal growth rate is a function of the rate of both processes.

Spry et al. [9] provides a detailed review of the dependence of growth rate on such factors as supersaturation, temperature, relative velocity of crystal and solution, nature and concentration of impurities, and the nature of the crystal surface. The manner in which these factors influence the mechanism of crystal growth are discussed. For evaporative crystallization, the mass transfer solutions are strongly rate-controlling and high supersaturation levels are required for good growth of crystals. For all conditions in pure sucrose solution, the rate of growth is strongly dependent on the crystal surface incorporated and not on the rate of solution uptake. In solution growth, both rate-limited to a limit of approximately 4000 ppm, it was not possible to remove completely the contribution of mass transfer to the overall crystal growth rate. Mortaghie [10] studied the effect of a number of inorganic salts and inert supercooling on crystal growth rate in pure sucrose solution. Crystallization due to the addition of individual component was found to be effective in increasing the differences in growth rate in the mixture of the impurities.

\[ SC = \frac{5.75}{T\text{C}} (0.1 + 0.28 \text{RS/ash}) \]
**FIGURE 2.** Solubility coefficients of molasses from different regions.
The effect of impurities on the crystal growth rate is complex as changes in both the sucrose solubility and the growth mechanism result and these effects must be separated. Smythe\textsuperscript{21} characterized the effect of impurities on the growth of sucrose crystals into two categories viz, those which predominantly affect growth rate by reducing the rate of mass transfer by increasing viscosity and lowering diffusion coefficient, and those which have their predominant effect by reducing the rate of the surface incorporation step by being absorbed on specific surfaces of the sucrose crystal. Substances in the former group include invert sugar and inorganic salts. Substances in the latter group are principally oligosaccharides which, by producing changes in the relative growth rates of the different pairs of faces, alter the shape of the sucrose crystal.

For a sugar solution at a given temperature and supersaturation, the presence of impurities of either type increases the viscosity of the solution and lowers the diffusion coefficient of the sucrose. This increase in viscosity increases the thickness of the stagnant film about the crystal at the same conditions of relative motion between the crystal and bulk solution. The combined effect of the impurities is thus to retard the mass transfer process and so decrease the rate of crystal growth. Thus, the mass transfer mechanism is more rate determining under normal factory boiling conditions for impure sucrose solutions, particularly in the absence of oligosaccharides.

Smythe\textsuperscript{20} found that at a given supersaturation for growth at 40–60°C in a solution containing invert sugar, the growth rate varied with the molasses viscosity as

\begin{equation}
G = \text{constant} \cdot \mu^{-1.4}
\end{equation}

while Van Hook\textsuperscript{22} proposed a direct dependence with impurity to water ratio as

\begin{equation}
G \propto \exp(-\text{constant} \cdot 1/W)
\end{equation}

Results of Growth Rate Measurements

The main interest in the growth rate measurements was to determine:

(i) if the growth rate mechanism remained unchanged as the concentration of impurities increased;

(ii) if the composition of the impurities in the different molasses retarded the absolute growth rate of each to a different degree, all other factors including total impurity concentration being equal.

Level of supersaturation

The coefficient of supersaturation of the molasses for rate measurement is
calculated using the following formula:

\[
SS = \frac{(S/W) \text{ pure sucrose } 65^\circ\text{C} \times SC_{65^\circ\text{C}}}{(S/W) \text{ pure sucrose } 50^\circ\text{C} \times SC_{50^\circ\text{C}}}
\]

\[
= 1.185 \times \frac{SC_{65^\circ\text{C}}}{SC_{50^\circ\text{C}}}
\]  

(Solubility data for pure sucrose according to Charles\textsuperscript{3})

Thus the level of supersaturation will be a function of the total impurity concentration and the impurity composition of the molasses. Measurements of the solubility coefficient have indicated that as the I/W ratio increases, the influence of temperature on the solubility of sucrose is greater i.e., \( \frac{SC_{65^\circ\text{C}}}{SC_{50^\circ\text{C}}} \) increases. This effect is greater at higher RS/ash levels. The overall effect is to increase the supersaturation by 2–4% in molasses of low RS/ash for the range of I/W over which growth rate measurements were made and up to 6% in molasses of high RS/ash. It is assumed that, within the accuracy associated with the growth measurements, the supersaturation for each molasses is constant for all I/W. The average value of supersaturation for mill areas A–C is 1.22 ± .01 and for mill area D is 1.24 ± .02.

\textit{Growth rate data}

The average rates of growth of crystals in molasses samples A–D (Table 1) are plotted in Fig. 3 (a), Regions A and D, and Fig. 3 (b), Regions B and C, against the total I/W concentration. Growth rate measurements are shown for stirrer speeds of 400 and 2000 rpm.

As expected, the influence of stirrer speed on the growth rate is greater at higher I/W concentrations as the diffusion of sucrose molecules through the stagnant film is more strongly rate-determining in this condition. In general, the growth rate was retarded proportional to the exponential of the I/W concentration i.e. as for relationship (7). This dependence was observed for operation at both rates of fluid shear.

From growth rate measurements in natural circulation pans in a Queensland factory (for molasses with RS/ash = 1.3), Wright and White\textsuperscript{2,5} found a similar dependence on I/W and the correlation they proposed is also indicated on Fig. 3 (a) and 3 (b). It appears that the functional form of the dependence of growth rate on I/W is similar despite the difference in shear rates. Molasses, from mill area D only, showed a change in dependence on I/W at higher I/W concentrations.

A marked difference in the average growth rates at the same I/W ratio and same shear rate is evident for the different molasses samples. For example, from Fig. 3 (b) for area samples B and C with similar RS/ash ratios (0.79 and 0.92 respectively), a two-fold difference in growth rate exists. This can be explained simply in terms of the differences in the respective molasses viscosities. Fig. 4 (a) and
4 (b) show log-log plots of growth rate against molasses viscosity for the data at the two stirrer speeds at which growth measurements were made. The viscosities of the molasses were measured over a range of shear rates and these were adjusted to a standard shear rate of 5 s\(^{-1}\) according to the dependence given in relationship (12) to follow. It is evident the effect of the different impurities on the growth rate in each of the molasses can be attributed to the change the impurities produce in the molasses viscosity at this supersaturation level; there being little difference between the data for the individual mill areas. This indicates that diffusion has a strong influence in limiting growth rate. Specific impurities influence the molasses viscosity at fixed (super) saturation conditions both directly by influencing the molecular mobility and indirectly by affecting the sucrose solubility.

Each of the molasses from the different mill areas shows a strong influence of the viscosity of the molasses on the growth rate. However, this dependence is not as marked as was proposed by Smyth\(^{-10}\) in relationship (6) for molasses containing invert sugar only. The results given in Figs. 4 (a) and 4 (b) show slight departure from the linear dependence of log growth rate on log viscosity. The growth data at both stirrer speeds show similar curvilinear form. Perhaps this indicates an increasing relative importance of the surface incorporation process in controlling the overall growth rate at high impurity concentration levels.

Since such a particular set of growth conditions has been investigated in this study, it is considered premature here to propose a correlation between crystal growth rate and molasses viscosity.

**Molasses viscosity measurement**

Knowledge of the rheological properties of molasses is desirable to aid good design for feed distribution pipe systems to pans, crystallizers and tanks and for sizing molasses pumps. It is also useful in studying the crystal/molasses separation in fugal operation. Investigations into the rheological properties of massecuite also require this information.

Natural cane molasses usually shows non-Newtonian flow behavior. Kot et al.\(^{-10}\) have shown that molasses (and massecuite) will flow under all shear conditions, even at very low shear rates. However, the apparent viscosity \(\mu\) given by the ratio of the shear stress \(T\) to shear rate \(\dot{\gamma}\) depends on the rate of shear.

The flow behavior for a non-Newtonian fluid is suitably described by the power law model

\[ T = K\dot{\gamma}^n \quad (9) \]

where \(K\) = consistency factor
\(n\) = flow behavior index

Thus for a non-Newtonian fluid

\[ \mu = K\dot{\gamma}^{n-1} \quad (10) \]
Both molasses and massecuits behave as a pseudoplastic fluid by which the 'viscosity' decreases as the rate of shear increases i.e. $n < 1$. 

**FIGURE 3(A).** Effect of impurity to water ratio on rate of crystallization for molasses from regions A and D.
Bhattacharyya et al.\textsuperscript{2} indicated that it is important for good design that the flow behavior be evaluated in the appropriate range of shear rates; for most practical molasses flow systems, the shear rates of interest would lie in the range \(1-10 \text{ s}^{-1}\).
The importance of this was demonstrated in their rheological studies of Queensland molasses samples where, over a wide range of shear rates (0.05–150 s\(^{-1}\)), a change in the value of the flow behavior index was observed. Over a limited range of shear rates e. g. one decade or so a constant value is sufficiently accurate.

Other variables affecting molasses viscosity are molasses composition and temperature. The apparent viscosity increases rapidly with the solids concentration and several workers (Micheli and de Gyulay\(^{14}\), Kelly and McAntee\(^{8}\), Payne\(^{17}\) and King\(^{9}\)) have reported data for cane molasses. Non-sugar constituents also influence the viscosity of the molasses although no well defined behavior has been determined. Payne\(^{17}\) reported that many inorganic salts and organic matter increase the viscosity. As a result, molasses from different sources with the same total solids content show different viscosities at the same temperature, purity and shear rate. As well, it is known that polysaccharides present in molasses from stale cane greatly increase the viscosity (Miller and Wright\(^{15}\)).

The purity of the molasses at the same total solids also appears to influence the viscosity. A number of workers (Micheli and de Gyulay\(^{14}\), Kelly and McAntee\(^{8}\)) have found that decreasing the purity increased the viscosity at the same total solids concentration. This suggests that sucrose produces a lesser change in the viscosity than the average of the contained impurities. Naturally, the extent of this effect would depend on the impurities present in the molasses.

The viscosity decreases sharply with a rise in temperature. Data presented in the International Critical Tables\(^{9}\) indicate that for pure sucrose solutions the sensitivity of viscosity to changes in temperature is greater at lower temperatures and at higher solids concentrations.

**Results of solubility coefficient measurements**

Viscosities have been measured on molasses samples from the five mill areas A—E (Table 1) over the following range of conditions:

| Dry substance | 74–87% |
| True purity   | 42–80% |
| Temperature   | 40–60\(^\circ\)C |
| Shear rate    | 0.2–34 s\(^{-1}\) |

No attempt was made to deaerate the molasses as little entrapped air was observed. A total of nearly 400 determination was made.

Some interactions were involved in the measurements due to:

(i) the preparation of the samples using the equilibration method for the solubility studies. Samples at the higher dry substance were of lower purity and, conversely, at lower dry substance levels, samples were of higher purity. However, samples covered the total range of purities in the middle range of solids concentration (dry substance 78–83).
FIGURE 4(A). Variation of rate of crystallization at 2000 rpm with molasses viscosity.
FIGURE 4(B). Variation of rate of crystallization at 400 rpm with molasses
(ii) the limited range of shear rates over which the viscosity of a particular molasses sample can be determined due to the interdependence of shear rate and torque in Brookfield viscometers. For each sample viscosities were generally measured at three shear rates giving about a six-fold variation. Naturally, measurements at higher rates of shear were performed on the samples with lower total solids.

Multi-linear regression analyses on the viscosity measurements for each mill area indicated that the variables which influence the measured molasses viscosity are, in order of decreasing significance, dry substance, temperature, purity and shear rate. Only sample B showed any variation, with purity being of lesser significance than shear rate.

A suitable form for a correlation which describes the effect of these parameters on the viscosity of a molasses is:

\[
\mu = k_1 \text{Pty}^{k_2} \gamma^{k_3} \exp\left(\frac{k_4 \text{DS}_*}{k_5 - \text{DS}_*}\right)
\]

where \(\text{DS}_* = \text{DS} - k_6 (T-50)\)

The symbols contained in this expression, together with the units chosen in the development of dimensional correlations, are:

- \(\mu\) = Viscosity of molasses (Pa s)
- \(\text{DS}\) = dry substance of molasses (%)
- \(\text{Pty}\) = true purity of molasses (%)
- \(T\) = temperature of measurement (°C)
- \(\gamma\) = shear rate of measurement (s \(^{-1}\))

This relationship provides a strong correlation with the viscosity data for each mill area and the results of the regression analysis are given in Table 2. Each molasses showed pseudoplastic flow characteristics with the value of the flow index, \(n\) [expressions (9) and (10)] ranging from 0.81 to 0.88. At lower purity levels the viscosity of each molasses increased. The 'predicted' viscosity of the molasses from each source is plotted in Fig. 5 as a function of the dry substance for the specific conditions indicated.

The molasses from the different regions exhibit considerably different viscosities (vary by up to 100%) at similar conditions of dry substance, temperature, purity and shear rate. Presumably, these differences are due to variations in the composition of the impurities. Even so, the rate of change of viscosity with dry substance is similar for each molasses; similar findings to this have been reported by several workers (Payne\(^{14}\)).

Obviously, the development of a suitable general correlation for viscosity of molasses from all sources in the Queensland sugar industry requires an index to relate the effect of impurity components in the molasses. Unfortunately, no corre-
Regression equation:
\[
\mu = k_1 P \gamma k_2 k_3 \exp \left( \frac{k_4 DS_a}{k_5 - DS_a} \right)
\]
where \(DS_a = DS - k_6 (T - 50)\)  
The units are specified in expression (11) in text.

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<th>(k_3)</th>
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<td>± 19%</td>
</tr>
<tr>
<td>D</td>
<td>1.078</td>
<td>-1.7</td>
<td>-0.13</td>
<td>3.2</td>
<td>112</td>
<td>0.20</td>
<td>0.997</td>
<td>± 13%</td>
</tr>
<tr>
<td>E</td>
<td>0.310</td>
<td>-1.5</td>
<td>-0.19</td>
<td>3.9</td>
<td>115</td>
<td>0.18</td>
<td>0.998</td>
<td>± 13%</td>
</tr>
</tbody>
</table>

**Table 2.** Results of Multi-Linear Regression Analysis on Viscosity Data From Different Mill Areas
lation between the concentration of specific impurities in the molasses (see Table 1) and the variations in viscosity has been determined from this study.

In the absence of this "impurity index", a multi-variable search on the values of the coefficients in expression (11) has been conducted for the combined viscosity data from all sources. This indicates the relationship

\[ \mu = 0.111 \, P_{T}^{1.3} \, \nu^{-0.16} \, \exp \left( \frac{3.7 \, DS_{*}}{113.5 - DS_{*}} \right) \] (12)

where \( DS_{*} = DS - 0.19 \, (T - 50) \)

provides a reasonable fit with a standard error of ±27%. An indication of the closeness of the fit provided by this correlation is shown in Fig. 6 where the logarithm of the measured value of viscosity (corrected for purity and shear rate according to expressions (12)) is plotted against \( DS/(113.5 - DS) \). The viscosity data determined at 40, 50 and 60°C are compared with the predicted values. This plot shows an increasing rate of change of viscosity with dry substance at higher dry substance levels. The change in viscosity due to a change in temperature is also greater at higher solids concentrations and at lower temperature levels. These effects agree with the viscosity data for pure sucrose given in the International Critical Table 4. Correlation (12) predicts this same pattern.

![Regression curves for molasses viscosity for individual mill regions](image)
FIGURE 6. Test of correlation (12) for viscosity data on molasses from five mill areas.
As a guide to the importance of each variable, the approximate change to cause a 100% increase in the viscosity is given below:

- Increase in total solids by 1.3% dry substance (in region of DS* = 85)
- Decrease in temperature by 7°C (in region of DS* = 85)
- A reduction in purity by 40% of the present value
- An 80-fold decrease in shear rate.

CONCLUSIONS

The impurity composition in molasses has been shown to influence the sucrose solubility, the crystal growth rate and the viscosity. The variation in these properties due to changes in the total impurity concentration and the impurity components has been studied for molasses from different mill areas.

Over the limited range of data, a correlation has been proposed for solubility coefficient in terms of the impurity/water ratio, RS/ash and temperature. The effect of impurity constituents on the molasses viscosity has been found to be quite marked although their influence could not be associated with specific impurities in the molasses samples. A correlation for molasses viscosity as a function of dry substance, temperature, purity and shear rate has been suggested.

Impurity constituents have also been found to influence the crystal growth rate. For the most part, the change in growth rate was a direct result of the associated change in molasses viscosity due to the variable impurity composition among samples.

Further work is required before definitive correlations can be proposed for each of these properties and it is intended the results presented here will form part of a continuing investigation.

REFERENCES


CARACTERISTICAS DE SOLUBILIDAD–CRISTALIZACION DE MELAZA DE QUEENSLAND

R. Broadfoot and R. J. Steiridl

RESUMEN

Melaza de cinco regiones diferentes plantadas a caña por la costa de Queensland se estudiaron por examenes de laboratorio para caracterizar la dependencia de la solubilidad, viscosidad y rapidez de crecimiento de cristales de la sucrosa en composición y concentracion de impuridades, después de un extenso programa experimental, un análisis estatistico de los resultados se hizo.

Sobre latitudes definidas, los valores del coeficiente de solubilidad de melaza fueron correlados con la relacion de impuridades/agua, la relacion de azucar reducido/ceniza y la temperatura de la melaza con expresion envolviendo la raiz del promedio cuadrado de error de 0.017 en su ajuste al data. Rapidez de aumento de cristales, medida en una
version modificada del aparato de Smythe\textsuperscript{3}, disminuyó linealmente de la relación impureza/agua y también mostró dependencia en la viscosidad de melaza, condiciones de crecimiento indicando una fuerte y limitada difusión de régimen de crecimiento. El tranco de crecimiento de cristales se midieron en dos diferentes medidas de shear. Medidas de la viscosidad de la melaza fueron correladas con concentración de sólidos de melaza, temperatura, pureza de melaza y el “rate” (tranco) de viscometro shear con un normal de error de 27\%. 