Measurement and analysis of the mannitol partition coefficient in sucrose crystallization under simulated industrial conditions

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1. Introduction

When postharvest deterioration of sugarcane occurs the juice quality is lowered, which concomitantly reduces the quality of the raw sugar end-product. Postharvest deterioration occurs any time sugarcane is physically injured including cutting at harvest, and varies from country to country, with environmental conditions, and by how the cane is managed. There are three types of postharvest deterioration of sugarcane leading to the degradation of sucrose and formation of unwanted degradation products or impurities: (1) chemical, (2) enzymatic, and (3) microbial.\textsuperscript{1} However, the latter is mostly responsible for the deterioration of sugarcane.\textsuperscript{1} The major (but not sole) contributor to microbial deterioration of sugarcane, particularly in areas where humid and warm conditions prevail, is infection by Leuconostoc mesenteroides.\textsuperscript{2}\textsuperscript{3} The effects of dextran include an increase in the viscosity of downstream factory products that causes a decrease in the rate of crystallization of sucrose,\textsuperscript{3} and sucrose crystal elongation across the c-axis.\textsuperscript{4} Factories try to mitigate the detrimental effects of dextran on processing by hydrolyzing it with commercial dextranase in the juice.\textsuperscript{5}

In recent years it has emerged that mannitol, a sugar alcohol (C\textsubscript{6}H\textsubscript{14}O\textsubscript{6}; mol. wt 182.2), is also a major product of L. mesenteroides.\textsuperscript{2} The effects of dextran include an increase in the viscosity of downstream factory products that causes a decrease in the rate of crystallization of sucrose,\textsuperscript{3} and sucrose crystal elongation across the c-axis.\textsuperscript{4} Factories try to mitigate the detrimental effects of dextran on processing by hydrolyzing it with commercial dextranase in the juice.\textsuperscript{5}

Mannitol is a major deterioration product of Leuconostoc mesenteroides bacterial metabolism of sucrose and fructose from both sugarcane and sugar beet. The effect of crystallization conditions on the mannitol partition coefficient (K\textsubscript{eq}) between impure sucrose syrup and crystal has been investigated in a batch laboratory crystallizer and a batch pilot plant-scale vacuum pan. Laboratory crystallization was operated at 65.5 °C (150 °F), 60.0 °C (140 °F), and 51.7 °C (125 °F) with a 78.0 Brix (% refractometric dissolved solids) pure sucrose syrup containing 0%, 0.1%, 0.2%, 1.0%, 2.0%, 3.0%, and 10% (at 65.5 °C only) mannitol. Organic dextranase (100,000 units) was added to the feed syrup to ensure complete digestion of dextran. The effect of dextran on the partition coefficient was also studied in a crystallizer operating on a 78.0 Brix (% refractometric dissolved solids) feed syrup containing 0%, 0.1%, 0.2%, 1.0%, 2.0%, 3.0%, and 10% (at 65.5 °C only) mannitol. The crystallization conditions were 60.0 °C (140 °F) and 51.7 °C (125 °F) with a 78.0 Brix (% refractometric dissolved solids) pure sucrose syrup containing 0%, 0.1%, 0.2%, 1.0%, 2.0%, 3.0%, and 10% (at 65.5 °C only) mannitol.

Mannitol incorporation into the sucrose crystal results mostly from liquid syrup inclusions but adsorption onto the crystal surface may play a minor role at lower mannitol concentrations. When postharvest deterioration of sugarcane occurs the juice extracted from deteriorated cane.\textsuperscript{7} Large amounts of mannitol have been found in downstream factory products including syrups, massecuites (crystals in mother liquor), and molasses.\textsuperscript{7} Greater than 24,000 ppm/Brix mannitol has been found in a hard-to-boil massecuite produced in a factory from juice extracted from deteriorated cane.\textsuperscript{2} Large amounts of mannitol...
have also been found in betaine (125,858 ppm/Brix or 12.5% on solids) chromatographically separated from sugar beet molasses (19,623 ppm/Brix) in a US factory which had processed severely deteriorated sugar beets after a freeze. The effect of mannitol on sucrose crystallization in the factory is unknown. Unfortunately, unlike dextran, mannitol cannot be broken down at the factory by a commercial enzyme.

Typically at sugarcane factories, sucrose crystals are grown under a vacuum not exceeding 84.7 kPa (25 in. Hg) at sea level, which means operating temperatures of ~65.5–71.1 °C depending on purity. At these temperatures, unwanted sucrose degradation reactions are minimized. The rate of crystal growth in a supersaturated sucrose solution is dependent on the rates of two successive processes: the diffusion of sucrose molecules through the layer of syrup surrounding the crystal, and the accommodation of the sucrose molecules into the proper position in the crystal lattice. The slower process determines the rate. The driving force for crystallization of molecular species is the relative supersaturation (ξ), which can be defined as:

\[
x = \frac{C - C^*}{C^*} \tag{1}
\]

where \( C \) is the sucrose concentration as a mass fraction, and \( C^* \) is the sucrose solubility at the experimental temperature. The rate of crystallization is greatly influenced by impurities and depends not only on the concentration of the impurity but also on the nature of the impurity.\(^4\)

During sucrose crystal growth at the factory, impurities can incorporate into the crystal by three mechanisms: (1) adsorption–occlusion, (2) inclusion, and (3) co-crystallization. Typically, the amount of impurities trapped in the crystal increases with crystal size.\(^10\) For a general review of sucrose crystallization see Vaccari and Montovani.\(^11\) The adsorption–occlusion mechanism of impurity incorporation into the crystal occurs when the impurity may be able to occupy the adsorption sites on the surface of the crystal, with the integration kinetics depending on its concentration, mobility, and physical–chemical affinity with the sucrose crystal surface. The inclusion mechanism of impurity incorporation is the physical capture of syrup (mother liquor droplets) inside the crystal. Thus, inclusions normally have a liquid content with a composition which is similar to the feed syrup from which the crystals grew at the time the inclusion was formed. Liquid inclusions are a major cause of impurities in crystal products, and in many cases can be simply caused by particular crystal growth conditions\(^14\) that destabilize the crystal surface creating hollows able to capture the mother liquor. In particular, high supersaturation levels or systems with very large temperature fluctuations give rise to liquid inclusions.\(^13\) Growth rate is generally recognized\(^14,15\) as being one of the more important factors for the introduction of impurities into crystals, with fast growing crystal faces showing more inclusions. Co-crystallization from liquid solutions occurs under conditions where there is a different solid (impurity) form with a lower free energy (lower solubility) than that of the other solid (sucrose) in the process.

Mannitol is much less soluble than sucrose at all temperatures\(^16\) due to a greater preponderance of sugar–sugar interactions over water–sugar interactions.\(^17\) For example, at 60 °C sucrose solubility is 283 g/100 ml whereas mannitol is only 56 g/100 ml. The relatively low solubility of mannitol implies a relatively low saturation viscosity level which enhances the diffusivity of the solution (the diffusion coefficient is inversely proportional to viscosity).\(^17\) Thus, mannitol has a very high nucleation rate or narrow metastable zone width (MSZW) in supersaturated solutions compared to sucrose.\(^17\) Recently, it was reported that at >10% mannitol levels in sucrose solutions of 71 Brix, mannitol needle crystals become prevalent.\(^18\)

This study was undertaken to determine how, and to what degree, mannitol partitions between sucrose crystals (solid phase) and mother liquor (liquid phase), and how mannitol affects boiling and crystallization by undertaking laboratory and pilot plant-scale experiments. As no greater than 2.5% mannitol on a Brix basis (equivalent to 25,000 ppm/Brix) has been reported in hard-to boil massecuets at sugarcane factories, mannitol only up to 3% on a Brix basis was investigated. Laboratory experiments were undertaken first to underpin later pilot plant studies.

2. Experimental

2.1. Chemicals and reagents

A high purity (>99.9%) sucrose was used in the laboratory crystallization experiments, obtained from EMD Chemicals Inc. that was ACS reagent grade. A low purity raw sugar (95.75%, 0.26%, and 0.26% sucrose, glucose, and fructose purity, respectively) was used in the pilot plant experiments, and kindly donated by Mr. Timmy Charlet of Cora Texas factory, White Castle, LA. D-Mannitol was reagent grade from Sigma–Aldrich. Deionized water (<18 Ω resistance) was used to prepare syrups. Isopropyl alcohol and polyethylene glycol (PEG-300 MW) were analytical grade from J.T. Baker and Sigma, respectively.

Grain crystals of approximately 0.18 mm size are used in raw sugar manufacture to ‘seed’ the pans, after confectioners sugar is used at the start of the processing season to form the first grain.\(^4\) Because of this, and that the effect of impurities is typically greater at larger crystal sizes,\(^10\) a fine, white sugar was used in this study as seed. Most commercial fine, white sugars are bimodal in size distribution. To ensure uniformity in the crystallization experiments, more uniform grain crystals of Domino Refinery Baker Special Sugar™ were used that were kindly donated from Mr. Fred Goodrow, of Domino Sugar Refinery, Chalmette, LA. Mean particle size of the grain was 0.223 mm and the range of particle sizes was 0.575 mm. A particle size distribution (PSD) of the grain crystals is shown in Figure 1.

2.2. Crystallization experiments

2.2.1. Seed grain production

Into a beaker (30 ml) the Domino Baker Special™ grain crystals (0.1 g) were added then PEG-300 (10 ml) was added and stirred with a magnetic bar for at least 30 min until the syrup was ready to be seeded.

2.2.2. Laboratory crystallization

The laboratory crystallization apparatus used is illustrated in Figure 2. The solution in the 1 L glass crystallizer was stirred with a laboratory triple-blade propeller mixer (Arrow 1750™, Hillside, NJ) at 600 rpm. The solution was heated over a heating isomantle (Glas-Col™, Terre Haute, US). Temperature control was provided by a thermostat (Powerstat™ Variable Autotransformer) and the temperature of the solution measured with an Oaktron™ RTD thermometer probe. The sugar solution (78 Brix) was first prepared in a glass beaker then poured into the crystallizer vessel. A sub-sample (~5 ml) was removed at this point for Brix measurement. The syrup solution was maintained at constant temperature with constant stirring. The house vacuum (84.7–91.4 kPa) was applied, and it was ensured that all the bubbles were removed. Also, a light was shone through the solution to check that no crystal nucleation had occurred. Vacuum was then removed. Seed grain (0.1 g/10 ml PEG-300) was then added to the syrup via the sample port shown in Figure 2. The timer was immediately started and crystals were allowed to grow with constant stirring. After 100 min, the massecu-
ite (crystals in mother liquor) formed was recovered for subsequent analyses. Preliminary experiments were undertaken to ensure sufficient crystal growth had occurred after 100 min.

2.2.3. Effect of mannitol and temperature on laboratory crystallization of sucrose syrups

After initial experiments to optimize the laboratory crystallization procedure, the effects of different mannitol concentrations in the initial syrup solution at different crystallization temperatures were investigated. At 65.5 °C, concentrations of 0.0%, 0.1%, 0.2%, 1.0%, 2.0% and 3.0% mannitol on a Brix basis in syrup were studied; final syrup Brix was 78. Because effects at 0.1% mannitol were negligible, studies at 60.0 and 51.7 °C were conducted only at 0.0%, 0.2%, 1.0%, 2.0% and 3.0% mannitol in syrup (78 Brix). As Eggleston et al.18 observed that mannitol needle crystals are visible at 10% mannitol in sucrose syrups (71 Brix), this mannitol concentration was also studied for comparison purposes at 65.5 °C (typical temperatures of industrial crystallization).

2.2.4. Pilot plant crystallization

Pilot plant-scale experiments were conducted on a batch vacuum pan (130 L full capacity) manufactured by Honiron™ (Jeanette, LA).19 The pan was a calandria (rising film) pan similar to those conventionally operated in the US and was operated at 65.5 °C under 84.7 kPa vacuum to simulate raw sugar manufacturing conditions. Feed syrup created from a low purity raw sugar (65 Brix; purity 95.75%) was fed into the pan at the bottom by suction until it covered just above the calandria tubes. The syrup was then boiled with constant feeding at 65.5 °C under 84.7 kPa vacuum and constant agitation until ~78 Brix was obtained to keep the syrup in the metastable zone and, therefore, limit false grain (nucleation) formation. Boiling was stopped and the same seed crystals (88 g/88 ml isopropanol, typical seed mixtures in a factory) as for the laboratory crystallization experiments were immediately added into the pilot vacuum pan, also from underneath. Five minutes after seeding, the boiling inside the pan began again and the volume of massecuites inside the pan was increased ~two-fold by adding feed syrup (65 Brix) to allow the crystals to grow. The Brix of the pan syrup was maintained ~78, that is, in the metastable zone. Once the grain crystals had grown to ~0.28 mm mean size (and little syrup was available for further growth) the grain produced was ‘cut’, that is, was dropped out of the pan at the bottom, leaving enough grain to just cover the calandria tubes. Feed syrup (65 Brix) was then fed into the pan again until the volume had increased two-fold, and the mixture allowed to boil. The second and final ‘cut or strike’ was dropped after further crystal growth to ~0.4 mm (and little syrup was available for further growth). Under these pilot plant conditions, concentrations of 0%, 1%, 2%, and 3% mannitol on a Brix basis were studied. To ensure complete dissolution of mannitol in the syrup, the syrup was first heated to ~65.5 °C.

Figure 1. Particle size distribution (PSD) graph for seed grain used in the crystallization experiments. q = volume of crystals.

Figure 2. Scheme of laboratory crystallization apparatus.
2.2.5. Separation of crystals and mother liquor

The crystals and mother liquor in the masscesuicites formed were separated in an IEC™ (Milford, MA) Clinical Centrifuge. Inside the centrifuge basket was placed a screen (41 cm length × 5 cm wide; hole size 0.3 × 0.08 mm) by cutting a piece of used, undamaged screen from a C Centrifugal in a LA factory. Between 100 and 500 g of weighed masscesuicites were placed in the basket and then centrifuged at 2850 rpm speed for 3 min (for pilot plant masscesuicites this was increased to 6 min). If all the mother liquor had not been removed then another 2 min of centrifugation occurred. To obtain accurate estimates of the mannitol partition coefficient it was necessary to very cleanly remove all mother liquor adhering to the crystal surface without dissolving any of the crystalline material. Thus, crystals were finally washed with saturated methanol, then saturated ethanol, and finally isopropyl alcohol to clean the crystals of all remaining mother liquor clinging to the surface of the crystal.13 The crystals obtained were then dried at room temperature to remove all the remaining alcohol.

2.3. Particle laser scattering analysis

Particle size analysis (PSA) was conducted on a Partica Laser Scattering Particle Size Distribution Analyzer LA-950V2 by Horiba™ (Kyoto, Japan). Crystals or massecuite (15 g) were added to isopropyl alcohol (10 ml) in a beaker and mixed with a spatula. Before using the instrument it was washed with isopropyl alcohol. The mixture was added in the liquid mode of the instrument. Using Horiba LA-950 software (Ver. 5.), it was ensured that the % transmittance was in the valid range. The crystals obtained were then dried at room temperature to remove all the remaining alcohol.

2.4. Brix (percent dissolved refractometric solids)

The mean Brix of triplicate samples was measured using an Index Instruments TCR 15–30 temperature controlled refractometer accurate to ±0.01 Brix.

2.5. Mannitol concentration

This was measured using ion chromatography with integrated pulsed amperometric detection (IC-IPAD). IC chromatograms were obtained on a Dionex (Sunnyvale, CA) instrument. Mannitol was separated from sucrose on Dionex CarboPac PA-1 analytical and guard anion-exchange columns at 30 °C in a LC25 Chromatography Oven. Flow rate was 1.0 ml/min. Eluent conditions were: 100 mM NaOH isocratic (0.0–1.1 min; inject 1.0 min), a gradient of 0–150 mM NaOAc in 100 mM NaOH (1.1–20 min) and return to 100 mM NaOH (20.1–25.0 min) to re-equilibrate the column. Mannitol (from 100 μl injections) was detected with a ED50 detector. Using a refrigerated ASS5™ autosampler and Dionex Chromelone (Ver. 6.8) chromatography software, runs were accumulated of multiple samples. Mannitol was quantitated in reference to a standard curve between 0 and 15 ppm mannitol using peak heights. Juices of ~14 Brix of either the crystals or the mother liquor were first prepared and these were then diluted in de-ionized water. Triplicate samples were analyzed. For crystals, 2- to 100-fold dilutions were required to measure mannitol. For the mother liquor, 250- to 1000-fold dilutions were required and adjusted accordingly.

2.6. Calculation of mannitol partition coefficient (K_{eff})

Mannitol is typically measured using units of ppm/Brix or mg mannitol/kg total dissolved refractometric solids in the solution. In this quantitative study on mannitol incorporation into the crystal the partition coefficient between the liquid phase (mother liquor) and solid phase (crystals) (K_{eff}) can be defined as the ratio of ppm/Brix mannitol in the crystal product to ppm/Brix mannitol in the mother liquor:

![Graph showing partition coefficient (K_{eff}) of mannitol in sucrose crystallization as a function of mannitol concentration and temperature in the feedstock syrup (liquid phase) and temperature (laboratory crystallization). See Section 2.6 for how K_{eff} was determined.](image-url)
\[ K_{eff}(\%) = \frac{\text{Mannitol ppm in crystals}}{\text{Mannitol ppm in mother liquor}} \times 100 \]  

(2)

### 2.7. Sugar moisture content

Sugar (~3 g) was placed in a Sartorius (Edgewood, NY) Mark 3 Moisture Analyzer. Sugar was dried until constant weight at 105–125 °C for at least 10 min. After 5 min the temperature increased from ~105 to 125 °C in the program. The moisture content after 5 min indicated surface moisture, while final moisture at 125 °C was surface moisture + entrapped moisture. Total moisture content was surface moisture + entrapped moisture. Results stated are an average of duplicate samples.

### 2.8. Viscosity

The viscosity of sucrose syrups (~66 Brix; 100 g samples), with varying amounts of mannitol and/or calcium (as CaCl₂) on a Brix basis, was measured on a Brookfield (Middleboro, US) DV-II+ rotational viscometer at 65.5 °C. Temperature of the sample was maintained via a jacketed adaptor sample cell (16 ml) which was connected to a water bath accurate to ±0.1 °C. The shear rate applied was 90 rpm. Viscosity in centipoise (cP) was calculated as % torque \times the spindle factor. Preliminary experiments were undertaken to ensure repeatability of the method applied.

### 2.9. Digital microscopy

Crystals were inspected with an Olympus MIC-D™ digital microscope (Center Valley, US) and multiple photomicrographs were taken.

### 2.10. Differential scanning calorimetry (DSC)

DSC was performed on a TA Instruments (Houston, TX) DSC Q100 thermal analytical device. The standard experiment consisted of heating the sample (~5 mg) from 35 to 210 °C at 10°/min. Each sample was run in duplicate.

### 3. Results and discussion

Sugar solutions (syrups) of 78 Brix (354.5 parts sucrose per 100 parts water/454.5 = 78 wt/wt) were chosen for this study as this represents a concentration of pure sucrose that is in the metastable phase of supersaturation (i.e., 1.0–1.20) at 65.5 °C. It is in the metastable phase in which seed crystals grow in size, but no new ones form.

### 3.1. Mannitol partition coefficient

During the growth process of sucrose in industrial sugar manufacture, mannitol, like other impurities may be able to incorporate into the sucrose crystal through adsorption–occlusion at the surface, liquid inclusions, or co-crystallization. The degree of mannitol incorporation is indicated by the partition coefficient \( K_{eff} \) between the mother liquor and the sucrose crystal. At the beginning of this research it was unknown if (a) mannitol incorporated into the sucrose crystal and (b) if it did, then by what mechanism?

Values of the mannitol \( K_{eff} \) under laboratory crystallization conditions, plotted against the mannitol concentration in the feed syrup are shown in Figure 3. The temperature had a significant effect on the \( K_{eff} \) for mannitol, with the higher temperatures resulting in more mannitol partitioning into the crystal. However, lower partitioning would be expected at lower relative supersaturation. The greater partitioning at the higher temperatures, particularly at 65.5 °C, indicates the growth rate of crystallization had an effect. It is well known that high crystal growth to 51.7 °C. This may be attributed to the 78 Brix sucrose solution being in the supersaturation zone of 1.0–1.25 at both 60.0 and 65.5 °C, whereas at 51.7 °C the supersaturation was higher at 1.25–1.30. However, lower partitioning would be expected at lower relative supersaturation. The greater partitioning at the higher temperatures, particularly at 65.5 °C where most industrial crystallization of sucrose occurs, indicates the growth rate of crystallization had an effect. It is well known that high crystal growth

<table>
<thead>
<tr>
<th>% Sucrose on a Brix basis</th>
<th>% Mannitol on a Brix basis</th>
<th>% Calciumb on a Brix basis</th>
<th>Avg. Viscosityb at 65.5 °C (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>25.30</td>
</tr>
<tr>
<td>99</td>
<td>1</td>
<td>0</td>
<td>23.63</td>
</tr>
<tr>
<td>98</td>
<td>2</td>
<td>0</td>
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<td>5</td>
<td>0</td>
<td>22.32</td>
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<td>0</td>
<td>17.41</td>
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<tr>
<td>87.0</td>
<td>12.3</td>
<td>1</td>
<td>26.44</td>
</tr>
</tbody>
</table>

a Calcium was added as calcium chloride.

b Viscosity was normalized to 67.16 Brix for all samples.

Figure 4. Digital micrographs of sucrose crystals grown in a laboratory crystallizer with 10% mannitol on a Brix basis in a 78 Brix syrup at 65.5 °C. In (a) and (b) needle-like crystals of mannitol were ubiquitous present. In (b) clumping of small crystals is visible and possible elongation of larger sucrose crystals.
rates promote the formation of liquid inclusions.\textsuperscript{14,15} These results indicate that, at least, liquid inclusions are one of the mechanisms for mannitol incorporation in growing sucrose crystals.

The mannitol partition coefficients were lower than for those reported for dextran\textsuperscript{13,20} under similar sucrose crystal growth conditions (Table 1). Therefore, mannitol does not incorporate into sucrose crystals to the degree of dextran. This is an important result for the sugar industry as it indicates that measurement of mannitol concentrations in raw sugar by the refiner is not equivalent to the dextran concentration. Raw sugar manufacturers are penalized by refiners for high dextran concentrations in raw sugar. Promraska et al\textsuperscript{13} reported that the concentration of dextran impurity did not have an effect on the dextran $K_{\text{eff}}$ although it did have a strong effect on the amount of dextran in the crystal. In strong contrast, in this study the concentration of mannitol had a marked effect on $K_{\text{eff}}$, and this varied with temperature (Fig. 3).

Although the crystals were grown under constant conditions of temperature, supersaturation, and agitation in the laboratory crystallizer, the measurement of mean size growth rates could not be assumed in this study as there were indications that some false grain production occurred on the PSD graphs. This made the effect of mannitol on growth rates difficult to discern. However, it can be generally stated that concentrations of mannitol up to 2\% did not have a marked affect on the growth rates of the sucrose crystals. This is in contrast to dextran, which has been reported to lower the growth rate because it is a polysaccharide that increases the solution viscosity.\textsuperscript{3} Higher solution viscosities reduce the rate of crystal growth because of the lower diffusivity. In comparison, low MW mannitol has a relatively lower solution viscosity than dextran and even sucrose.\textsuperscript{17} Therefore, mannitol would not be expected to have significantly lowered the growth rates of sucrose crystals in the high purity solutions in the laboratory crystallizations in this study. The effect of mannitol on slightly lowering the viscosity of sucrose solutions is further illustrated in Table 2.

Grimsey and Herrington\textsuperscript{12} using laboratory crystallizations showed that the presence of a melanoidin color impurity, glucose glycine, decreased the viscosity of sucrose because it did not form complexes with sucrose and did not affect the sucrose growth. Furthermore, glucose–glycine had a low crystal transfer factor through the surface adsorption mechanism and was mainly found as liquid inclusions in the crystal. However, the presence of calcium (a cation that is abundantly present in factory syrups because of the addition of lime during the juice clarification process) did increase the solution viscosity in the presence of mannitol (Table 2).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Particle size distribution of sucrose crystals grown in a laboratory crystallizer with (a) 0\% and (b) 10\% mannitol on a Brix basis in a 78 Brix syrup at 65.5 °C. $q =$ volume of crystals. Needle-like crystals were visually observed in the mixture containing 10\% mannitol.}
\end{figure}
This was most likely because of the formation of calcium–sucrose complexes and possibly calcium–mannitol adducts. Thus, in the impure syrup feedstocks encountered in a raw sugar factory, mannitol through complexing or bonding with calcium and other possible impurities, may not be reducing the viscosity and even slightly increasing it. Overall, because up to 2% mannitol had little effect on the crystal growth rate of sucrose, liquid inclusions may not be the only mechanism for mannitol occurrence in the crystals at the lower concentrations and as there was no evidence of co-crystallization there may have been some adsorption/occlusion of mannitol.

At 65.5 °C and a 10% concentration of mannitol it was visually observed that mannitol co-crystallized with sucrose because needle-like mannitol crystals were present (Fig. 4). At the 10% mannitol concentration the growth rate of mean size crystals was 3.40 μm/min, which was markedly lower than 3.92 μm/min measured for the control (100% sucrose at 65.5 °C). Furthermore, the mannitol $K_{\text{eff}}$ was 23.3%, which was considerably higher than the $K_{\text{eff}}$ values presented in Figure 3 for 0.1–3% mannitol concentrations at 65.5 °C. Such a high $K_{\text{eff}}$ cannot be explained by liquid inclusions and/or adsorption alone. The PSD profile for the crystals grown from sucrose syrup containing 10% mannitol was also dramatically different to the control (compare Fig. 5a and b), as a much greater amount of small crystals <100 μm were formed (Fig. 5). The large peak centered at 15.2 μm can be attributed to the majority of needle-like crystals that formed (Fig. 4). Some large crystals (0.6–1.4 mm) were also evident in the PSD profile (Fig. 5) and photomicrographs (Fig. 4). From Figure 4 there was also visual indication of some clumping of mannitol crystals around sucrose crystals, but it was not clear if any elongation of the sucrose crystal occurred. The corresponding DSC thermal profile for the crystals is shown in Figure 6. Pure mannitol crystals have been reported to melt at ~165–167 °C and pure crystalline sucrose at ~188–190 °C. At the 10% mannitol concentration, separate melting peaks were observed at 160.2 and 169.4 °C (Fig. 6), which confirmed that the mannitol crystallized out separately. The presence of the 160.2 °C peak suggests that some mannitol crystals incorporated some impurities (sucrose or water), causing depression of the melting point. Other impurities have been known to depress the mannitol melting point. Another explanation for the slightly lower than expected melting temperature at 160.2 °C, could be the slight production of amorphous mannitol. The melting peak at 169.4 °C was most likely pure mannitol crystals, and the higher temperature than reported in the literature may be because of a calibration difference in the DSC instruments or, because it is broader than the first melting peak it may indicate that some mannitol was also incorporated into the sucrose crystal matrix. A small and relatively broad sucrose melting point peak was observed at 204.7 °C (Fig. 6), which was also higher than reported in the literature for pure sucrose crystals. This peak further suggests that at least some co-crystallization of mannitol and sucrose occurred.

The massecuites formed from syrup that contained 10% mannitol were also very difficult to centrifuge. Overall, the co-crystallization of mannitol with sucrose impeded the growth of sucrose crystals. Because of the considerably lower solubility of mannitol than sucrose, the mannitol may have crystallized early and nucleated the crystallization of sucrose on the mannitol crystal itself keeping the sucrose crystals small and reducing the growth rate.

### 3.2. Pilot plant-scale crystallization experiments

To further understand the effect of mannitol on the crystallization of sucrose under conditions that better simulate raw sugar manufacture in the factory, pilot plant-scale experiments were undertaken. Pilot plant crystallization more closely reflected industrial-scale crystallization as continuous feed addition occurred, and growth rates were higher under the pilot plant than laboratory conditions. Mannitol $K_{\text{eff}}$ results from the pilot plant crystallizations are listed in Table 3, and followed a similar trend to the $K_{\text{eff}}$ values obtained from the laboratory crystallizations.

### Table 3

The mannitol partition coefficient for various concentrations of mannitol in sucrose syrups (78 Brix; 95.7 purity) at 65.5 °C under 84.7 kPa vacuum pilot plant conditions

<table>
<thead>
<tr>
<th>Feed syrup % mannitol</th>
<th>Partition coefficient ($K_{\text{eff}}$) %</th>
</tr>
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<tbody>
<tr>
<td>1.0</td>
<td>1.33</td>
</tr>
<tr>
<td>2.0</td>
<td>2.177</td>
</tr>
<tr>
<td>3.0</td>
<td>3.02</td>
</tr>
</tbody>
</table>

**Figure 6.** Differential scanning calorimetry thermal profile of sucrose crystals grown in a laboratory crystallizer with 10% mannitol on a Brix basis in a 78 Brix syrup at 65.5 °C.
Figure 7. Digital micrographs of crystals formed in pilot plant-scale vacuum pan at 65.5 °C, 84.7 kPa vacuum and constant agitation with mannitol concentrations of (a) 0, (b) 1.0, (c) 2.0 and (d) 3.0 and (e) 3.0% on a Brix basis in 78 Brix raw sugar (95.7% purity) syrup. Micrograph (d) highlights the possibility of elongated crystals and (e) highlights conglomeration of crystals. At 3% mannitol, conglomerates were more predominant and elongated crystals were occasionally visible that may be mannitol crystals.

Figure 8. Particle size distributions of sucrose crystals formed in pilot plant-scale vacuum pan at 65.5 °C, 84.7 kPa vacuum and constant agitation with 0 to 3% mannitol concentrations in 78 Brix raw sugar (95.7% purity) syrup.
undertaken at the same mannitol concentration and temperature (65.5 °C) (Fig. 3). Furthermore, for both the pilot plant and laboratory crystallizations at 65.5 °C, the $K_{eff}$ values became progressively similar to the mannitol concentrations of the feed syrup as themannitol concentration increased. This is a strong indication thatmannitol was incorporated into the crystals as liquid inclusions.11,13

When mannitol was present, the massecuites in the vacuum pan were harder to boil, that is, the crystals were more difficult to grow, and the growth rates of the mean size crystals were lower than the control, and this became progressively worse with increased concentration ofmannitol. As seen in the digital photomicrographs of Figure 7, conglomeration (sticking together) of crystals was much more prevalent when mannitol was present. Conglomeration also became progressively worse with increased concentration of mannitol, especially at the 3% mannitol concentration (Fig. 7d and e). Once formed, conglomerates remain until the end of the strike. Conglomerate groups of crystals are objectionable in the factory and refinery because impurities and dirt lodge in the crevices and prevent proper washing and drying, and they yield a low quality sugar.4 Also, conglomerates detract from the number of properly sized grain and are detrimental to the centrifugal purging properties of a massecuite. However, in the factory where syrups are often less pure than in this study, the tendency for crystals to stick together or clump and grow as a conglomerate grain would be lower.

Increased conglomeration reduces the number of final crystals produced so that the mean crystal size increases. Likewise the range of crystal sizes increases because the conglomerate grain grows larger in size at the expense of individual clean crystals. This is evidenced in the PSD graphs of the pilot plant grown sucrose crystals grown from feed syrup containing 0–3%mannitol (Fig. 8). From 0% to 1% mannitol concentrations the crystal growth was impaired because of conglomerate formation, but this became worse from 1% to 3% mannitol. Progressively worse conglomeration was evidenced when the mean and median size crystal sizes or range of crystal sizes were plotted against %mannitol in the syrup feedstock, in Figs. 9 and 10, respectively.

3.3. Mechanism

Because mannitol $K_{eff}$ results from both the laboratory and pilot plant crystallizations at 65.5 °C became progressively similar to the mannitol concentrations of the feed syrup as the mannitol concentration increased, liquid inclusions must be the predominant mechanism of mannitol incorporation into the crystal at the higher mannitol concentrations. Attempts were made to verify this by measuring the moisture content in the crystals produced in the pilot vacuum pan and also subjecting them to differential scanning calorimetry (DSC). The moisture results are listed in Table 4. A linear relationship ($R^2 = 0.948; y = 0.0078x + 0.125$) existed between surface moisture of the crystals (y axis) and the mannitol concentration in the feed syrup (x axis). In contrast, the relationship between entrapped water and the syrup mannitol concentration was more polynomial ($R^2 = 0.945; y = 0.005x^2 – 0.0152x + 0.0695$). Thus entrapped water became progressively worse as the syrup mannitol concentration increased. Similarly, the linear correlation ($R^2 = 0.951; y = 0.0072x + 0.1331$) between the mannitol $K_{eff}$ and the amount of surface moisture was stronger than between the $K_{eff}$ and entrapped moisture ($R^2 = 0.757; y = 0.0155x + 0.0386$) (polynomial fits could not be calculated as only three data points were available). Because entrapped moisture also became progressively worse as the mannitol concentration in the feed syrup increased, this is further evidence that inclusions of syrup became more prevalent. In particular, inclusions at the 3% mannitol impurity level were the predominant mechanism of impurity incorporation into the crystals. The dark areas observed in Figure 7d and e (crystals grown in syrup feed containing 3% mannitol) further indicate some inclusion of liquid where clumping of the crystals occurred.

The DSC profiles (not shown) of the pilot plant crystals did not vary much, although the lowest melting point was at 3% mannitol concentration. There was a slight trend to a lower $\Delta H$ melting enthalpy with increased mannitol concentrations (average $\Delta H$ values were 1423, 1441, 1309, and 1373 W/g at the 0%, 1%, 2%, and 3% mannitol concentrations, respectively) that indicated it became easier to melt the crystals, most likely because of the increased conglomerations, and inclusions of mannitol and entrapped water.

4. Major conclusions

The degree of mannitol partitioning into the product sugar strongly depends on the supersaturation, mannitol concentration in the feed syrup, and to a lesser extent the crystallization temperature. Mannitol effects on sucrose crystallization are not the same

![Figure 9](image_url) Effect of mannitol on the median and mean crystal sizes grown under pilot plant conditions.

![Figure 10](image_url) Effect of mannitol on the range of crystal sizes grown under pilot plant conditions.
as HMW dextran effects,\textsuperscript{13,19} which is not overly surprising as mannitol is a considerably LMW molecule which imparts lower viscosity. Less mannitol partitions into the crystal than dextran and does not cause marked elongation. Although dextran concentration in syrup has an effect on the amount of dextran incorporated into the sucrose crystal it does not strongly affect the sucrose crystal growth rates.

At a 10\% concentration of mannitol in the 78 Brix feed syrup at 65.5 °C, co-crystallization of mannitol occurred and there was a marked reduction in the growth rate of the mean crystal size. Needle-like crystals of mannitol were observed with digital microscopy, which melted at 160.2 and 169.4 °C.

Under laboratory-scale crystallization conditions, at the 3\% mannitol concentration in the feed syrup, crystallization of sucrose was more difficult. Overall, laboratory crystallizations suggested that liquid inclusion was at least one of the mechanisms for mannitol incorporation in growing sucrose crystals, but at the lower (<1\%) mannitol feed concentrations some adsorption may occur. In the pilot plant crystallizations that better simulated industrial-scale conditions, crystal growth rates were higher. It was more difficult to boil the syrup with mannitol present at 1–3\% concentrations under pilot plant conditions, and this became progressively worse with increased concentration of mannitol. Conglomeration (sticking of crystals) also became progressively worse.

It must be noted that when mannitol occurs in sugarcane juice that is processed at the factory, then dextran will be present and vice versa. Thus, future studies are still needed to determine their effects and possible interaction-effects on crystallization when both impurities are present.

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