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Increasing our understanding of supersaturation and the use of massecuite dry substance in pan control – part 1

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Abstract Australian sugar factories currently use massecuite conductivity to control the feed rate of syrup and molasses to pans. The system works well but does not provide a signal that describes either the mother molasses supersaturation or the crystal content that are the key variables for control of crystallisation. The signal is a combination of these two parameters, but its value is also strongly affected by other factors, notably the conductance of the impurities, which changes with variations in the cane supply and with some processing operations. In practice, the pan stage operators must closely monitor the massecuite condition and, when needed in order to maintain appropriate massecuite conditions, change the conductivity set points. Substantial gains in pan stage productivity could be achieved if independent measurements (or reliable estimations) of supersaturation and crystal content could be made. Currently, neither of these parameters are able to be measured directly. The use of available correlations to define suitable operating ranges for supersaturation that would achieve fast crystal growth rates but avoid fine grain formation is investigated. Correlations for the mother molasses dry substance are proposed for the run-up and pan drop operations for the range of boiling duties. The measurement of massecuite dry substance using microwave technology is being increasingly adopted in overseas factories and refineries, and the suitability of this measurement for pan control in Australian factories is investigated. The paper provides data for a further two parts to this investigation - Part 2 progresses the investigation into the use of massecuite dry substance measurement for pan control, and Part 3 examines the profiles for massecuite dry substance for the various pan boiling duties. Comparison is made in Part 3 to the conventional use of conductivity for pan control. The overall aim of this three-part study is to provide a foundation for improved methods for controlling pan boiling operations in Australian factories.

Key words Vacuum pan boiling, sucrose crystal growth, nucleation, supersaturation control, mother molasses dry substance

INTRODUCTION

Successful boiling of a massecuite strike requires the pan stage operator to control the solids concentration of the mother molasses in the pan to be at sufficiently high supersaturation to provide fast enough crystal growth rate but not so high that nucleation (fine grain formation) occurs. Fine grain is less likely to form if the massecuite has sufficient crystal content. Australian factories use the measurement of massecuite conductivity to guide the operator on the condition of the massecuite. The difficulty for the operator is that the conductivity value is influenced by the mother molasses supersaturation, the crystal content, temperature, and, notably, the conductance of the impurities, which changes with variations in the cane supply and some processing operations such as lime addition. Despite these difficulties, massecuite conductivity has been used effectively by Australian factories as the single process variable for controlling the massecuite condition for more than 60 years (Foster *et al.* 1960).

Substantial gains in pan stage productivity could be achieved if independent measurements of supersaturation (or a parameter closely related to supersaturation) and crystal content could be made. Advanced control procedures have been promoted that would allow the supersaturation value to control the steam rate to the calandria and the crystal content value to control the syrup/molasses feed rate (Batterham *et al.* 1973; Wilson *et al.* 1987; Schneider 2003; Schneider and Vigh 2004). However, no advancement has been made into using these two parameters as independent parameters for control on Australian pan stages. In practice, there is no direct measure of the supersaturation of the mother molasses, even though this is fundamentally the most important control variable for regulating crystal growth rates while avoiding nucleation. The independent measurement of crystal content is also very problematic (Batterham *et al.* 1974).

Some overseas factories use two or perhaps three measurement techniques e.g., massecuite dry substance (by microwave), mother molasses refractive index and boiling point elevation to provide estimates of supersaturation (Rozsa 2008; Rozsa 2011). This procedure still requires knowledge (or reliable estimations) of the mother molasses purity, crystal content and solubility characteristics to provide reliable estimations of the supersaturation. The procedure is more readily implemented in sugar refinery pans because the mother molasses purity changes by only a small amount during a refinery white sugar strike, and the solubility characteristics are reasonably similar to those for pure sucrose, thus allowing supersaturation to be estimated. The situation in raw sugar massecuite production is substantially different owing to the large changes in mother molasses purity and sucrose solubility within a single massecuite strike, and across the different boiling duties on the pan stage.

Here, we provide an improved understanding of the appropriate operating ranges for supersaturation in Australian raw sugar factories in order to achieve fast crystal growth rate while avoiding the formation of fine grain. Correlations are proposed for the typical dry substance of the mother molasses during pan run-up and at pan discharge conditions. In addition, a modified correlation for the supersaturation at which nucleation is expected to form is proposed. Improved understanding of the various relationships affecting supersaturation will ideally lead to improved control methodologies being applied and the productivity of the pan stage increased.

A follow-on paper (Part 2) (Broadfoot and Fraga 2023a) applies the outcomes from this paper to define suitable operating ranges for massecuite dry substance for the various process operations undertaken on the pan stage. In a further application of the results (Part 3) (Broadfoot and Fraga 2023b), the profiles of massecuite dry substance that are currently used in the conventional high-grade seed and A, B and C massecuite production in Australian factories are examined. This third part compares the use of massecuite dry substance and conductivity for pan control.

SATURATION, SUPERSATURATION AND OVERSATURATION

General descriptions and definitions

Just as the saturation concentration of a pure sucrose solution is strongly influenced by its temperature, so is the saturation concentration of impure sucrose solutions. In addition, both the concentration and the composition of the impurities in cane syrups and molasses affect the saturation conditions and hence also affect the solids concentration of the supersaturated solution. For an impure sucrose solution (e.g., mother molasses), the effect of impurities on supersaturation (SS) is taken into account relative to the saturation conditions for pure sucrose by incorporating a solubility coefficient (SC). Thus,

Supersaturation (SS) =

$$\frac{\frac{S}{W} \text{ in the mother molasses}}{\frac{S}{W} \text{ in a saturated pure sucrose solution at the same temperature} \times \text{Solubility Coefficient (SC)}} \quad \text{Eqn 1}$$

where S/W = sucrose/water mass ratio in the solution.

For a mother molasses at saturation SS = 1.0 and for a supersaturated mother molasses SS > 1.0.

The SC defines the extent to which the impurity concentration and composition affect the saturation condition of the mother molasses. SC is also influenced by the temperature. The higher the value of SC the greater is the solubility of sucrose in the syrup/molasses.

Researchers have undertaken extensive investigations of the SC for beet syrup and molasses (Wagnerowski *et al.* 1962; Schliephake and Ekelhof 1983; Carter 2013) and established that it can be described by an expression of the form

$$\text{Solubility Coefficient (SC)} = m \frac{I}{W} + b + (1 - b) \exp\left(-c \frac{I}{W}\right) \quad \text{Eqn 2}$$

where the coefficients m , b and c are functions of temperature, impurity/water (I/W) mass ratio and specific impurity components (e.g., raffinose). A feature of Eqn 2 is that an inflection point exists at a certain I/W value, where the dependence of SC on I/W changes from negative to positive.

Investigations by SRI have shown that the form of Eqn 2 is also suitable to describe the saturation conditions for impure cane syrups and molasses (Broadfoot and Steindl 1992; Miller and Beath 1999).

In order for crystals to grow, the supersaturation of the solution needs to exceed the saturation condition by a certain amount, which is termed the limiting supersaturation value (SS_{Lim}) (Smythe 1971; Wright 1984). Oversaturation (OS) is the extent of supersaturation above SS_{Lim} and defines the driving force for crystal growth. Thus,

$$OS = SS - SS_{Lim} \quad \text{Eqn 3}$$

The rate of growth of the sugar crystals has been found to vary linearly with OS (Smythe 1971, Broadfoot and Steindl 1992). Thus, OS is the key parameter which determines the rate of sucrose deposition, the boil-on rate of the feed syrup or molasses, and the production rate of the pan.

In practice, the supersaturation of the mother molasses is not readily used for control in factory pans as neither the S/W ratio (as given by the purity and dry substance of the mother molasses) nor the SC are known at any time during the pan's boil-on or heavy-up operations.

It is noteworthy that the method for calculating supersaturation values has changed as specific data on solubility coefficients and its dependence on I/W have been determined. Measurements of supersaturation in high-grade boilings by Foster *et al.* (1960) used the expression

$$\text{Supersaturation} = \frac{\frac{S}{W} \text{ in the mother molasses}}{\frac{S}{W} \text{ in the mother molasses when saturated at the same purity and temp}} \quad \text{Eqn 4}$$

The different denominators in Eqn 1 and Eqn 4 affect the calculated value of supersaturation. For high purity boilings, the supersaturation values reported using the SC expression (Eqn 1) will provide higher values than reported using Eqn 4.

Methods to measure the Solubility Coefficient

Three methods can be used to provide information on the Solubility Coefficient.

Equilibration method. The test molasses is equilibrated to saturation at constant temperature by tumbling a sample that was initially undersaturated with an excess of sucrose crystals (Miller and Beath 1999). At the completion of the equilibration time (normally 20 h), the mother molasses is separated by pressure filtration and analysed. The temperature dependence of SC can be determined by conducting the tests at different equilibration temperatures. However, because of the degradation resulting from the Maillard reaction for tests at high temperature, equilibration temperatures are usually limited to a maximum of 65°C. A substantial limitation of the 'Equilibration method' is that the measured value of SC for a particular molasses is always at lower I/W than the I/W for pan boiling at the supersaturated condition. Overall, the 'Equilibration method' limits the I/W values to 2.5 or slightly higher at typical pan boiling temperatures and certainly much lower than the I/W range for C massecuite processing (typically 3.5 to 5.0).

Exhaustion method. This method determines a pseudo-saturation condition by exhausting an initially supersaturated test molasses in a constant temperature stirred vessel for a long period e.g., 48 h (Rouillard 1980; Lionnet and Rein 1980). Because the crystallisation rate becomes very slow at low supersaturation values, the calculated SC is inflated relative to the values from the 'Equilibration method', with the largest difference being for low purity molasses at high I/W. One benefit of the exhaustion method is that it provides data at substantially higher I/W values than the 'Equilibration method'.

Heating to undersaturation method. An approximate value of supersaturation can be obtained by taking a sample of mother molasses and heating it slowly till the saturation point is reached (as determined by the initial rounding of crystals) (BSES 2001, Method 23). A variation of this method is the *Saturation cell* method. The test molasses is pre-mixed with fine crystals and heated until dissolution occurs. The onset of dissolution can be observed through a microscope or using a photocell to monitor the change in light transmission (Wright 1980). While the concentration of the original sample and the sample at saturation are the same, information on the differences in SC at the two temperatures is not known and the erroneous assumption is made that the solubility coefficient is temperature independent (BSES 2001, Method 23). The error will be greater for low purity molasses at high I/W.

SRI favours the 'Equilibration method' to determine the SC as it defines the true saturation condition at the nominated temperature of interest; temperature having a strong influence on the concentration of the saturated (and supersaturated) syrup/molasses. The use of the limiting supersaturation then defines the condition of zero growth and, hence, the oversaturation that strongly influences the crystal growth rate.

Correlations for the parameters

Table 1 shows two correlations (labelled SC-1 and SC-2) for solubility coefficient developed using the 'Equilibration method'. The table also shows the range of data used in these determinations¹. In the absence of sufficient data at I/W values above the inflection point, it was proposed that the slope (m) in Eqn 2 in the high I/W region is constant i.e., independent of RS/ash ratio as shown by Rouillard (1980) from tests using the 'Exhaustion method'. Table 1 also provides correlations for the solids concentration of pure sucrose at saturation (as a function of temperature) and for SS_{Lim}.

Table 1. Correlations for Solubility Coefficient using the Equilibration method, the saturation correlation for pure sucrose and correlation for SS_{Lim}.

Parameter	Correlation	Range of data for development of the correlations	Reference
SC-1	Equation 2 with $m = 0.04111 + 0.0001 T$ $b = 0.61181 + 0.00233 T - 0.04926 \text{ RS/ash}$ $c = 0.84269 + 0.00055 T$ where T = temperature, °C	Equilibration tests undertaken at 65 and 70°C for 5 molasses samples adjusted through a range of purities with RS/ash in the range 0.7 to 1.28. The I/W values at saturation ranged 0.4 to 1.5. The data used in the development of SC-2 were included in the determination of SC-1.	Miller and Beath (1999).
SC-2	Equation 2 with $m = 0.011 + 0.00046 T$ $b = 0.67 + 0.0021 T - 0.07 \text{ RS/ash}$ $c = 0.54 + 0.0049 T$	Equilibration tests undertaken at 40, 50 and 60°C for final molasses samples with RS/ash values of 0.74 and 0.63; six molasses samples at 50°C with RS/ash values in range 0.45 to 1.7; four molasses samples at 50 and 65°C with RS/ash values in range 0.68 to 1.71 (Broadfoot & Steindl, 1980). Maximum I/W value of tests was 2.8.	Broadfoot and Steindl (1992); Steindl <i>et al.</i> (2001). This correlation was used in the development of the SRI cooling crystallisation model.
Dry substance of pure sucrose at saturation	$\text{Sol} = 64.407 + 0.07251 T + 0.0020569 T^2 - 9.035 \times 10^{-6} T^3$ where sol = mass percent sucrose in the solution		Charles (1960) but with first term changed from 64.397 to 64.407 as the latter provides a better fit.
SS _{Lim}	$\text{SS}_{\text{Lim}} = 1.057 + 0.036 \text{ I/W} - 0.0012 T$	Exhaustion tests on C massecuite in stirred pilot crystalliser for temperatures between 40 and 50°C for 48 to 72 h. The calculation of SS _{Lim} used SC-2 correlation to determine the SS value. The data were forced to align with data for SS _{Lim} for pure sucrose (Smythe 1971).	Broadfoot and Steindl (1992).

¹ The correlations used here are based on the following methods of analyses (Sugar Research Australia 2014): Dry substance by vacuum oven drying at 60°C for 16 h using Method 19; Sucrose by double polarisation method using Method 18; Reducing sugars by the constant volume determination of the Lane and Eynon method using Method 20; Ash by double sulphation method using Method 27. Purity values quoted are true purity (=100 x sucrose/dry substance).

Correlation SC-1 is considered to provide a better general representation of the saturation behaviour of Australian cane sugar molasses than correlation SC-2, at least in the range of I/W from 0 to 2.8. The Root Mean Square Error for SC-1 was 0.02.

The form of the SC-1 correlation is shown in Figure 1 for temperatures of 65 and 70°C and RS/ash values of 0.5, 1.0 and 1.5. The point of inflection in SC values occurs at an I/W in the range 2.0 to 2.5. Marked on Figure 1 are the usual ranges of I/W values for high grade seed massecuite, and A, B and C massecuite production, as produced in the Australian three massecuite boiling flowscheme. For each boiling duty the minimum value of I/W corresponds to the footing condition and the maximum value of I/W to the pan cut-out or discharge condition.

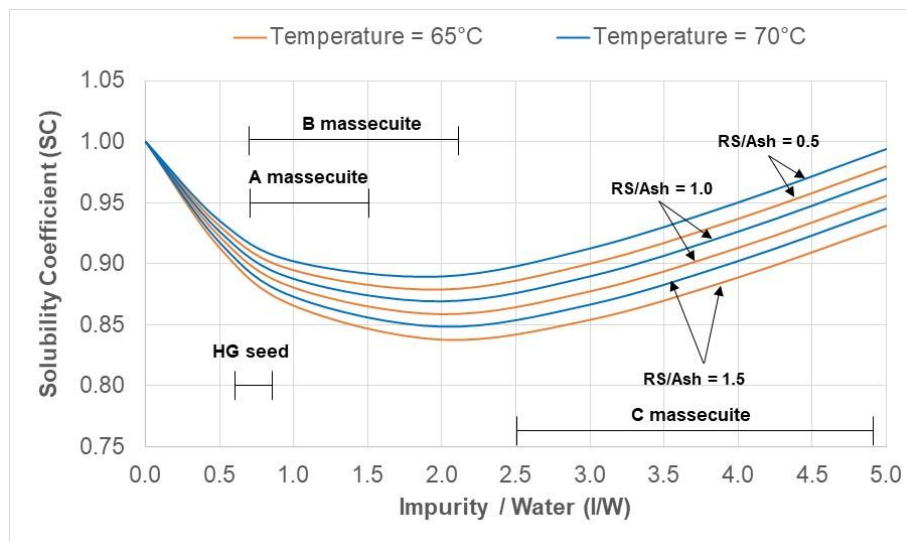


Figure 1. Solubility coefficient values provided by correlation SC-1 for 65 and 70°C and RS/ash ratios of 0.5, 1.0 and 1.5.

As is evident in Figure 1, and supported by saturation studies for cane molasses by several researchers, SC is dependent on:

- Process temperature. SC, when determined by the 'Equilibration method' is lower at lower process temperatures². Thus, at higher temperatures, such as experienced during the heavy-up of massecuites, the solubility increases, and a higher solids concentration is required in order to maintain the level of supersaturation;
- Concentration of impurities expressed in terms of I/W. There is a distinct difference in the effects of increasing I/W on SC for the high and low purity massecuite boiling duties.
 - For high grade massecuites, the SC decreases for an increase in I/W; and
 - For C massecuites, SC increases for an increase in I/W.
- Composition of the impurities. Higher concentrations of reducing sugars are known to reduce the solubility of sucrose (attributed to their attraction to water molecules) (Rouillard 1980), while various cations are thought to increase the solubility of sucrose through complexing compounds with sucrose. While individual compounds will contribute different melassigenic effects on the sucrose solubility in molasses, the dependency on impurity composition is generally described in terms of the RS/ash ratio of the mother molasses. For molasses with higher RS/ash ratio the solubility of sucrose in the molasses is reduced.

²SC data provided by Rouillard (1980) show that sucrose in cane molasses is more soluble at lower temperatures. However, this result, obtained using the 'Exhaustion' saturation method is likely confounded by a large oversaturation component remaining after crystallisation in low purity molasses at the lower holding temperatures. In essence solubility coefficient values obtained by the 'Exhaustion method' incorporate the effects of SS_{Lim} . This would account for the very high solubility coefficient values reported by Rouillard (1980) for C massecuites during cooling crystallisation, such as values of 1.05 for I/W 4.5, RS/ash = 1.0 and temperature 45°C.

For conditions that reduce the solubility of sucrose in molasses, the dry substance at saturation (and any specific level of supersaturation) is lower (as shown through application of Eqn 1).

Ideally, in order to estimate supersaturation values for pan control, SC values would need to be determined regularly on the syrup and molasses for the current cane supply. However, only tedious, time-consuming laboratory methods are available, and they only provide data for a limited range of I/W. The expression SC-1 is expected to provide a reasonable description of sucrose solubility for Australian cane molasses on the basis that the data included wide ranges of RS/ash ratios (0.45 to 1.7) and temperature (40 to 70°C). Even though it is three decades since its development, the SC-1 expression is still likely to be suitable as a general correlation as the compositions of the reducing sugars and ash have probably not changed substantially in that time and the RS/ash ratio would provide an adequate description of the influence of the impurities. The potential error in using SC-1 in high purity boilings is expected to be relatively low as the impurity concentration is low.

There is more doubt over the validity of the SC-1 correlation for C massecuite boilings as:

- The operating range for I/W is above the maximum I/W value in the experimental determinations (I/W = 2.8) and well above the inflection point. The magnitude of this potential error in SC increases for C massecuites of high I/W (e.g., 4.5 to 5.0); and
- Any substantial change in the impurity composition, other than accommodated by the RS/ash ratio, could change the saturation conditions and these changes will manifest more strongly in the C massecuite processing owing to the higher concentration of impurities.

The implications of variations in boiling temperature and RS/ash ratio in the mother molasses are discussed by Broadfoot and Fraga (2023b).

CRITICAL SUPERSATURATION AND NUCLEATION

The formation of sucrose nuclei in the mother molasses is thought to occur when a cluster of sucrose molecules becomes a stable entity, and ultimately attracts other sucrose molecules to establish the crystal lattice (Ostwald 1903). The minimum supersaturation in the mother molasses at which the nuclei are expected to form (defined as the nucleation boundary condition) is termed the Critical Supersaturation. Rozsa (2008) indicated the Critical Supersaturation for pure sucrose is ~1.20. In practice, pan operators aim to maintain the conditions of the mother molasses at high enough supersaturation for strong crystal growth rates, but below the Critical Supersaturation. Of course, the variability of massecuite conditions in the pan, particularly when the massecuite is at high brix, compounds the difficulty for the pan stage operator in maintaining a high but safe supersaturation condition.

Studies by SRI by concentrating syrup/molasses in a stirred laboratory vacuum pan till nucleation was observed determined two correlations for the Critical Supersaturation (labelled SSNuc-1 and SSNuc-2), which are presented in Table 2, along with the range of process conditions used in the investigations. Ideally, the Critical Supersaturation would have been measured in molasses of lower purity but difficulties with dark solutions and the presence of sludge made it too difficult to detect the small nuclei.

Table 2. Correlations for the Critical Supersaturation.

Parameter	Correlation	Range of test conditions for development of the correlations	Reference
SSNuc-1	$SSNuc-1 = 1.12889 - 0.2841 (I/(S+I)) + (2.333 - 0.0709 (T-60)) (I/(S+I))^2$	Molasses purity 60 to 80; temperature 60 and 71°C; crystal content 10 to 30% massecuite	Correlation in Broadfoot and Wright (1972) using the data of Penklis and Wright (1963)
SSNuc-2	$SSNuc-2 = 2.864 - 3.516 (S/(S+I)) + 1.81 (S/(S+I))^2 - 0.00177 CC$ where CC = crystal content %massecuite	Molasses purity 70 to 100; temperature 60 and 71°C; crystal content 2 and 15% massecuite	Broadfoot and Wright (1972)

The investigations undertaken by Batterham *et al.* (1975) covered a wider range of conditions than shown in Table 2 and included: true purity 55 to 100, temperature 38 to 79°C, crystal content 0 to 50%, crystal size 0.19 to 0.78 mm. The Critical Supersaturation value was found to be higher when processing at:

- Lower temperature;
- Lower purity mother molasses;
- Lower crystal content;
- Smaller average crystal size; and
- Lower speed of mechanical agitation.

Batterham *et al.* (1975) did not propose a correlation for the Critical Supersaturation in terms of the process variables. Importantly, their work included trials in low purity molasses and indicated that higher safe supersaturations can be accommodated in C massecuite boilings because of the effects of lower purity, lower crystal content and smaller average crystal size. Higher temperature of C massecuite boiling would counteract these effects to some extent.

Figure 2 shows plots for SSNuc-1 for 65, 70 and 75°C as a function of the purity of the mother molasses. Data for SSNuc-2 are also shown with values calculated using realistic crystal contents, as shown in Table 3 for high-grade seed massecuite and run-up and pan drop of A, B and C massecuites. The data shown in Figure 2 for the C massecuite boilings are extrapolated beyond the data range determined in the experimental investigations for these two correlations, but are supported by the results of Batterham *et al.* (1975).

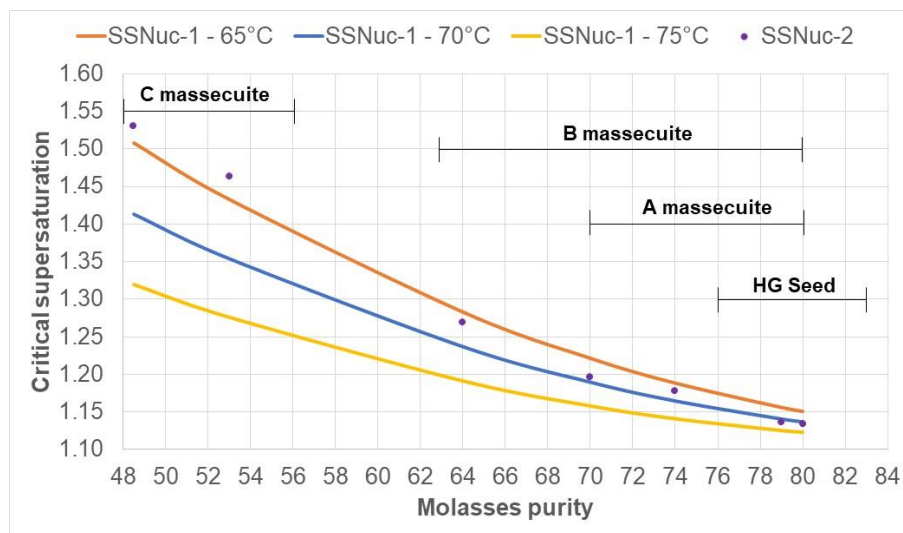


Figure 2. Comparison of the correlations for Critical Supersaturation at typical pan boiling temperatures.

Table 3. Typical crystal content values in pan boiling duties on Australian pan stages.

Masseccuite	Status	Mother molasses purity	Crystal content % masseccuite
HG seed	Run-up	80	42
A	Run-up	79	44
	Pan drop	70	52
B	Run-up	74	42
	Pan drop	64	48
C	Run-up	53	25
	Pan drop	48.5	30

Observations from the two correlations in Figure 2 include:

- The Critical Supersaturation values are quite low for the high-grade seed and early stages of A massecuite boiling. It is expected that values higher than 1.20, as reported by Rozsa (2008) for pure sucrose, would apply.
- For the low purity boilings, temperature has a strong influence for SSNuc-1, with nucleation predicted to form at lower superaturation values at higher temperatures (as typically experienced during C massecuite heavy up). As mentioned above, Batterham *et al.* (1975) also found the Critical Supersaturation was lower at higher temperature.

As a general observation, in industrial sugar boiling there is a reduced likelihood of forming nuclei if the crystal content is maintained at a high level. This observation is opposite to the results determined in the laboratory investigations. However, for industrial sugar boiling the operating supersaturation is determined largely by the net evaporation rate and when the crystal content is high there is more surface area for sucrose deposition and there is a reduced likelihood of reaching the high supersaturations to form nuclei.

Overall, the value of the Critical Supersaturation is not well defined and there is uncertainty in the suitability of either correlation for industrial massecuite production, partly due to the change in the method of calculation of supersaturation, as described above. Its specification for factory pans is made even more difficult by the massecuite conditions in factory pans being non-uniform.

DRY SUBSTANCE OF MOTHER MOLASSES FOR A RANGE OF FACTORY PROCESSING CONDITIONS

Calculation of dry substance of mother molasses at saturation and at supersaturated conditions

For a mother molasses of given purity, RS/ash ratio and boiling temperature, the dry substance (DS) of the mother molasses at saturation, or at any nominated supersaturated condition, can be calculated iteratively from the following equations Eqn 5 and Eqn 6, with Eqn 2 (with the coefficients for SC-1 in Table 1).

$$SS = \frac{\frac{Purity \times DS}{100 - DS}}{100 \times \frac{S}{W_{pure}} \times SC} \quad \text{Eqn 5}$$

where, from Table 1, $S / W_{pure} = Sol / (100 - Sol)$

$$\frac{I}{W} = \frac{(100 - Purity) \times DS}{(100 - DS)} \quad \text{Eqn 6}$$

For operation in industrial pans where the head space pressure is controlled to a set point value, the additional complication arises in that the mother molasses temperature varies through the course of the pan strike. The boiling point elevation is a function of the saturation temperature of the head space vapour and the purity and dry substance of the mother molasses. In addition, temperature directly influences S/W_{pure} and SC.

Dry substance of mother molasses at saturation and at supersaturated conditions

Figure 3 shows saturation data as a plot of dry substance of molasses versus mother molasses purity with RS/ash ratio of 1.0 for temperatures of 75, 70, 65 and 60°C, and solubility described by the SC-1 correlation. It also shows saturation data for pure sucrose and the typical range of mother molasses purities during the boilings of the different massecuites in the Australian three massecuite flowscheme.

Clearly, the dry substance at saturation for the impure cane sugar solutions is higher than for pure sucrose as would be expected owing to the presence of soluble impurities in the solutions. In addition, the dry substance at saturation is substantially higher at lower purities, as is well known when comparing boiling conditions for high and low purity massecuites. The rate of change of dry substance with change in molasses purity is greater for the low purity massecuites than for the high purity massecuites because of the associated increase in SC (increased solubility of sucrose) at the low purity conditions. Approximately, for the same process temperature, the saturation dry substance in A massecuites increases by approximately 1.7 units for each 10 units reduction in molasses purity while in C massecuite boilings the increase is approximately 2.8 units.

As for pure sucrose solutions, the dry substance of impure cane sugar solutions is strongly dependent on the temperature of the solution. The saturation curves through the range of molasses purities are almost parallel for the different temperatures. For a 10°C reduction in temperature, the saturation dry substance reduces by approximately 2.15 units. This value is similar to, but slightly lower than that for pure sucrose which shows an average 2.3 units reduction in dry substance for a 10°C reduction in temperature.

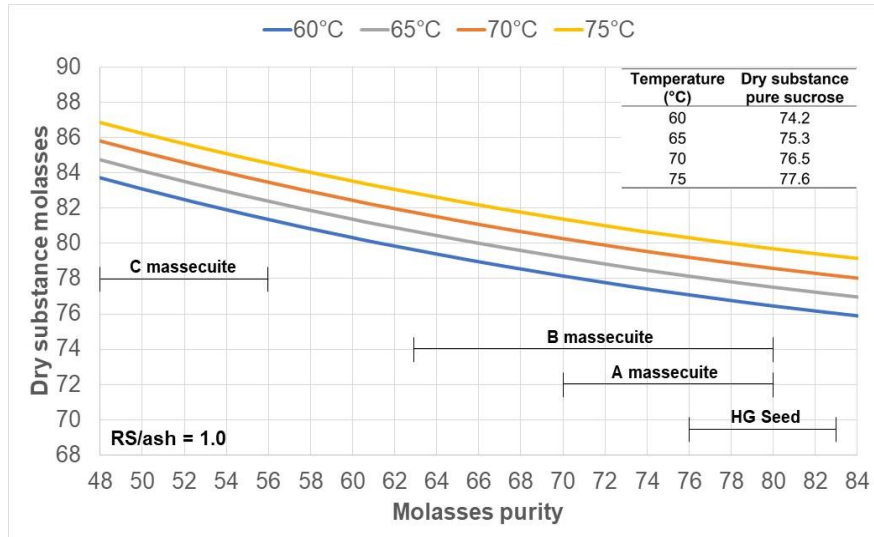


Figure 3. Saturation dry substance data for molasses at different purities having solubility characteristics of SC-1 and RS/ash ratio 1.0.

The effects of a change in RS/ash ratio on the saturation dry substance values are shown in Figure 4. The data are provided for temperatures of 65 and 75°C. As expected, because the solubility of sucrose is lower at high RS/ash ratio, the dry substance at saturation is lower for the high RS/ash values. The effect of a change in RS/ash ratio is greater in the low purity boilings due to the higher concentration of impurities. For an A massecuite boiling, the difference in dry substance for a variation in RS/ash ratio between 0.5 and 1.5 (the usual extreme limits for Australian cane supply) is 0.5 units, while for C massecuite boilings, the difference is 0.7 units. These differences are similar at both 65 and 75°C and also apply for mother molasses at supersaturated conditions.

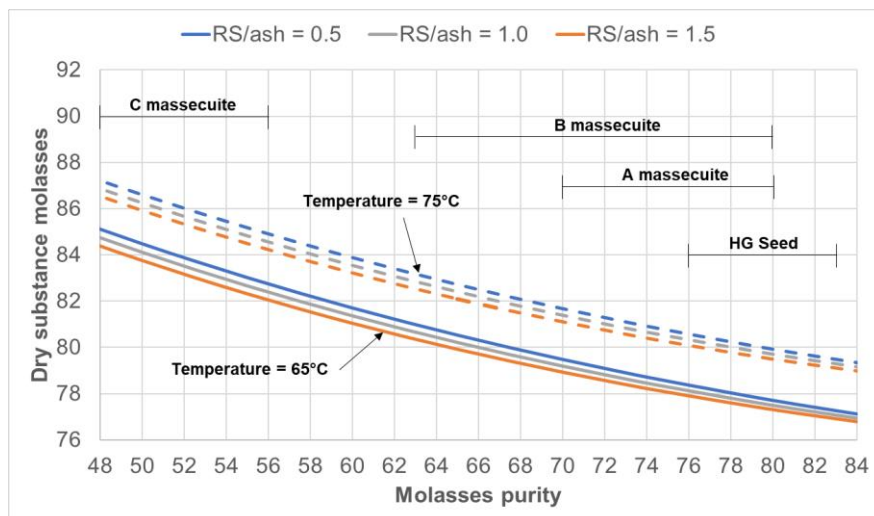


Figure 4. Effect of RS/ash ratio on the saturation dry substance values for molasses at 65 and 75°C.

In practice, massecuite boiling temperatures vary among mills primarily due to different head space pressures (mainly affected by condenser performance and temperature of the cooling water supply). The increase in boiling temperature resulting from the increase in boiling point elevation from footing to pan drop during a strike is also a significant factor (typically ranging between approximately 2°C for A massecuite and 6°C for C massecuite).

The impact of RS/ash ratio on the saturation dry substance of the mother molasses is the result of the effect on the solubility coefficient. Variations in the composition of impurities present in syrup and molasses on the pan stage are generally dampened to a large extent in the buffer storage tanks for juice and the pan stage stock tanks. Consequently, at least in the usual day to day operations, large variations in the solubility coefficient are unlikely to occur (perhaps by ± 0.2). However, across the total season, and particularly if a factory starts the season with immature cane or standover cane, the variation in RS/ash ratio could change over the range 0.5 to 1.5.

Based on these considerations and the data in Figures 3 and 4, it is expected that, in normal processing conditions, the temperature of boiling has a much stronger effect on the dry substance of molasses at the saturation (and supersaturated) conditions than the variation in RS/ash ratio. The implications for practical pan boiling are that, for a mother molasses of a certain dry substance, the boiling temperature will determine the supersaturation more strongly than the influence of the expected variation in RS/ash ratio on the solubility coefficient.

As a general observation also, the cane industry does not relate good or poor exhaustion performance on the pan stage to changes in RS/ash ratio. The industry only concerns itself with the effects of RS/ash on solubility in defining the Target Purity for exhaustion of the C massecuites (Smith 1995; Miller *et al.* 1998). Of course, the effects of RS/ash ratio are greatest under these conditions because of the high concentration of impurities in the molasses and the very high viscosities at the end of cooling crystallisation.

Figure 5 shows molasses dry substance data for a supersaturation of 1.2 at temperatures of 75, 70, 65 and 60°C and RS/ash ratio of 1.0. Compared with the saturation data the molasses dry substance is higher by ~2.55 units for A massecuite production and 2.4 units for C massecuites. As for the saturation data, the 1.2 supersaturation curves are almost parallel through the range of purities for the different temperatures. For a 10°C reduction in temperature, the supersaturated dry substance values reduce by approximately 2.0 units which is slightly less than the influence of a temperature change on saturation data. For a change in molasses purity there is also a very slight reduction in the sensitivity of molasses dry substance at the supersaturation of 1.2 compared to the effect of a purity change on saturation dry substance. Approximately, for the same process temperature, the dry substance at a supersaturation of 1.2 in A massecuites increases by approximately 1.6 units for each 10 units reduction in molasses purity, while in C massecuites the increase is approximately 2.7 units.

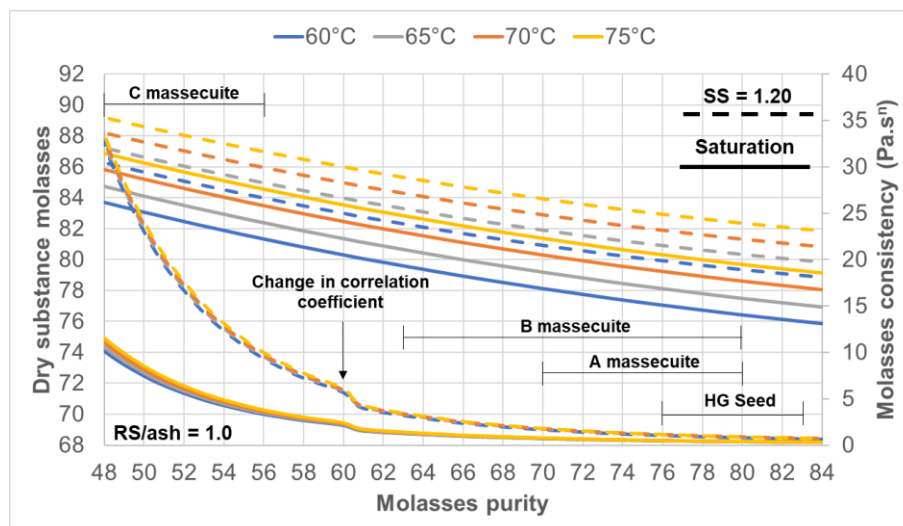


Figure 5. Molasses dry substance and consistency values at different temperatures at saturation and supersaturation of 1.2 for an RS/ash ratio of 1.0.

Figure 5 also shows consistency data (viscosity at a shear rate of 1 s^{-1}) for molasses at saturation and 1.2 supersaturation for the different temperatures. The correlation used for determining the consistency values in Figure 5 is given in Broadfoot *et al.* (1998). These data show a beneficial characteristic for practical pan boiling viz., the consistency of the mother molasses at a specified level of supersaturation is largely independent of the temperature of boiling. This occurs because of the counteracting effects on consistency of (1) higher dry substance (e.g. at a nominated supersaturation at higher temperature) increases the consistency and (2) at higher temperatures the consistency is lower.

Of note for the consistency data:

- The consistency is much greater for the lower purity massecuites, reflecting the strong dependence of consistency on molasses dry substance. For the same reason, the consistency of the mother molasses is much greater for C massecuite at a supersaturation of 1.2 compared with saturation.
- There is less variation of consistency with temperature at higher supersaturation values. This occurs because of the counteracting effects of dry substance and temperature on consistency and the stronger dependency of consistency on temperature at higher dry substance values.

If mother molasses consistency could be measured in a pan (requiring separation from crystal), it may provide an accurate measure of supersaturation, at least for C massecuite boilings, although dextran and other polysaccharides would add to the uncertainty when processing stale cane or standover cane.

The fact that the consistency of the mother molasses at a given level of supersaturation is largely independent of the boiling temperature means that the upper supersaturation limits for pan run-up and pan drop conditions are defined by the circulation characteristics of the pan, as well as to avoid fine grain formation. For pans with poor circulation characteristics, the average mother molasses concentration must be maintained at a lower dry substance in order to maintain adequate circulation and, hence, the average supersaturation is lower.

The consistency data in Figure 5 suggest that the circulation movement in the pan at the same mother molasses purity, supersaturation level and crystal content will not be strongly affected by the head space pressure. This observation is largely borne out in practice for operation of pans at the same steam rate but at different head space pressures. Changes in circulation in the pan are likely influenced more by the volume of vapour bubbles in the massecuite for the different head space pressures than differences in mother molasses (and massecuite) consistency at desired supersaturation conditions for run-up and pan drop.

The above discussion shows that, under normal crushing conditions, the RS/ash ratio will likely have a smaller influence on the determination of the supersaturation for a mother molasses of given composition, compared with the boiling temperature. Under abnormal cane supply conditions, large changes in the RS/ash ratio may influence the supersaturation to a significant extent, and so affect the target dry substance for the mother molasses.

Dry substance of mother molasses during run-up and at pan drop

The considerations above have determined that the boiling temperature and the molasses purity are the two factors having greatest influence on the mother molasses dry substance at saturation and supersaturated conditions. The influence of changes in RS/ash ratio appeared to be of lesser importance, at least within the typical range experienced by Australian mills under normal cane supply conditions.

Correlations are presented for typical dry substance values during pan run-up and at the pan drop condition as functions of mother molasses purity and massecuite boiling temperature. These correlations were developed from experimental data across several studies in Australian factories and also included mother molasses compositions representing high productivity results for the pan stage i.e., high crystal growth rates during run-up and high massecuite exhaustion at pan drop. The correlations are considered appropriate for the typical range of RS/ash ratios averaging around 1.0, experienced in Australian factories:

$$DS_{\text{Run-up}} = 84.1976 - 0.2198 \times \text{molasses purity} + 0.1989 \times \text{temperature } (^{\circ}\text{C}) \quad \text{Eqn 7}$$

$$DS_{\text{Pan drop}} = 88.9164 - 0.2405 \times \text{molasses purity} + 0.1630 \times \text{temperature } (^{\circ}\text{C}) \quad \text{Eqn 8}$$

As mentioned, the $DS_{\text{Run-up}}$ relationship applies to conditions for reasonably high crystal growth rates viz., high supersaturation condition (but safe with respect to the likelihood of nucleation) and the $DS_{\text{Pan drop}}$ represents well exhausted massecuite at pan drop i.e., heaved to a high dry substance in the mother molasses at drop. In practice, for a range of circumstances, the chosen dry substance values used for run-up and pan drop may be lower than defined in Eqn 7 and Eqn 8.

These circumstances include:

- Targeting low boil-on rates e.g., using low steam rates when syrup/molasses stocks are low;
- Using low-pressure vapour supply to the calandria, thus limiting the evaporation rate (and supersaturation) that can be achieved; and
- Boiling massecuites in a pan with poor circulation characteristics as a wider range of supersaturation would exist within the pan and a lower average supersaturation would be appropriate in order to avoid nucleation (and also to assist circulation).

The range of dry substance for the mother molasses between that corresponding to SS_{Lim} (zero crystal growth rate) and DS_{Run-up} defines the operating oversaturation range for growth of the crystals during the syrup/molasses feed on phase.

During the feed-on of A molasses to A and B massecuite boilings and the feed-on of B molasses to C massecuite boilings, the mother molasses purity reduces and, to maintain a required level of supersaturation, the mother molasses dry substance and I/W are increased. As a consequence, the boiling-point elevation increases during the strike and, for the head space pressure being controlled to a fixed set point, the massecuite boiling temperature increases. With the increasing temperature as the strike progresses, both the saturation dry substance for pure sucrose and the solubility coefficient (see Figure 1) increase. Both these parameters (in the denominator of the supersaturation expression Eqn 1) increase, and so the dry substance (and I/W) must increase further in order to maintain a desired level of supersaturation to achieve the required rate of crystal growth. The increase in temperature is faster during the heavy up phase because of the rapid increase in dry substance.

The influence of increasing I/W on SC differs for the high and low purity massecuite production, as noted in the discussion on Figure 1. For the high purity boilings, the increasing I/W (associated with the reducing mother molasses purity as the strike proceeds) reduces the solubility and so there is a counteracting effect to limit the extent of increase in mother molasses dry substance and I/W to maintain supersaturation as the temperature increases. For C massecuite boilings, the increasing I/W increases the solubility of sucrose which augments the effect of increasing solubility associated with the increasing temperature.

The boiling temperature in the pan has a large influence on the mother molasses dry substance required to supply a desired operating supersaturation. Conversely, a change in the dry substance of the mother molasses affects the boiling point elevation and the massecuite boiling temperature, and, hence, the supersaturation. Both these effects are well known to pan stage operators.

In practice, the massecuite temperature approximates the saturated temperature of the vapour in the head space plus the boiling point elevation plus superheat in the massecuite. The boiling-point elevation is estimated from the relationship given by Saska (2002) and is a function of the saturation temperature of the vapour in the head space and the mother molasses purity and dry substance. The experimental data used by Saska (2002) covered the purity range 58 to 100 and dry substance range 65 to 80. Unfortunately, the data did not extend to the high dry substance values, particularly relevant to C massecuite boiling. The value of superheat of 2°C is assumed as this provided massecuite boiling temperatures that aligned reasonably with measurements in factory pans. Batterham and Norgate (1975) measured superheat values averaging 3.3°C for a floating calandria pan and noted that superheat is a function of several parameters, including massecuite boiling height, heat input and crystal content. The circulation characteristics of the pan would also affect the magnitude of superheat.

PROPOSED RELATIONSHIP FOR CRITICAL SUPERSATURATION

There is little data available to better define the conditions for initiation of nucleation in industrial pans. It is known that at most pan drop conditions, at least for well exhausted A and B massecuites, the final stages of heavy-up are likely to show initial evidence of nucleation. Thus, it appears likely that the Critical Supersaturation would be only slightly above the supersaturation at the pan drop condition defined by Eqn 8. It is proposed that, for mother molasses of purity above 60 (i.e., for high grade seed, A and B massecuites) the operating supersaturation at pan drop is 90% of the Critical Supersaturation. Thus, for the molasses above 60 purity:

$$SS_{Nuc} = 1 + ((SS_{pandrop} - 1) / 0.9) \quad \text{Eqn 9}$$

It is more difficult to define the Critical Supersaturation that applies to C massecuite boilings. This is partly because the data in Table 2 are not based on experimental data in the low purity region. Also, the apparent strong dependence of $SS_{Nuc}-1$ on temperature, as shown in Figure 2 appears to be unrealistic showing Critical

Supersaturation values as high as 1.45 to 1.5 for well exhausted C massecuites of high I/W (and typical boiling temperatures above 72°C). The proposed SSNuc relationship (which is based on the same functional form as SSNuc-1) is given in Eqn 10:

$$\text{SSNuc} = 0.958 + 1.712 (I/S+I) + (-3.130 + 0.0154 \times (T + 7.1)) \times (I/S+I)^2 \quad \text{Eqn 10}$$

SUPERSATURATION VALUES DURING TYPICAL BOILING DUTIES

Figure 6 shows supersaturation data and expected boiling temperatures for massecuites at the run-up and pan drop conditions (Eqn 7 and Eqn 8, respectively), at a head space pressure of -86 kPag. The data are for a RS/ash ratio of 1.0. Also shown on Figure 6 are the SSNuc-1 relationship and the proposed SSNuc relationship, with both determined at the expected pan drop massecuite temperature. The differences in supersaturation between the run-up condition and at pan drop are evident. At the typical pan drop mother molasses purities for A, B and C massecuites, the differences in supersaturation between typical run-up and pan drop conditions are 0.07, 0.09 and 0.10, respectively.

The data in Figure 6 suggest that there is reduced likelihood of forming fine grain in C massecuite boilings. However, the variation in supersaturation is likely to be greater in C massecuites because of the inherently worse circulation than in high-purity boilings.

For the high-purity boilings, the operating supersaturations for run-up and for pan drop increase with reducing mother molasses purity. However, during the run-up and heavy-up of C massecuites there is a decline in supersaturation with reducing mother molasses purity which is a consequence of several compounding effects:

- Increasing SC as the mother molasses purity declines and the I/W increases;
- Increasing mother molasses dry substance associated with the increasing solubility of sucrose;
- Increasing boiling temperature at the higher mother molasses dry substance; and
- Further increase in mother molasses dry substance at saturation conditions at the higher boiling temperature (resulting from both terms in the denominator of Eqn 1).

Figure 6 also shows the magnitude of the increase in temperature during run-up and heavy up which, as expected, is greater for the C massecuite boilings. This strong increase in temperature for the C massecuite boilings (during both run-up and at pan drop) is the primary reason for the decline in supersaturation as C massecuite boilings progress through to pan drop.

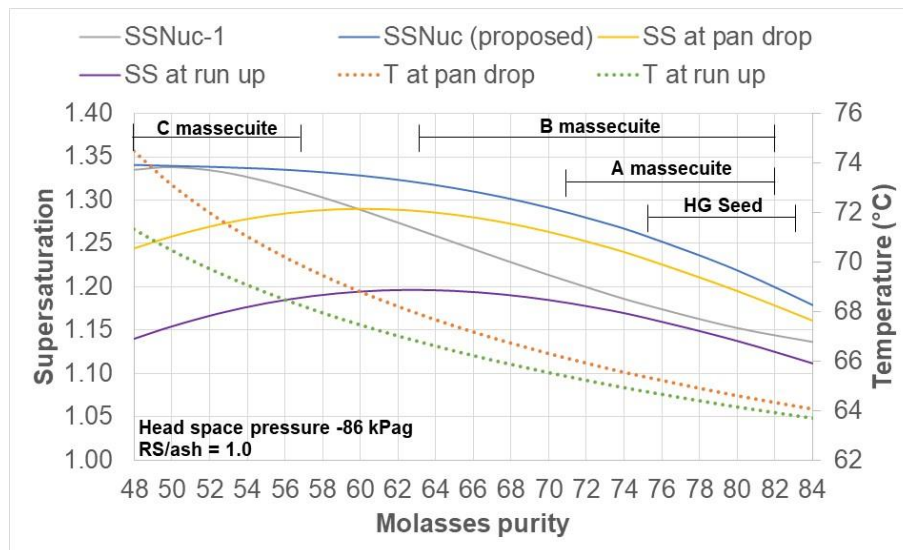


Figure 6. Supersaturation values for run-up and pan drop conditions and values of Critical Supersaturation.

It should be noted that the boiling point elevation for C massecuites at the final stages of run-up and at pan drop are at conditions outside the range of data investigated by Saska (2002) and may be slightly overestimated³ e.g., by 1°C or slightly more. If this were the case, the reduction in supersaturation during run-up for the final stages of C massecuite boiling and for pan drop may be overstated slightly in Figure 6.

TYPICAL MOTHER MOLASSES DRY SUBSTANCE DURING BOILINGS IN THE AUSTRALIAN THREE MASSECUIE FLOWScheme

Figure 7 shows the dry substance values at different mother molasses purities for saturation, for supersaturation at 1.10, 1.20 and 1.30, for SS_{Lim} and for the typical run-up condition using Eqn 7 for the situation where the head space pressure in the pan is controlled to -86 kPag throughout the strike. The data are for a RS/ash ratio of 1.0 and SC defined by correlation SC-1. Also shown on Figure 7 is the estimated mother molasses temperature at the run-up condition. It should be noted that all saturation and supersaturation data shown in Figure 7 correspond to the estimated boiling temperature of the mother molasses at their specific conditions for a head space pressure of -86 kPag. For example, for a mother molasses of 70 purity at the run-up condition the temperature is estimated at 65.5°C, whereas for a 70 purity molasses at saturation the boiling temperature is estimated to be 63.8°C, because of the lower boiling point elevation.

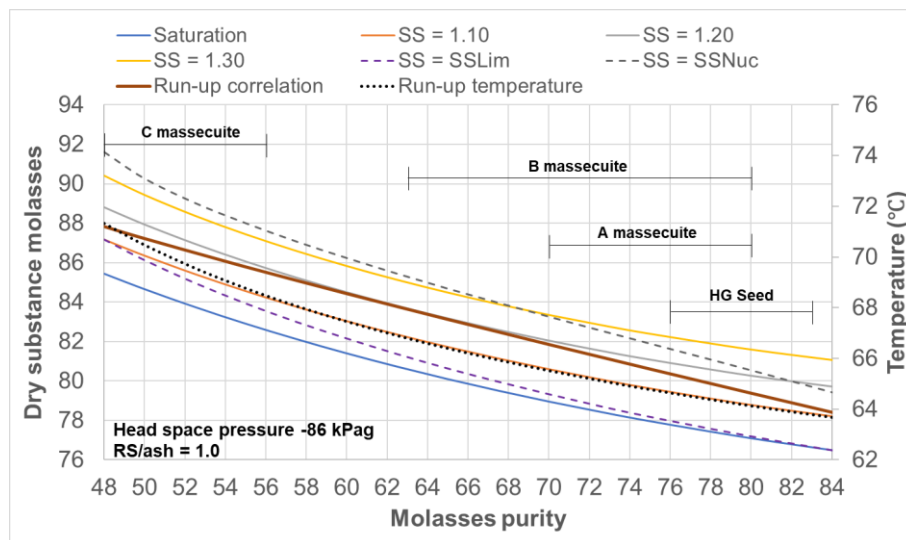


Figure 7. Process data for pan run-up at the predicted actual temperatures for head space pressure -86 kPag and RS/ash ratio 1.0.

Several observations are made from the data presented for run-up operations in Figure 7:

- As shown for the saturation data in Figure 3 and Figure 4, each strike of lower purity in the three massecuite scheme operates at a higher mother molasses dry substance for run-up of the strike. This behaviour is also evident for the run-up within an individual strike as the mother molasses purity decreases. For example, for a C massecuite strike with the mother molasses purity reducing from 56 to 50 during run-up, the mother molasses dry substance would increase from 85.5 to 87.2. Pan stage operators are familiar with this change in mother molasses condition;
- For the A and B massecuite boilings the typical supersaturation during run-up is 1.15 to 1.19. These supersaturation values are higher than values more typically quoted (say 1.15) but this is most likely because previous estimates ignored the value of the solubility coefficient in the determination of supersaturation (see BSES 2001, Method 23).
- For the high-grade boilings the difference in mother molasses dry substance between the run-up condition and SS_{Lim} (i.e., the range of operation for crystal growth) is reasonably consistent across the full range of

³ For C massecuites at pan drop with mother molasses purity 48, the mother molasses dry substance is 89.5, the boiling point elevation 18.1°C (at a head space pressure of -86 kPag) and the massecuite boiling temperature 74.5°C.

boiling conditions, being ~ 2.3 units. For C massecuite boilings this difference in dry substance steadily reduces from the start of the strike, being 2.3 units (for mother molasses 56 purity) to being 1.1 units at pan full (for mother molasses purity 50). This reduction in driving force is one of the factors contributing to the very low crystal growth rates experienced towards the end of C massecuite boilings.

Figure 8 shows a similar plot to Figure 7 but at the estimated pan drop conditions as given by Eqn 8. As in Figure 7, the saturation and supersaturation data shown in Figure 8 correspond to their specific conditions at a head space pressure of -86 kPag. Comparison of the boiling temperatures in Figure 7 and Figure 8 for a given mother molasses purity shows the increase in temperature owing to the higher dry substance at pan drop, compared with the run-up conditions. These same temperature values for run-up and pan drop were shown in Figure 6. As discussed previously, the pan drop temperature is substantially greater for C massecuite boilings than for the high purity boilings.

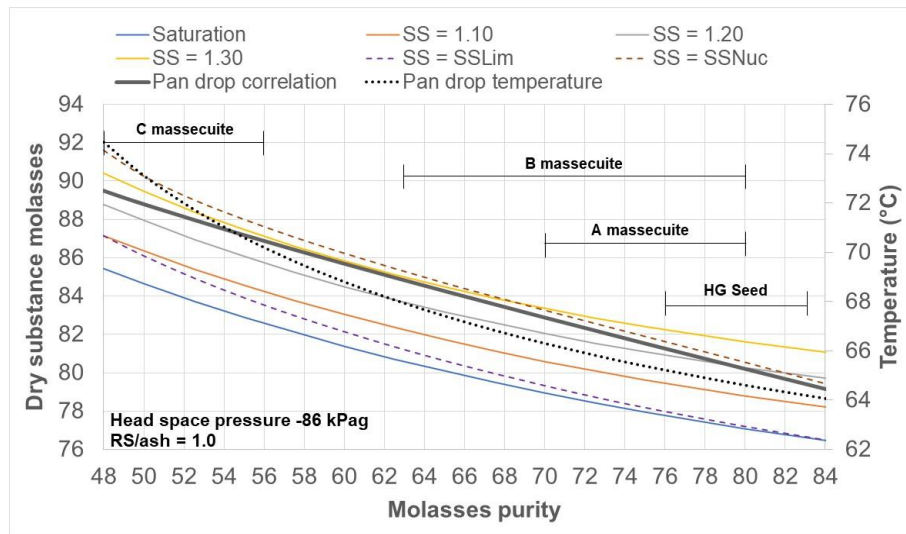


Figure 8. Process data for pan drop conditions at the predicted actual temperatures for head space pressure of - 86 kPag and RS/ash 1.0.

Observations from the pan drop data in Figure 8 are:

- For the typical pan drop conditions for A, B and C massecuites the supersaturation values are 1.26, 1.28 and 1.24, respectively. The differences in mother molasses dry substance at pan drop and those corresponding to the Critical Supersaturation are 0.4, 0.5 and 2.1 units, respectively;
- The lower supersaturation value for C massecuite at pan drop is a consequence of the large increase in temperature as heavy-up progresses to lower mother molasses purities. The main contributing factor is the increase in solubility of sucrose at higher I/W in C massecuite boilings.

The signal from a process refractometer could be adjusted to provide a reliable estimate of the mother molasses dry substance and hence used in control procedures to follow the profiles described in Eqn 7, Eqn 8, Figure 7 and Figure 8. For process refractometers it is important that the flow of material across the prism is fast enough to provide a useful control response. Miller and Skippen (1989) discussed the positioning of process refractometers in raw sugar pans and, while successful for a high grade massecuite, the slower circulation in a C seed duty produced a very slow response from the instrument. The measurement of mother molasses dry substance as a single process variable to regulate the massecuite composition is not sufficient as no indication of the crystal content is provided. Massecuite dry substance does provide a combined signal affected by mother molasses dry substance and crystal content and its measurement is the focus of Part 2 (Broadfoot and Fraga 2023a).

DISCUSSION AND CONCLUSIONS

The supersaturation of the mother molasses is an important control parameter during vacuum pan boiling and determines the rate of crystal growth, the time for a pan to boil-on till full, the exhaustion of the pan drop massecuite, and uniformity of the size distribution. Ideally, supersaturation would be able to be measured accurately and in real time. However, there is no transducer which provides a suitable measure of supersaturation as there are several process variables which influence its value. In addition, there are several factors that prevent reliable estimates of supersaturation from being made and used for pan control including:

- The solubility of sucrose varies during pan operations as changes occur in the concentration of impurities and the boiling temperature. In addition, sucrose solubility is affected by the composition of impurities, but these are expected to be relatively consistent, at least in the short term. Adding to the complexity, changes in the impurity concentration in the mother molasses affect the sucrose solubility differently in high and low purity massecuites; and
- The purity and dry substance of the mother molasses are required to calculate the sucrose/water ratio. Dry substance may be able to be measured using an on-line process refractometer, but there is no current method to measure the mother molasses purity in real time in factory pans.

Correlations for saturation conditions for pure sucrose, solubility coefficient for cane syrups and molasses, and boiling point elevation have been applied to determine supersaturation values for typical pan boiling run-up and pan drop conditions in high-grade seed massecuites and A, B and C massecuites. The calculated supersaturation values are higher than usually stated for the high purity boilings as, for previous methods of calculation, the value of solubility coefficient was often ignored (i.e., assumed to be 1). The supersaturation values for the C massecuite are lower than usually stated.

The solubility coefficient has been found to be affected in the following manner:

- Increasing solubility at higher temperatures;
- Reducing solubility for increasing impurity/water ratio in high grade seed and A and B massecuites;
- Increasing solubility for increasing impurity/water ratio in C massecuites; and
- Lower solubility for molasses having higher RS/ash ratio.

For normal processing conditions, the temperature of boiling was determined to have a much stronger effect on the dry substance of molasses at the saturation (and supersaturated) conditions than the variation in RS/ash ratio. The implications for practical pan boiling are that, for a mother molasses of a certain dry substance, the boiling temperature will determine the supersaturation more strongly than the influence of the expected variation in RS/ash ratio on the solubility coefficient. However, under abnormal cane supply conditions e.g., when crushing standover cane, large deviations in the RS/ash ratio from the more typical values (e.g., 1.0) may influence the supersaturation to a significant extent.

The consistency (viscosity at a shear rate of 1 s^{-1}) of the mother molasses at a given purity (and the consistency of the massecuite at a given crystal content) was closely correlated to the level of supersaturation and largely unaffected by the boiling temperature (and hence head space pressure). Consequently, the appropriate pan run-up and pan drop conditions are defined to a large extent by the circulation characteristics of the pan, as well as the need to avoid fine grain formation. This result is obviously well known to pan stage operators.

Correlations for the mother molasses dry substance as functions of mother molasses purity and temperature for the run-up and pan drop operations have been proposed. The run-up correlation represents strong growth rate conditions and the pan drop correlation aligns with the production of well exhausted, high-brix massecuites. It may be that the factory would elect to run-up at a slightly lower growth rate condition, and perhaps drop the massecuite at a slightly lower dry substance, depending on the operating circumstances of the factory and the circulation characteristics of individual pans.

Available laboratory-determined correlations for Critical Supersaturation were unsuitable for predicting the onset of nucleation in industrial pans when used in conjunction with supersaturation values determined for industrial run-up and pan drop conditions. A new correlation for Critical Supersaturation is proposed.

Overall, for high grade boilings, there is scope to make reasonable estimates of the expected operating range of supersaturation in industrial pans. Because the impurity concentration is low, variations in impurity composition are likely to have only a small effect on the saturation conditions. In addition, for high-grade boilings, as the mother molasses purity reduces (and I/W increases) the boiling temperature increases (when operating at a control set point of head space pressure) and these two counteracting effects tend to reduce the variation in

saturation concentration. However, for C massecuite boilings, the potential error in estimating the operating range of supersaturation is considerably larger. Firstly, the correlations for both the solubility coefficient and boiling point elevation are being applied beyond the range of experimental data used for developing the correlations. Secondly, as the mother molasses purity reduces and the impurity/water increases during run-up and heavy up, there are compounding effects of increasing sucrose solubility and increasing temperature.

A follow-on paper (Part 2) (Broadfoot and Fraga 2023a) applies the outcomes from this paper to define suitable operating ranges for massecuite dry substance for the various process operations undertaken on the pan stage.

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