REVIEW PAPER

A REVIEW OF SUCROSE SOLUBILITY IN IMPURE CANE SUGAR SOLUTIONS USED IN RAW SUGAR FACTORY PAN STATIONS

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Abstract

Crystallisation is a crucial step in the production of crystalline sucrose within raw sugar factories, and this is typically achieved in multiple stages across a factory's pan station. The majority of the crystallisation occurs in vacuum pans and it is widely accepted that the main driving force during crystallisation is the supersaturation of the mother liquor. Therefore, optimal control of the mother liquor supersaturation in vacuum pans is essential to achieve the highest crystallisation rates while minimising the risk of false grain formation. Hence, it is vital to understand both the solubility at saturation and the metastable zone supersaturation limit of the mother liquor being processed, which are strongly influenced by the nature and quantity of impurities. However, limited sucrose solubility data is available for South African raw syrups and molasses. Consequently, there is a large reliance on factory-scale trial-and-error solubility experimentation in vacuum pans and pan boiler experience to adapt pan boiling procedures to variations in impurity levels resulting from varying sugarcane quality throughout the crushing season, which is not ideal.

In 2024, the Sugar Milling Research Institute NPC (SMRI) upgraded its steam-heated 50 l pilot pan by equipping it with an online pan microscope (ITECA SOCADEI CrystObserver), which presented an opportunity to utilise this equipment for solubility measurements. This paper provides a comprehensive review of the available sucrose solubility data, outlining the common methods for measuring the saturation and metastable solubility limits of impure cane sugar solutions, and the potential application of the fully-equipped SMRI pilot pan as a tool for solubility assessment.

Keywords: Crystallisation, solubility, saturation, metastable limit, pan boiling, pilot pan

Introduction

Crystallisation is a necessary recovery and purification step in raw sugar factories for producing crystalline sucrose (or sugar) of the required quality. Crystallisation typically occurs in multiple steps in a raw sugar factory and involves the use of evaporative crystallisation (or pan boiling) and cooling crystallisation. The majority of the crystallisation is performed during pan boiling and this process generally utilises batch vacuum pans, or a combination of batch and continuous vacuum pans. The objectives of pan boiling include (1) recovering the maximum amount of crystalline sucrose efficiently, (2) production of massecuite crystals of the required size and a narrow size distribution for efficient separation in the centrifuge station and (3) production of sugar that meets the customer quality specifications. South African raw sugar factories typically employ the partial-remelt pan boiling scheme (see Figure 1) to produce very high pol (VHP) sugar.

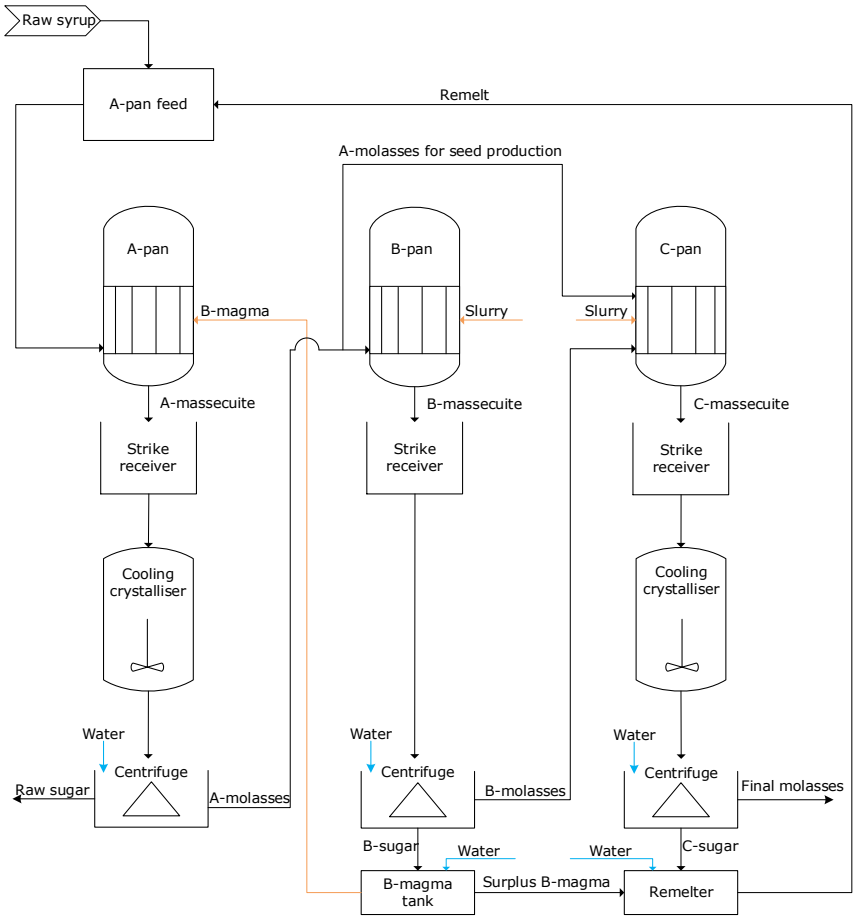


Figure 1. Process flow diagram of the partial-remelt boiling scheme (Rein, 2007)

In this boiling scheme, the A-pans are typically seeded with B-magma, while the B-pans and C-pans are seeded with ball-milled slurry (i.e. finely-milled refined sugar suspended in alcohol). Pan boilers strive to achieve true seeding (i.e. only the seed crystals grow into product crystals and there is no crystal dissolution nor spontaneous crystal formation) during pan boiling as this feeds into Objective (2) of the process.

Good pan station performance largely depends on controlling the mother liquor supersaturation which is the main driving force during pan boiling. Therefore, objectives (1) and (2) of pan boiling ideally require a sound knowledge of the solubility of sucrose in impure cane sugar solutions. This ensures that pan boiling proceeds at the fastest rate while reducing the risk of forming new crystals (or false grain). There is a large variation in the solubility data for impure cane sugar solutions (Rein, 2007) and very limited data for South African cane sugar process streams (i.e. raw syrup, A-molasses and B-molasses) is available. Therefore, pan boilers have limited information with which to adjust the concentration of the mother liquor. There is therefore a large reliance on trial and error and pan boiler experience to adjust pan boiling control to accommodate for cane quality changes throughout the crushing season. Consequently, there is a risk of long boiling times, production of poor quality massecuite and increased usage of energy that adversely affects factory throughput, boiling house recovery and energy efficiency, respectively. There is certainly a need to generate reliable solubility data for South African impure cane sugar solutions as this may assist with optimisation and automation of the pan boiling process, and the upskilling of pan boilers, especially when there is poor succession planning between pan boilers.

The Sugar Milling Research Institute NPC (SMRI) owns a fully-instrumented 50 l pilot pan capable of simulating industrial pan boiling behaviour (Love and Walthew, 2002 and Rahiman *et al*., 2023). The pan is equipped with an ITECA online pan microscope that may potentially be used for generating solubility data similar to the visual technique reported by Chen (1985) and Honig (1959). The objective of this paper is to critically review the available solubility literature for impure cane sugar solutions and the common methods used to measure solubility. This paper also discusses the assessment of the technical viability of using the SMRI 50-l pilot pan to generate solubility data.

Available solubility literature for cane sugar solutions

Understanding how the solubility of sucrose in aqueous solutions changes with temperature and dissolved impurities is the foundation of sucrose crystallisation. Raw sugar factory boilings are typically performed between 60 and 70°C (Penklis and Wright, 1963 and Rein, 2007) and the boiling temperature is typically reduced from the A-pans to C-pans to slow down the undesirable Maillard reaction. Rein (2007) states that the Maillard reaction thrives under high dissolved solids, high temperature and low purity conditions, and therefore recommends boiling temperatures of <63°C particularly for the C-pans.

Solubility of pure sucrose solutions

Sucrose is highly soluble in water as about two thirds by mass of sucrose can dissolve in onethird by mass of water at room temperature (25°C – Anon, 1985). The solubility of pure sucrose in aqueous solutions primarily depends on the temperature of the solution. Mathlouthi and Cedus (1995) provide a comprehensive review of the solubility of pure sucrose solutions showing that the solubility of sucrose increases with temperature (i.e. more sucrose can dissolve in a unit mass of water at higher temperatures). A saturated aqueous sucrose solution is a solution that is in a state of equilibrium with its undissolved solid sucrose phase, and as such, it contains the maximum amount of dissolved sucrose at a given temperature.

The sucrose solubility review by Mathlouthi and Cedus (1995) stated that the Charles (1960) and Vavrinecz (1962) empirical solubility correlations for a pure sucrose solution were recommended by the International Commission for Uniform Methods of Sugar Analysis (ICUMSA – Heitz, 1974), which is in agreement with Rein (2007). The Charles (1960) correlation (Equation 1) is applicable for a temperature range from 0 to 86°C whereas the temperature range of the Vavrinecz correlation (Equation 2) is from -13 to 100°C. Rein (2007) states that the Charles (1960) correlation may be used up to a temperature of 90°C, and this is in agreement with the South African Sugar Technologists' Association (SASTA) manual (Anon, 1985). Equations 1 and 2 assume that the dissolved solids are equivalent to the refractometric brix (B) of the pure solution. Both the SASTA manual and Rein (2007) recommend the use of Equation 1.

$$B_{sat} = 64.397 + 0.07251T + 2.0569 \times 10^{-3}T^2 - 9.035 \times 10^{-6}T^3 \quad \text{..... Equation 1}$$

$$B_{sat} = 64.447 + 0.08222T + 1.6169 \times 10^{-3}T^2 - 1.558 \times 10^{-6}T^3 - 4.63 \times 10^{-8}T^4 \quad \text{..... Equation 2}$$

Where B_{sat} is the saturation brix of the solution (°Bx) at a given temperature, T (°C).

Supersaturation and supersaturation coefficient

Crystallisation of sucrose can only be achieved in a supersaturated sucrose solution, which is a solution that contains more dissolved sucrose than at its equilibrium state at the same temperature. Supersaturated solutions in sugar factories may be produced by increasing the concentration of sucrose at a given temperature through evaporation of water (via pan boiling) or by cooling a saturated solution (via cooling crystallisation). Supersaturation is the main

driving force in crystallisation and the extent of supersaturation is referred to as the supersaturation coefficient (SSC). The SSC of a sucrose solution may be determined by using Equation 3.

$$SSC = \frac{\frac{S}{W}}{\left(\frac{S}{W}\right)_{sat}} \quad \text{..... Equation 3}$$

Where S is the mass percent of sucrose (%), W is the mass percent of water (%) and the subscript 'sat' refers to saturation (i.e. the S/W ratio at saturation at a specific temperature). Hugot (1960) proposed the following equation to determine the SSC of a solution at a given purity and temperature.

$$SSC = \frac{\frac{B}{100-B}}{\frac{B_{sat}}{100-B_{sat}}} \quad \text{..... Equation 4}$$

Equation 4 is a convenient form as it utilises brix and may be used with Equation 1 to determine the SSC of a pure sucrose solution.

Figure 2 was constructed using Equations 1 and 4, and shows the three zones of supersaturation (Chen, 1985, van der Poel *et al*., 1998 and Love *et al*., 2016) that are described as follows:

- Metastable zone (1.0<SSC<1.2) – only crystal growth occurs in this zone.
- Intermediate zone (1.0<SSC<1.3) – new crystals form in the presence of existing crystals.
- Labile zone (SSC>1.3) – new crystals form spontaneously in this zone.

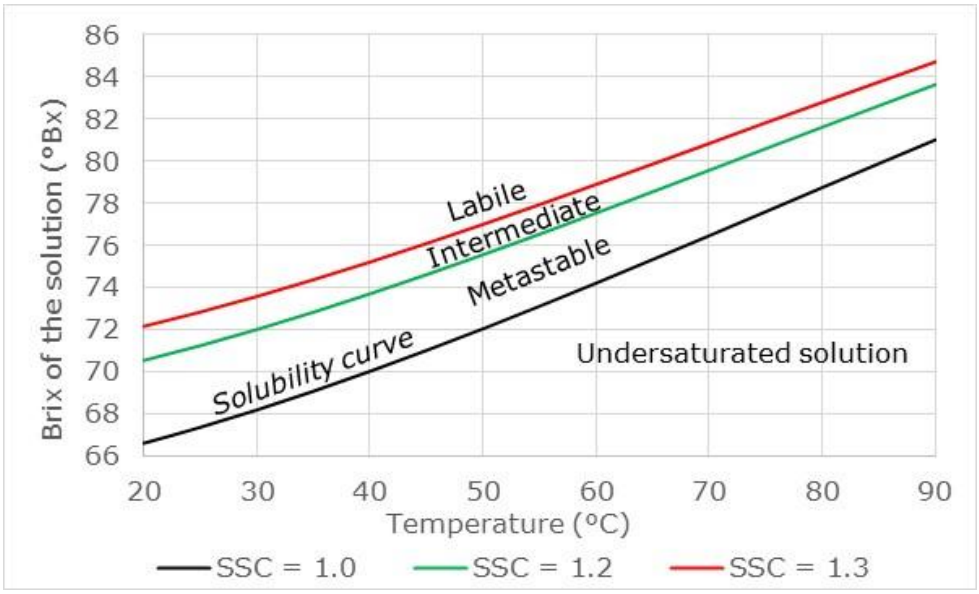


Figure 2. Solubility and zones of supersaturation for a pure sucrose solution

It is desirable for pan boilers to operate at the upper region of the metastable zone so that the crystallisation rate is maximised without the risk of false grain formation.

Solubility of sucrose in impure cane sugar solutions

The non-sucrose content of cane sugar syrups and molasses is the difference between the total dissolved solids and the sucrose contents. Non-sucrose alters the solubility of sucrose in water, and the effect of non-sucrose depends on the type and quantity that is present (van der Poel *et al*., 1998 and Rein, 2007). The effects of non-sucrose are complicated and the type of non-sucrose may be different in various regions of South Africa and may change with sugarcane varieties. Therefore, having a good understanding of the effect of non-sucrose on raw sugar factory syrups and molasses, particularly in South Africa, is of great practical importance during crystallisation.

Mathlouthi and Cedus (1995) and van der Poel *et al*. (1998) provide good reviews of the key aspects of the solubility of sucrose in impure beet and cane sugar solutions. According to Mathlouthi and Cedus (1995), the non-sucrose in cane sugar solutions may affect sucrose solubility by either binding water and/or sucrose molecules. Rein (2007) states that the reducing sugars (i.e. fructose and glucose) typically decrease the solubility of sucrose in water and van der Poel *et al*. (1998) states that Vavrinecz (1978/79) shows that the effect of reducing sugars increases with decreasing temperature. The ions present in cane juice, specifically, the potassium, sodium, calcium and magnesium cations, increase the solubility of sucrose. There are differing opinions on which cation is the most melassigenic: van der Poel *et al*. (1998) reports on the experimental data from Vavrinecz (1978/79) and shows the melassigenic effect of the following cations in descending order:

$$K^+ > Na^+ > Li^+ > Ca^{2+} > Mg^{2+}$$

Sahadeo (1998) showed the melassigenic effect of the following cations in descending order using South African raw sugar factory molasses:

$$Na^+ > Ca^{2+} \text{ and } Mg^{2+} > K^+$$

Interestingly, sodium was found to be the most melassigenic cation on a mg/kg dry solids in molasses basis; however, potassium is expected to create more molasses as it is the most abundant in molasses (Sahadeo, 1998). The cations (and anions) are typically measured collectively as conductivity ash in raw sugar factories. Generally, the reducing sugars and ash are grouped as the reducing sugar to ash (RS/Ash) ratio when considering their impact on solubility (Rein, 2007). Although it may be considered convenient to use the RS/Ash ratio given the limited analytical capability of sugar factories for analysing ions, the ash composition may change from region to region and/or season to season, and therefore it may be appropriate to focus on specific ash components, particularly if the analysis can be done rapidly.

The effect of non-sucrose on sucrose solubility is typically expressed as the Solubility Coefficient (SC), as defined by Equation 5.

$$SC = \frac{\left(\frac{S}{W}\right)_{sat,impure}}{\left(\frac{S}{W}\right)_{sat,pure}} \quad \text{..... Equation 5}$$

It is clear from Equation 5 that the sucrose-to-water ratio of an impure solution at saturation may be determined if the solubility coefficient and the sucrose-to-water ratio of a pure solution at the corresponding temperature are known. The value of SC strongly depends on the Non-Sucrose to Water (NS/W) ratio and is defined mathematically by Lionnet and Rein (1980) as follows:

$$\frac{NS}{W} = \frac{DS\left(1-\frac{P}{100}\right)}{100-DS} \quad \text{..... Equation 6}$$

Where DS is the total dissolved solids (%) and P is the true purity (%). Lionnet and Rein (1980) showed that the solubility coefficient for C-massecuite crystallisation was strongly-dependent on the NS/W and RS/Ash ratios, and a regression analysis revealed that the two parameters were significant at a 95% confidence interval. Other sources of literature (Mathlouthi and Cedus, 1995, van der Poel *et al*., 1998 and Rein, 2007) mainly show the dependence of SC on the NS/W ratio and the standard form (Rein, 2007 and Rosza, 2000) of the equation that relates these two parameters is as follows:

$$SC = m \times (NS/W) + b + (1-b) \times e^{-c\times\left(\frac{NS}{W}\right)} \quad \text{..... Equation 7}$$

Where m, b and c are constants. The constant 'm' is at times referred to as 'a' in earlier literature (Mathlouthi and Cedus, 1995 and van der Poel *et al*., 1998); however, m was chosen as this symbol as it is typically used to denote the gradient of a straight line. It is clear from Equation 7 that the SC vs NS/W ratio curve is made up of a straight line and an exponential term (see Figure 3). Figure 3 was constructed using the recommended SC constants from Rein (2007) and a RS/Ash ratio of 0.97 (the South African industry average value for the 2023 season). Furthermore, note that an increasing NS/W ratio corresponds to a decreasing purity, starting at 0 (100% purity) and increasing to 6 (C-boiling purity range). Therefore, using the SC vs purity trend reported by Rosza (2000), Figure 3 shows the approximate ranges for the various types of boilings in sugar factories.

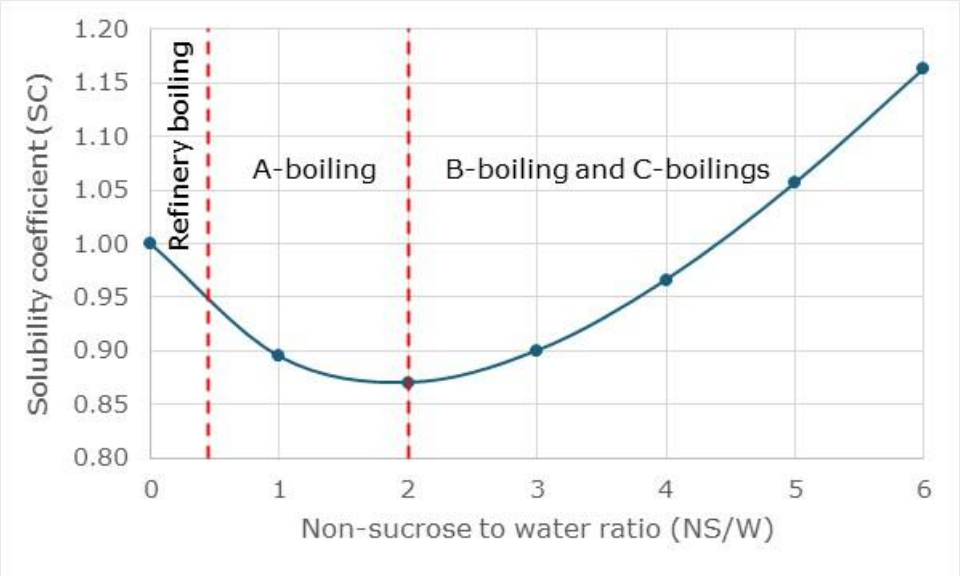


Figure 3. SC versus NS/W ratio for cane sugar solutions

Generally, the shape of the SC vs NS/W ratio curve is similar to Figure 3 in most of the cited literature (Mathlouthi and Cedus, 1995, van der Poel *et al*., 1998 and Rein, 2007). The non-sucrose tends to reduce the solubility of sucrose at low NS/W ratios (<2) and increases the solubility of sucrose at high ratios (>3). However, Rosza (2000) reports a deviation from the general SC versus NS/W curve using the comprehensive Thieme solubility data for cane sugar solutions (Hugot, 1960). Rosza (2000) reports that the cane sugar solutions that were used by Thieme behaved differently from beet solutions with a general linear decline in the SC from a NS/W ratio of zero. The RS/Ash ratio seems to have a profound effect on the SC when considering the SC correlation proposed by Rein (2007), and it is possible that Thieme's data

was obtained at high RS/Ash ratios (>2) as Chen (1985) implicitly reported a similar SC vs NS/W graph (at a RS/Ash ratio of 2.42) to that reported by Rosza (2000).

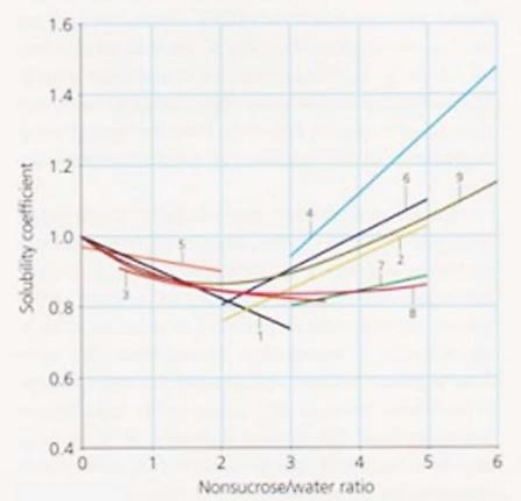
There has been some contention in literature about the impact of temperature on the solubility coefficient. Van der Poel *et al*. (1998) reports that Wiklund (1946) discovered that the solubility coefficient was independent of temperature and there seems to be a consensus in literature about the validity of this discovery (Vavrinecz, 1978/79, Lionnet and Rein, 1980, Chen, 1985 and Mathlouthi and Cedus, 1995). However, Steindl *et al*. (2001) report that the SC constants (m, b and c) are affected by the temperature of the cane sugar solution. Love (2002) conducted solubility experiments that indicated minimal variation in the solubility coefficient of cane syrups within a temperature range of 60 to 70°C, up to a NS/W ratio of approximately 2.5. However, data for NS/W values exceeding 2.5 suggest that the solubility coefficient increases with rising temperature. It remains unclear whether the observed differences at higher NS/W ratios fell within the method's uncertainty as the relative standard deviation for the data points was not provided. Table 1 is a summary of the m, b and c constants from a range of authors.

Table 1. Summary of m, b and c solubility coefficient constants

Reference	**m or a**	**b**	**c**	**NS/W range**	**T (°C) range**	**RS/Ash range**
*van der Poel *et al*., (1998) – Grut's data	0.178	0.820	2.1	0.3 to 3.0	20 to 90	n/a
*Mathlouthi and Cedus (1995) – Vavrinecz average data	0.292	0.691	1.80	0.2 to 7.0	20 to 98	n/a
Rosza (2000) – based on the corrected and extended Thieme's data	-0.063	0.982	-2.1	0 to 2.6	70 to 80	n/a
Steindl *et al*. (2001)	0.011+ 0.00046T	0.670 + 0.0021T - 0.007(RS/Ash)	0.540 + 0.0049T	0 to 5.0	40 to 60	0.5 to 1.0
**Rein (2007)	0.14	0.45 – 0.2(RS/Ash)	0.4	0.5 to 7.3	34 to 65	0.6 to 1.7

*The solubility coefficients from these authors are applicable to the beet sugar factory products.
**The NS/W, temperature and RS/Ash ranges were not explicitly mentioned by Rein (2007), the ranges were obtained by considering all the references quoted by the author (see Figure 4).

Figure 4 has been extracted from Rein (2007) and shows the variability of solubility coefficient data in literature. Furthermore, it is uncertain whether the solubility data presented is applicable to raw syrup and molasses currently being processed in South African raw sugar factories. Therefore, given the above-mentioned concerns with the existing solubility data, there is certainly a need to perform solubility tests to confirm the applicability of the constants detailed in Table 1 or to propose a revised set of constants.



Correlations proposed by different investigators for the solubility coefficient in cane sugar solutions (where the correlation equations require it, temperature is specified as 50 °C and $q_{MS/A}$ or $q_{NS/A}$ = 1.0).
1 *Batterham* et al. (1974); 2 *Maudarbocus* and *White* (1978); 3 *Broadfoot* and *Steindl* (1980); 4 *Lionnet* and *Rein* (1980); 5 *Rouillard* (1980); 6 *Rouillard* (1980); 7 *Broadfoot* (1984); 8 *Steindl* et al. (2001); 9 Equation (18.5)

Figure 4. Summary of SC vs NS/W curves (Rein, 2007)

The metastable supersaturation limit of impure cane sugar solutions

During pan boiling, it is imperative that there is a good understanding of the metastable zone's upper supersaturation limit so that pan boilers can avoid false grain formation during crystallisation. The absence of false grain is required if the boiling is expected to approach full seeding and the size distribution of the crystals is to be kept at an acceptable level [i.e. a sieve analysis size coefficient of variation <35% (Rahiman *et al*., 2023)]. Furthermore, it is desirable to maximise the rate of crystallisation without the risk of false grain formation, and therefore, operating near the upper level of the metastable region is necessary to ensure that pan throughput is kept at an optimum.

The metastable limit for pure sucrose solutions is widely accepted as 1.20 SSC (Chen, 1985, van der Poel *et al*., 1998, Pan boiling, 2015 and Rein, 2007). However, the limit of 1.20 SSC may not be applicable to impure cane sugar solutions. Hugot (1960) and Broadfoot and Wright (1972) report that the metastable limit increases as the purity of the cane sugar solution decreases. Broadfoot and Wright (1972) performed experiments using a laboratory vacuum pan to determine the metastable limit of cane syrup over a true purity range of 65 to 100%, a temperature range of 50 to 70°C, a crystal content (CC) range of 0.3 to 20% and at different rates of syrup concentration (range not specified). It was found that the true purity and CC showed a statistically significant effect on the secondary nucleation point, and the relationship was described by Equation 8.

$$\mathrm{SSC_m} = 2.864 - 3.516\left(\frac{\mathrm{S}}{\mathrm{S+NS}}\right) + 1.81\left(\frac{\mathrm{S}}{\mathrm{S+NS}}\right)^2 - 0.00177\mathrm{CC} \quad \text{..... Equation 8}$$

Where SSC_m refers to the metastable supersaturation limit and the term S/(S+NS) is essentially the true purity expressed as a fraction. Equation 8 suggests that the purity of the mother liquor is the major variable that influences the supersaturation limit. However, Broadfoot and Wright (1972) did mention that a standard error of ±0.036 SSC was obtained during this test due to the difficulty in reproducing the point of nucleation.

If slurry-seeding is considered, the crystal surface area after injection of the slurry crystals is negligible, and therefore the CC content term in Equation 8 may be omitted. Table 2 provides a summary of the metastable zone upper limit data obtained from Hugot (1960) and that obtained via Equation 8 (assuming negligible CC). It was assumed that the purity reported by Hugot (1960) was the true purity of the cane sugar solution.

Table 2. Summary of metastable zone upper limit data

True purity (%)	Hugot (1960)	Broadfoot and Wright (1972)
60	1.55	1.41
70	1.30	1.29
80	1.25	1.21

The metastable zone limits shown in Table 2 are substantially different, particularly for mother liquor purities of 60% and 80%. Broadfoot and Wright (1972) cited Davies and Yearwood (1944) from the data presented by Honig (1959), and state that the metastable limits were found to be 1.20 (determined by extrapolation) and 1.30 for pure sucrose solutions and 70% purity cane syrups, respectively. These results are close to the 70% purity metastable limit results detailed in Table 2; however, the results from Broadfoot and Wright (1972) implicitly suggest that the metastable limit for a pure sucrose solution is <1.20 (specifically 1.16 SSC). Clearly, there is large variation in the available metastable limit data for impure cane sugar solutions, and therefore, there is scope for exploring the metastable limit for South African cane syrups and molasses.

Methods of measuring the solubility of sucrose in impure cane sugar solutions

This section details some of the common analytical and optical methods described in literature to determine the saturation and metastable limit data for impure sugar solutions.

Determination of the solubility of syrups and molasses

The Polish test

A rapid method used for measuring the solubility of sucrose in impure solutions, particularly in the beet sugar industry, is the Wagnerowski method (or the Polish test) and this method is detailed by van der Poel *et al.* (1998). Samples of syrups or molasses are typically diluted or concentrated (under vacuum) to give NS/W ratios in the range of 1.6 to 3.0. After adjustment of the NS/W ratio, the samples are added to a vessel containing a mechanical stirrer and a predetermined amount of coarse sugar is added to the vessel and allowed to mix at a constant temperature for at least three hours (at this point the mother liquor is presumed to be saturated). McGillivray *et al*. (2003) used a temperature of 80°C and allowed the mixture to saturate for 24 h. It is expected that the minimum time to reach saturation would depend on the saturation temperature and the degree of mixing in the saturation vessel, and therefore the minimum time to reach saturation should be determined experimentally. The coarse sugar contains 8000 crystals in 1 g of sugar and this corresponds to crystals that have an average sieve aperture size of about 1.00 mm (Bubnik and Kadlec, 1992). The NS/W ratio of the saturated solution is not expected to change assuming that the coarse refined sugar used to saturate the mother liquor has negligible moisture content. Once the mother liquor is saturated, the mixture is filtered through a glass filter and the sucrose content and dry substance are determined. These analytes may then be used to determine the true purity and the NS/W ratio. Adequate data points are required at different NS/W ratios to assist with determining the m, b and c constants. The Polish test relies on the dissolution of sugar in an undersaturated solution to reach saturation as this occurs faster than the crystallisation of sucrose from a supersaturated solution to reach saturation. Since the solubility coefficient is independent of

temperature, which is the basis of the Polish test, equations 1, 5 and 7 may be used to determine the solubility of an impure solution at the desired temperature range.

Adaptation of the Polish test for the sugarcane industry

Love (2002) adapted the Polish test to determine the solubility coefficients of cane sugar factory molasses at various NS/W ratios. He showed the time benefit of approaching equilibrium via dissolution as opposed to crystallisation. The rate of dissolution is substantially faster than the rate of crystallisation as observed in Figure 5 (Wright, 1983). The abbreviation I/W refers to the impurity-to-water ratio which is the same as the NS/W ratio. It is clear from Figure 5 that at the pan boiling temperatures typically experienced in a raw sugar factory, the rate of dissolution is faster than the rate of crystallisation for the same level of oversaturation (defined as SSC-1), particularly as the purity of the mother liquor decreases (a negative oversaturation value implies that the solution in undersaturated). Interestingly, Figure 5 also shows that at NS/W ratios ≥2, the rate of crystallisation is almost independent of oversaturation and is close to the zero mm/h crystallisation velocity line (i.e. the red dashed line). This suggests that it may take a long while before the solution achieves saturation by crystallisation. Love's (2002) review of sucrose solubility reinforces this observation as the conclusions from the saturation tests reported by Charles (1960) for a pure sucrose solution at approximately 15°C revealed that reaching saturation by dissolution took approximately 45 min, whereas reaching saturation by crystallisation took about 75 h.

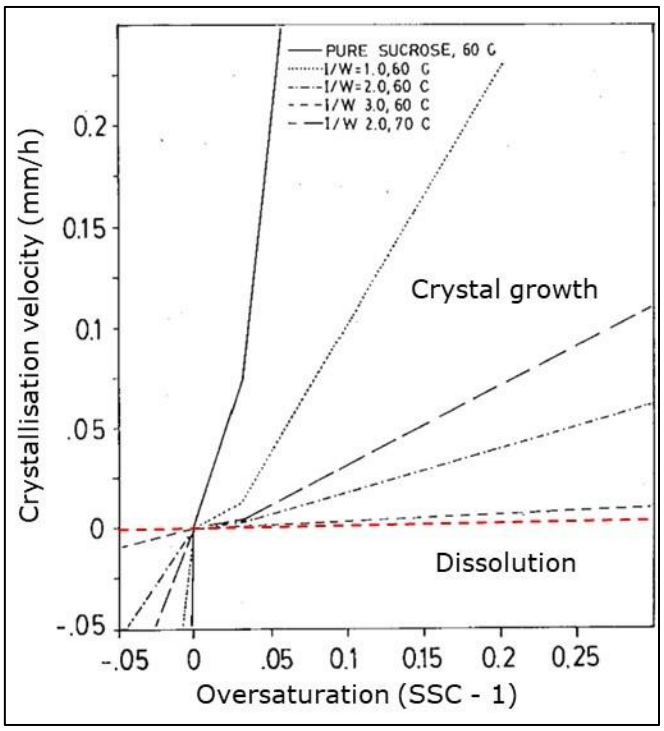


Figure 5. Dissolution and crystallisation rate of cane syrups at various NS/W ratios temperatures (Wright, 1983)

Love acknowledged that the temperature at which the Polish test is typically performed (80°C) may not be suitable for cane syrups and molasses as the non-sucrose components (particularly the reducing sugars) are prone to thermal degradation, especially via the Maillard reaction (Rein, 2007). Therefore, saturation tests would need to be conducted in the 60 to 70°C range that is typically used in raw sugar factories.

Love (2002) used the experimental set-up shown in Figure 6 to perform the saturation experiments. Six brass-jacketed pots, each with their own paddle stirrer operating at 62 rpm,

were connected to a temperature-controlled water bath to maintain the temperature of the syrup or molasses at the desired level. The pot design is the same as that used for the boil-down test performed at the SMRI. A summary of the procedure detailed by Love (2002) is provided in Appendix A.

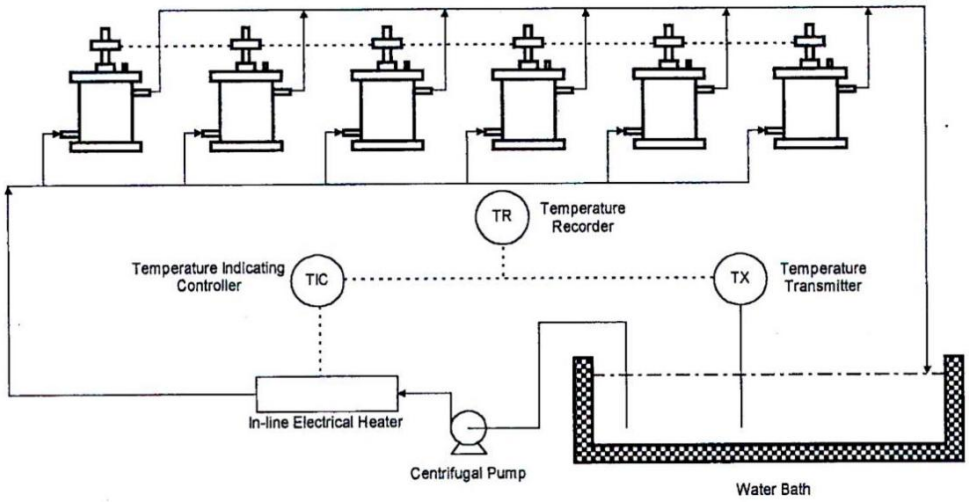


Figure 6. Six-pot saturation set-up used by Love (2002)

Love (2002) recommended that changes to the non-sucrose composition be assessed in future solubility work as it is undesirable to change the non-sucrose matrix during the saturation tests.

Solubility methods described by Honig (1959)

Honig (1959) discussed several methods to determine the solubility of sucrose in impure cane sugar solutions. The two methods that have fundamentally different approaches for determining the saturation limit are summarised below:

- *Kelly's (1954) method:* This method involves the saturation of pure or impure sugar solutions by the dissolution of crystalline sucrose. This method is similar to the Polish test; however, it typically involves the use of tightly-sealed tubes into which the mixture of crystals and mother liquor is poured and thereafter held in a constant temperature water bath. The water bath has to be equipped with a mechanism to rotate the tubes at a speed of at least 4 rpm. Approximately 20% more crystals than what is required to saturate the mother liquor should be added and the crystals should be in the size range of 0.8 to 1.0 mm. The method involves a saturation time of 14 days; however, this may be shortened if mixing conditions are improved. Furthermore, Honig (1960) reported that saturation temperature did affect the saturation time and it is expected to decrease as the saturation temperature increases. It is preferable to place a glass rod in the tubes containing viscous solutions to assist with mixing. After saturation, samples are allowed to stand in the constant temperature water bath for at least 24 h to allow the crystals to settle and thereafter the supernatant is decanted for analysis. Alternatively, pressure filtration may be used especially in the case of very viscous mixtures. Saturation by dissolution via Kelly's method may potentially be achieved using the crystallisation water bath system as reported by Rahiman and Mbuthuma (2023).

- *Harman's (1932) method*: This method is also referred to as the saturascope technique and employs microscopic examination of sugar crystals in molasses. The saturation cell is either jacketed or electrically-heated to provide good temperature control. A

sample of molasses of known composition is placed on a cover glass and the temperature of the molasses and saturation cell is such that the molasses is supersaturated. Finely-milled sugar is added to the molasses and a suitable microscope objective is used to observe the edge of the crystals as the temperature is increased at a rate of 1°C per minute. The temperature at which the edges of the crystals start to erode is recorded as the saturation temperature. Typically, the test is repeated at a slower rate of temperature increase (i.e. 0.33°C per minute) starting about 5°C away from the initially recorded saturation temperature to assist with accurate determination of the temperature. This technique is typically suited for syrup purities of ≤60% as the rate of crystallisation is slow and therefore the finelymilled seed crystals are not expected to significantly affect the mother liquor composition. by Honig (1960) also reported a variation of the saturascope technique by Taylor (1947) where a minimum of two large crystals (0.5 to 0.25 mm in size) were used to check erosion of the crystal edge and carefully calibrated thermocouples were used to increase the temperature at a rate of 0.02°C per minute. A further variation of the Harman method, known as the photometric saturation temperature method, is reported separately below as this method was not detailed by Honig (1959).

The photometric saturation temperature method

Wright (1978) detailed a variation of the Harman method in an attempt to reduce operator-dependency in determining the point at which crystal edges start to dissolve. This method (i.e. the photometric method) was used for determining the saturation temperature of cane sugar syrups and molasses across a wide purity range (45 to 99% true purity). The author noted that the Harman method was advantageous over the equilibrium test methods (such as the Polish test and the Kelly's method) as a small quantity of sample was required (approximately five grams of syrup or molasses) and that it could be easily incorporated as part of process control in sugar factories; however, the technique's major drawback was its operator-dependency. The photometric method detailed by Wright (1978) relies on the change in light transmission through a sample when dissolution occurs to assist with determining the saturation temperature, instead of relying on the operator's eye to determine the point when the crystal edges begin to round. The apparatus used to perform the photometric saturation test primarily comprised of two 13 mm (diameter) slide cover slips that were separated by a 13 mm metal washer permanently attached to one coverslip, a Gallenkamp MF 350 microscope hot stage (i.e. a temperature-controlled microscope stage) that controlled the temperature of the sample sandwiched between the two cover slips, a steady light source that provided light beneath the sample and a light-sensitive sensor (such as a photovoltaic cell or a phototransistor) that converted the transmitted light to an electrical signal that was presented by an x-y recording system. The apparatus was subsequently modified so that it was more compact than its precursor, and the light sensor electronics were optimised so that there was automatic regulation of the light source intensity. Appendix B provides details on the equipment and procedure used in the photometric method.

Initially there was a gradual rise in the recorder output voltage as the sub-sample temperature increased and this was followed by a steep decline in the voltage once the temperature exceeded the saturation point. According to Wright (1980), given the circuitry used in the equipment (see Appendix B - Figure B2), the steep fall in the voltage can be explained by the dissolution of the fine crystals whilst the gradual rise in the recorder output voltage was suggested to be due to the slight pre-crystallisation and/or tendency of the light transmission of the molasses sub-sample to decrease with a rise in temperature. Further investigation is required to understand exactly why the light transmission through the sample decreases as the temperature increases towards the saturation temperature point.

According to Wright (1978), initial scans were typically done at about 5 to 10°C per minute followed by repeat scans performed at 1 to 2°C per minute for high purity solutions (90 to 99%

true purity), and 0.5 to 1°C per minute for low purity solutions (45 to 58% true purity). Wright (1978) equilibrated molasses samples using excess sugar in a constant temperature water bath and then performed the photometric analysis of the sample to determine the saturation temperature. The saturation temperature results reported by Wright (1980) were in close agreement with the equilibration bath temperatures: temperature differences of 0.50 to 0.65°C for a 99% pure sucrose solution at 60.0 and 51.2°C equilibrium bath temperatures were achieved, respectively. The standard deviation of the temperatures from the repeat photometric scans ranged from 0.1°C to 0.3°C. These results are promising; however, the work done by the author seems to implicitly suggest that high temperature saturation tests (>50°C) require saturation of the samples using excess sugar in a constant temperature water bath before the photometric measurement and therefore adds to the analysis time as per the procedure mentioned above.

Qin and Wright (1992) further developed the photometric technique by using an infrared light source instead of an LED light source. The authors provided a detailed assessment of some of the factors that affected the accuracy of the saturation temperature measurement such as enhanced solubility of the sample due to the size of the seed crystals, pre-crystallisation of the sample, temperature lags and random errors that may arise from the analogue to digital conversion of the light transmission and temperature signals. It was concluded that the use of good equipment and technique may result in an uncertainty in the supersaturation measurement of as low as ±0.0015 SSC. Inaccuracies due to the stability of the infrared light source and photodetector, the presence of air bubbles and the effect of the seed dispersant were not quantified but were acknowledged. Furthermore, the authors considered the use of the photometric method as an online method to determine the saturation conditions during batch pan boiling; however, careful attention would need to be given to the factors affecting the accuracy of the measurement, the operating pressure of the sample being measured and the possibility of introducing fines into a vacuum pan.

Determination of the metastable zone limits of impure cane sugar solutions

A study detailing the method of determining the metastable limits of Australian syrup and molasses was reported by Penklis and Wright (1963). Raw syrups and molasses (apparent purity range of 55 to 80%) were used in a stirred laboratory vacuum pan and boiled at temperatures of 60 and 71°C. Raw sugar was added to the syrup or molasses of a certain purity such that the crystal content ranged from 2 to 35%. The evaporation rate was controlled above the saturation point such that the SSC increased at 0.004 per minute. Samples were taken using the pan's proof stick until a high concentration of fine grain was observed. These samples were centrifuged to determine the crystal content and obtain the mother liquor purity. Once a high concentration of fine grain was visible, the temperature was recorded and the mother liquor brix was measured followed by the determination of the supersaturation (i.e. using Equation 4). It is important to note that dry solids is a true indication of total dissolved solids and is generally equal to refractometric brix for pure solutions. However, according to Honig (1959), the dry solids of molasses that has a gravity purity of 40% is typically to 2 to 4 units lower than brix. Therefore, when using Equation 4, it is important to understand the dry solids and brix relationship, particularly for the mother liquor purities experienced in the B-station and C-station of a raw sugar factory.

Penklis and Wright (1963) discovered that the metastable zone limit increased steeply as the molasses purity decreased, and the oversaturation approximately doubled as the apparent purity decreased from 80% to 60%. Furthermore, there was not much alteration in the metastable zone limit over a crystal content range of 10 to 30%.

Factory-scale solubility and metastable width tests

Chen (1985) reported on the determination of the saturation and metastable limits in a full-scale pan. To determine the saturation point for raw syrup or molasses of a certain purity, coarse crystals that have sharp edges are added to a proof stick and exposed to the syrup or molasses in the pan during the concentration phase. As soon the crystal edge ceases to become round and begins to sharpen, saturation has been reached.

The metastable limit is obtained by concentrating massecuite to the point where new crystals begin to form. The massecuite is sampled and filtered, and the Nutsch molasses is analysed for dissolved solids and sucrose content. Pan boilers cannot afford to spend large amounts of time determining the saturation and metastable points as there are throughput and/or energy targets to be met. Instead, pan boilers rely on experience and existing solubility data to guide them during crystallisation. Therefore, there is certainly a benefit in determining and making available reliable solubility data that applies to South African syrups and molasses.

Potential use of the SMRI steam-heated pilot pan as a solubility measurement tool

The SMRI has a fully-instrumented 50 l steam-heated vacuum pan (Figure 7) capable of simulating industrial pan boiling (Rahiman *et al.*, 2023). The pilot pan is equipped with an online pan microscope (the ITECA SOCADEI CrystObserver) that is capable of detecting crystals as small as four microns (i.e. the size of ball-milled slurry crystals) and provides real time crystal growth and product quality data (i.e. the crystal mean aperture, size coefficient of variation and % fines in the massecuite). In addition to the real time crystal size results, the pan microscope system also records a video of the boiling which may allow the user to easily troubleshoot problems and/or optimise the process accordingly.

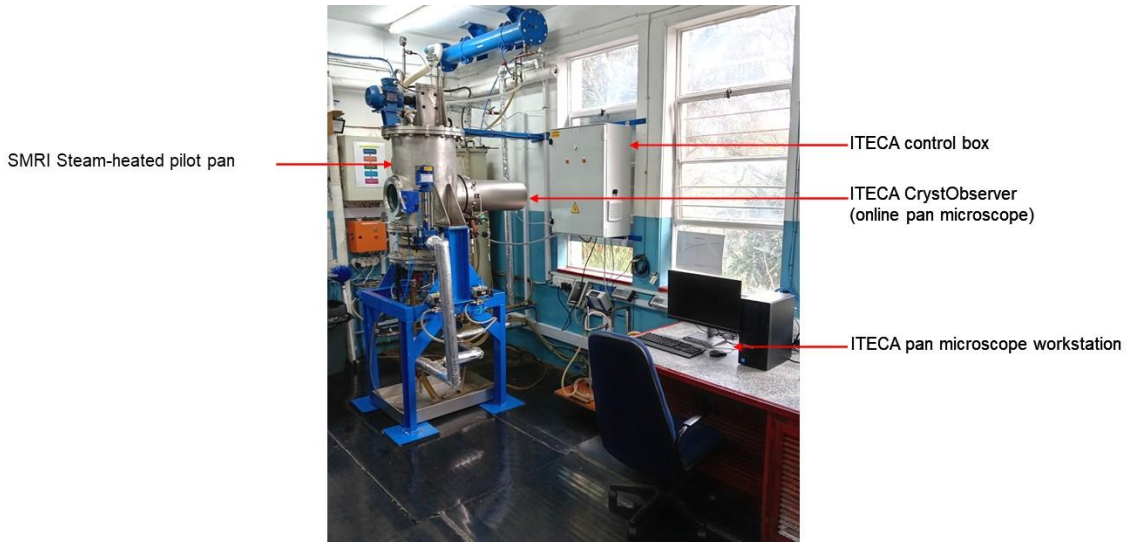


Figure 7. SMRI steam-heated pilot pan equipped with an online pan microscope

The pan microscope system may be used in a similar way to a saturascope, to determine the saturation limit of impure cane sugar solutions. In the case of the pan, the vacuum pressure may be held constant such that the raw syrup or molasses boils within the typical raw sugar factory pan temperature range (60-70°C) and it should be allowed to reach a state of supersaturation. The mother liquor supersaturation in the pan is controlled by maintaining the brix of the mother liquor and this is inferred from the Boiling Point Elevation (BPE) measurement. The BPE of the mother liquor is maintained at a constant value by adding water into the pan such that it matches the evaporation rate of the vapour exiting the pan. Thereafter, coarse sugar crystals (>0.5 mm) are added to the pan and the BPE reduced gradually until

the crystal edges begin to round. The massecuite in the pan is then sampled and filtered using a Nutsch filter so that the mother liquor dissolved solids and sucrose content can be measured. This may be done at various NS/W ratios by starting with C-molasses (40% purity) and thereafter adding pure sucrose solution to the C-molasses to change the NS/W ratio so that the range achieved is from 0.5 to 5. As mentioned in the above section, determination of the point of saturation by visual inspection by the operator may be subjective particularly when observing the roundness of the crystal edges. It would be convenient if the image analysis performed by the online pan microscope could determine the circularity of the particle using Equation 9 (Balter, 2017) to reduce subjectivity from analyst to analyst.

$$C = \frac{4 \times \pi \times A}{P^2} \quad \text{..... Equation 9}$$

Where C is the circularity (dimensionless), A is the crystal area (μm^2) and P is the crystal perimeter (μm). The circularity for a circle, square and rectangle (with length two times width) are 1.000, 0.785 and 0.698, respectively. A circularity real time trend could potentially be monitored to assist with determining the saturation point (i.e. the circularity of the sugar crystal is expected to increase with time when the mother liquor is undersaturated but should remain the same if the mother liquor concentration is increased to the saturation point). Secondly, to determine if the saturation point was determined correctly using the pilot pan system, the tests conducted using the pan would need to be validated using the Love's (2002) adapted Polish test or by the Kelly's (1954) method.

As mentioned above, the metastable supersaturation limit of cane syrup or molasses may be determined using the method described by Penklis and Wright (1963). The detection of false grain can easily be achieved since the SMRI pilot pan is equipped with a microscope capable of measuring crystals as small as four microns and can track the number of crystals throughout a pan boiling.

Conclusions

The literature review highlights the following key findings in summary form:

Pure sucrose solutions

- The solubility of sucrose in pure aqueous solutions is well understood and is dependent on the temperature of the solution. The two solubility correlations accepted by ICUMSA include the Charles (1960) and Vavrinecz (1962) equations of which the recommended equation for South African sugar factories is the Charles (1960) correlation. The Charles (1960) correlation is applicable across a temperature range from 0 to 86°C, however, Rein (2007) and the South African Sugar Technologists' Association (Anon, 1985) suggest that the equation may be extended to 90°C.

Impure cane sugar solutions

- The solubility of sucrose in impure cane sugar solutions depends on the temperature, and type and quantity of non-sucrose in the solution.
- The solubility of sucrose in impure cane sugar solutions is typically determined from the Solubility Coefficient (SC). The SC is the quotient of the S/W ratios of a saturated impure solution and saturated pure solution at the same temperature.
    - The SC is mainly dependent on the Non-Sucrose-to-Water (NS/W) ratio of the solution and the widely accepted SC correlation typically includes an exponential and linear term, the general form of equation is below:

      $$SC = m \times (NS/W) + b + (1 - b) \times e^{-c \times \left(\frac{NS}{W}\right)}$$

      Where m, b and c are constants. Some sugar technologists include the effect of the type of non-sucrose, mainly the reducing sugar and ash components, on the b constant in the above-mentioned equation.

  - There is contention in literature about the temperature dependence of the SC, majority of the literature suggests that the solubility coefficient is independent on temperature, however, it was found that one source includes temperature dependence.

- The literature on the solubility coefficient for cane sugar solutions was limited for South African raw sugar factory streams, and there is a large variation in the data across the same NS/W range. Furthermore, there is uncertainty as to whether the available solubility data is applicable to South African raw syrups and molasses being processed today.
- The metastable supersaturation limit data for impure cane sugar solutions was also found to be substantially different from one source to another and the data provided was not based on experiments using South African raw sugar syrups and molasses. However, there was agreement in literature that the metastable supersaturation limit of impure cane sugar solutions increased as the true purity of the solution decreased.

Common methods used to measure the saturation and metastable limits of sucrose in impure cane sugar solutions:

- There are various methods used to measure the saturation point of sucrose in impure cane sugar solutions and these methods may be broadly classified into two groups. Group 1 typically involves the saturation of impure cane sugar solutions at the different NS/W ratios by dissolution of crystalline sucrose at constant temperature. Whereas Group 2 involves observing a physical change in the sample to determine the saturation point (such as the slight rounding of the existing crystal edges when the mother liquor is close to the saturation point).
- The SMRI 50 l steam-heated pilot pan, equipped with ITECA online pan microscope, falls under Group 2 of the methods, and may be used to determine saturation data by observing the rounding of the crystal edges. Furthermore, the pan microscope can also detect new crystals and therefore is ideal for also determining the metastable supersaturation limit of impure cane sugar solutions.
- The Kelly's solubility technique (Honig, 1959) falls under Group 1 and the equipment required for this technique is readily available at the SMRI. Therefore, this technique may be an attractive option of potentially validating the saturation data obtained using the pilot pan.
- The review suggests that the SMRI pilot pan is an attractive tool for determining both the saturation and metastable limit data for impure cane sugar solutions, however, exploratory research will need to be conducted to practically determine the technical viability of using the pilot pan system, particularly for obtaining saturation limit data.

Future work

It is recommended that exploratory experiments be performed to practically assess the viability of using the SMRI pilot pan as a solubility measurement tool using the proposed method of determining the saturation and metastable limit data of impure cane sugar solutions.

Furthermore, it would be beneficial to perform solubility experiments to determine the effect of temperature on the solubility coefficient, preferably within the true purity (40 to 85%) and temperature (60 to 70°C) ranges used in a raw sugar factory station.

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Appendix A

Below is a summary of the procedure employed by Love (2002) to determine the solubility limit of impure cane sugar solutions:

- The base molasses (A-, B- or C-molasses), water and sucrose (starch-free icing sugar) were added together to obtain the desired NS/W ratio such that the concentration approximates saturation at the desired temperature (this was determined using an appropriate solubility coefficient correlation).
- The sucrose was dissolved in the molasses by heating using a microwave oven.
- The conditioned molasses was placed in the stirred jacketed pot to equilibrate at the desired temperature.
- Thereafter, large sugar crystals (between a mean aperture size of 550 and 880 µm) were heated to the same temperature as the molasses and were added to the pot. The mass of sugar was approximately 40% of the mass of the conditioned molasses used for saturation.
- The mixture of crystals and molasses was then heated to about 10°C higher than the saturation temperature to dissolve fines. The mixture was then cooled to 20°C lower than the saturation temperature so that sucrose may be exhausted from the mother liquor. Mixing at the temperature 20°C below saturation was performed for about 30 to 60 min. This was to ensure that when the temperature was raised to the desired saturation temperature, the mother liquor would be undersaturated and therefore saturation would occur by dissolution.
- The mixture of crystals and molasses was held at the saturation temperature for about 16 h and thereafter the mother liquor was separated by pressure filtration.
- A sample of the crystals in the mixture was analysed using a microscope to check that rounded crystal edges were obtained, thus confirming saturation by dissolution.

Appendix B

Figures B1 and B2 illustrate the assembly diagram of the hot stage and the light sensor set-up, and the general arrangement of the photometric apparatus used by Wright (1980), respectively.

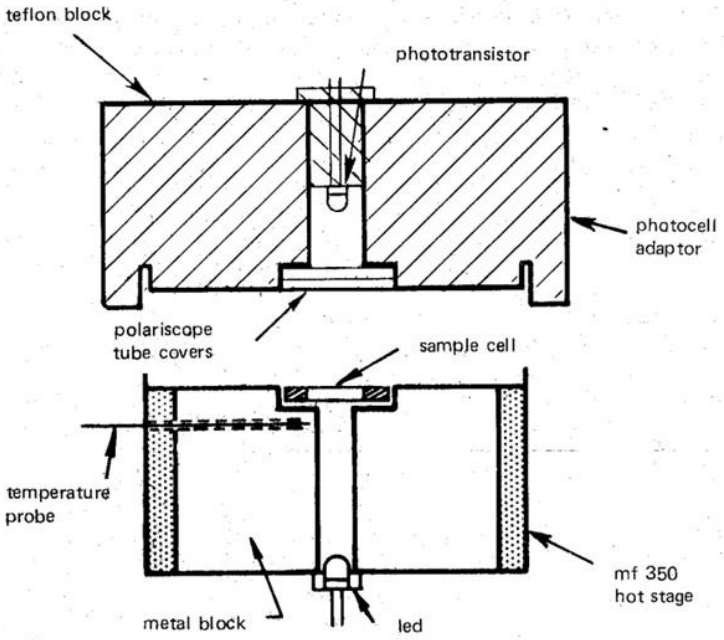

Figure B1. Assembly diagram of the hot stage and the light sensor set-up (Wright, 1980)

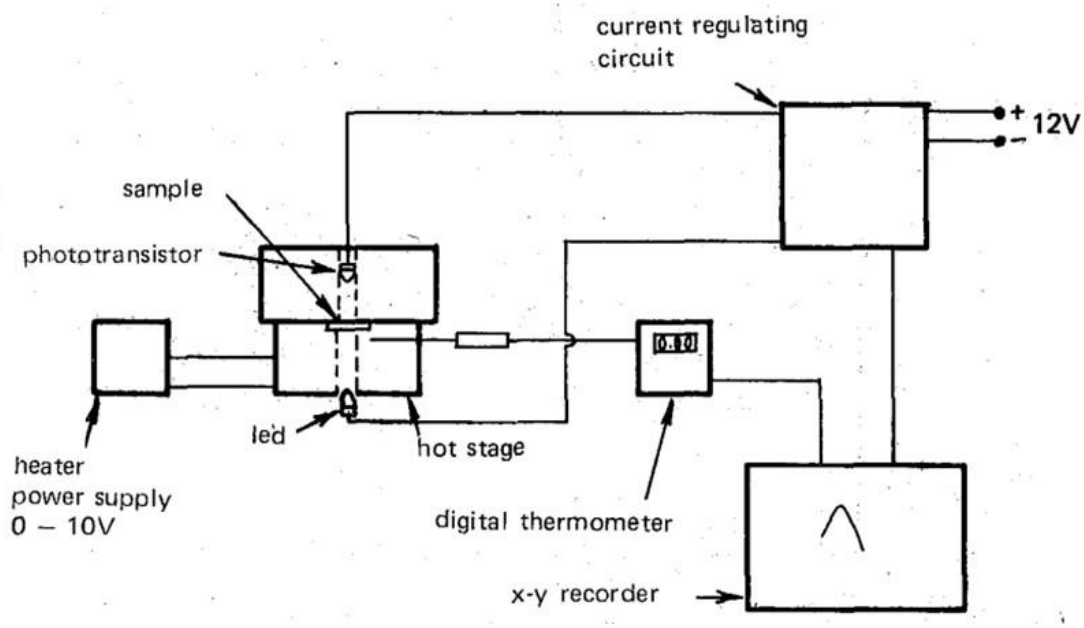

Figure B2. General layout of the photometric saturation temperature apparatus (Wright, 1980)

The procedure that was used to determine the saturation temperature was as follows (Wright, 1980):

- The molasses sample was preheated in a microwave oven to dissolve any crystals.
- The heated sample was removed from the microwave and stirred, and a sub-sample of approximately five grams was transferred onto a ceramic plate.
- The sub-sample was naturally cooled on the ceramic plate and thereafter about 250 to 500 mg of slurry crystals were added to the sub-sample and the mixture was stirred. The slurry was obtained by centrifuging conventional ball-milled slurry, the thick white paste left over after decanting the alcohol was used.
- Viewing slides were prepared using the molasses-slurry mixture. Careful attention was required in this step to minimise the presence of air bubbles in the sub-sample as this would interfere with the light transmission through the viewing slide.
- The metal block temperature (Figure B1) was controlled such that it was 10 to 20°C below the expected saturation temperature.
- The viewing slide (or sample cell) was placed in the photometric apparatus as shown in Figure B2, to be scanned, and the heating rate was adjusted based on the purity of the sample being processed. Note, it was desirable to scan the viewing slides shortly after the slides were prepared.
- The recorder generates a voltage versus temperature trace that may be used to locate the saturation temperature (i.e. the peak of the curve).
- Repeat analysis was performed by replacing the photocell adaptor shown in Figure B1 with a copper block to rapidly cool the hot stage to the initial temperature value. Thereafter, the procedure starting from the sixth bullet point was followed. Approximately six scans may be completed in an hour. It was recommended that each sample prepared for measurement be scanned once.