REFEREED PAPER

ASSESSING THE QUALITY OF BALL-MILLED SLURRIES

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Abstract

In a survey of the preparation method of ball-milled slurries in South African sugarcane factories, it was determined, from the ten participating mills, that only a single sugar factory still adhered to the method prescribed in the SASTA Laboratory Manual. This deviation raised some concern over the quality of slurry being prepared by the various mills and subsequently prompted an assessment by the Sugar Milling Research Institute.

The quality parameters for ball-milled slurries were identified as crystal density (or number of crystals), crystal size distribution and crystal habit (or shape) – each of which was assessed using an image analysis technique. The use of this method is recommended for sugar mills to evaluate the quality of the slurries produced and can be done using equipment mostly already available, together with free public domain software.

The method developed for the slurry assessment is described in this paper and the results of the analyses performed are given. Crystal mean sizes ranged from 5.8 to 9.4 μm and crystal densities from 1.95×10^8 to 1.07×10^9 nuclei per mL of slurry. Also reported on are the preliminary investigations of different analysis techniques available; these included laser diffractometry, the Coulter counter method and image analysis.

Keywords: slurry, crystallisation, pan boiling, crystal size distribution, coefficient of variance, mean crystal size

Introduction

The preparation of seed slurry by ball-milling has been used from as early as 1957 (Badley) and has since become the standard method of preparation globally for the graining of low grade rawhouse pans. Slurry produced by ball-milling involves crushing refined sugar suspended in an organic liquid for a specific amount of time and, as such, the process suffers from the intrinsic drawback of producing defaced crystals of various sizes. According to van der Poel *et al*. (1998), a key to obtaining a good crystal size distribution (CSD) of the product is to ensure that the seed used has a good CSD. This illustrates the importance of the slurry used, as its CSD influences the quality of the seed. An improved CSD would also require less grain conditioning in pans, which would lead to the steam savings associated with less movement water used (typically about 5% of the seed mass).

Madho *et al.* (2010) conducted a survey elucidating slurry usage and preparation in South African mills and showed that only a single mill adhered to the technique described in the South African Sugar Technologists' Association (SASTA) laboratory manual (Anon, 1985). The results of the survey have been updated and appear in Appendix 1, together with the SASTA prescribed method of preparation. It stands to reason that the different methods

adopted by the sugar mills would result in a variation of the slurry quality. However, to the knowledge of the authors of this paper, there was no documented literature on how to assess the quality of sugar factory ball-milled slurries.

This paper looks at the quality of the slurries being produced in some South African sugar mills. The method proposed for the assessment of the quality can be easily adopted by sugar mills, using equipment already available coupled with free software available in the public domain. The slurry quality is evaluated using three criteria, viz. CSD, crystal density (or the number of crystals in a millilitre of slurry) and crystal habit (or crystal shape). Also reported in the paper are the initial investigations into available particle analysis techniques, namely laser diffractometry, the Coulter counter method and image analysis.

Investigating various assessment techniques

The Sugar Milling Research Institute (SMRI) investigated the use of various available particle analysis techniques for slurry assessment. These are briefly described and the major findings of the evaluations are given.

Laser diffractometry

This method utilises angular variation of light scattered by particles, to obtain a size distribution of the suspension. Modern laser diffractometry follows the Mie scattering theory which includes sensitivity to sizes smaller than 20 µm and a wide opacity range (Horiba Scientific, 2012) and provides an equivalent diameter based on light scattering.

The sub-sampled slurry was initially suspended in glycerol, followed by further suspension in ethanol. The result obtained from the instrument is simply a volume distribution that can be fitted as a log-normal distribution. Figure 1 illustrates a typical slurry particle distribution obtained from laser diffractometry. The analyses were performed at the University of KwaZulu-Natal (Geology department) using a Malvern Mastersizer 2000 laser diffractometry instrument.

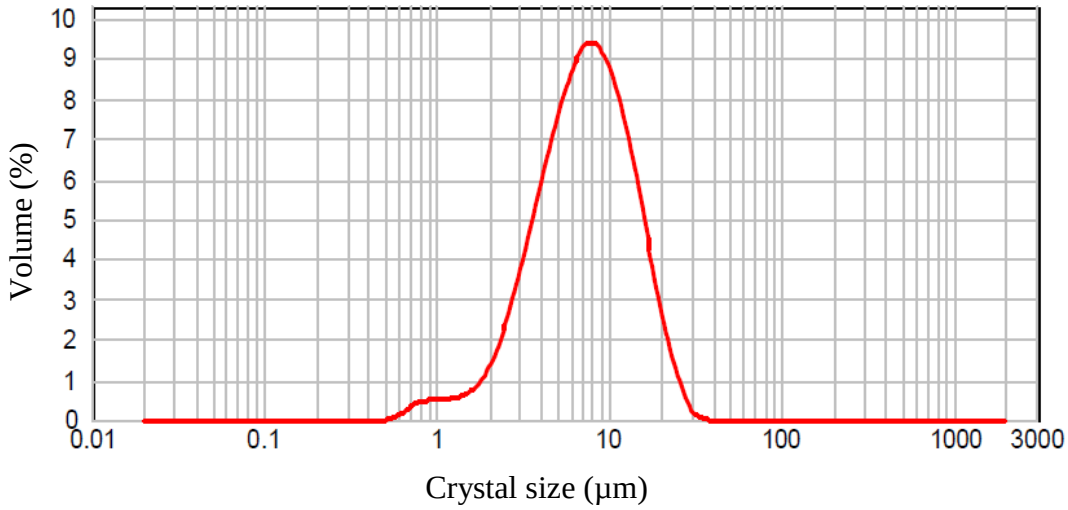

Figure 1. Laser diffractometry crystal size distribution of a ball-milled slurry.

The disadvantages of laser diffractometry are as follows:

- It ignores crystal habit and assumes a spherical shape;
- No direct evaluation of crystal density is obtained;
- A large amount of ethanol is required as a carrier for the particles and to avoid clusters of particles;
- Agglomerations are counted as single crystals (Horiba Scientific, 2012).

The advantages of this technique are that it is quick, repeatable and requires no calibration.

The Coulter counter method

This method was developed by WH Coulter in 1954 (Trottier *et al*., 2010), for the rapid counting of blood cells. According to Trottier *et al*. (2010), the principle involves passing a controlled volume of particles suspended in an electrolyte through a given orifice through which current flows. The particles flowing through the orifice change the impedance across the orifice and the number of changes in electrical resistance across the orifice is related to the number of particles; the extent of the change correlates to the particle size. This method requires the particles to be adequately suspended, since agglomerates are counted as one crystal. The results obtained are in the form of a number distribution and a particle count. The advantages of this method are that it is rapid and it can measure complex distributions. A disadvantage is that the instrument is difficult to calibrate for a sample that has a large CSD.

For this work, the tests were performed on a Beckman Multisizer 3 Coulter counter that was made available by Biological Control Products SA and was calibrated using 20 µm beads. The slurry was suspended in saturated glycerol followed by further suspension in an ammonium thiocyanate electrolyte (van der Poel *et al*., 1985). The results obtained from the Coulter counter tests were not repeatable and there were many instances where the orifice was plugged despite the attention to crystal dispersion prior to analysing.

Image analysis

This method is well known in the South African sugar industry as it is currently employed by the SMRI for CSD analysis of C-massecuites. The method utilises a transmittance light microscope equipped with a polariser and the relevant image analysis software (for the slurry analyses, Scope Photo® was the software used).

Due to the small visual differences in length and width of the slurry crystals in most samples, it was decided that the maximum distance across the crystal area be measured. The factory slurry was dispersed in saturated glycerol, and only 100 crystals were manually sized due to the hygroscopic nature of glycerol and the heat from the microscope dissolving smaller crystals when exposing the sample for too long. The crystal density was measured by capturing pictures of a well dispersed slurry sample at various points on the slide, followed by manual counting of the crystals.

Results show that a mean size range of 7-9 µm was obtained, with an average crystal density of 1.0×10^8 nuclei/mL of slurry. The crystals did not display defined crystal edges due to their small size and limitations to the available magnifications. The results of the image analysis compared well to the laser diffractometry results (also reported in a pharmaceutical application by Tinke *et al*., 2005); however, there were the added advantages, over laser diffractometry, of counting the number of crystals and evaluating their habit. Image analysis is a direct analytical method which allows measurement of various size parameters that may

consider particle shape in certain instances, which overcomes a major weakness of laser diffractometry. The image analysis method used in these initial tests was, however, very tedious and was limited due to the time taken to analyse the sample, as well as the dispersion of crystals when counting. These constraints were overcome in the development of the image analysis method by the automatic counting of crystals from photomicrographs and from determining the appropriate amount of saturated glycerol to be used for the purpose of crystal dispersion.

The development of an image analysis method for the assessment of ball-milled slurries

Work done by Love *et al*. (2004) encouraged the use of the Image J® software package to automatically size and count crystals. The software is available in the public domain (http://rsbweb.nih.gov/ij/index.html [accessed 2012]) at no charge.

A challenge using the software was to create a distinct contrast between the crystals and their background. This was overcome by means of polarisation and light manipulation (well known microscope techniques using standard equipment). For the assessment of the proposed method, three images of the slurry (with crystals dispersed in saturated glycerol) were captured and collectively measured using Image J®. The mean (average size), median (middle value of a distribution) and coefficient of variance (CV) (ratio of standard deviation to mean size expressed as a percentage) were then determined. A method of estimating the crystal density was also investigated using the settled volume of slurry crystals and the size distribution of the sample. This developed technique of estimating the crystal density is more time efficient than the initial method, and greatly reduced the effect of glycerol, and heat from the microscope light.

The development of this proposed method is described fully below and includes the development of the sampling technique, crystal density measurement and use of the image analysis tool. The repeatability of the sampling technique and the analyses are also reported.

Sub-sampling
The factory slurries were sampled as follows:

- The entire amount of slurry from a ball-mill was shaken until all the settled crystals were visually suspended.
- One litre of the slurry was then emptied into a separating funnel by intermittently shaking and decanting small amounts of the slurry.
- The sample from the funnel was shaken 20 times and inverted ten times before 10 g of sample was discharged into a sample bottle. This was repeated until a total sample mass of 30 g was obtained.

Microscope and Image J® analysis
The sub-sample was analysed as follows:

- The sub-sample was shaken manually for one minute. Thereafter 0.5 mL of the sample was withdrawn using a medicine dropper and emptied into a smaller vial.
- Approximately 6 mL of saturated glycerol was added to the slurry in the vial, followed by swirling of the mixture.

- A drop of the glycerol-slurry mixture was placed onto a large slide; thereafter an identical slide was placed on top of the sample to disperse the slurry.
- Once the slurry was dispersed, three photomicrographs were captured at three different points on the slide.
- Each picture was converted into a binary image (Image J® function that creates a white background and fills in solids in black) that was automatically analysed using Image J® to determine the Feret's diameter of all particles. The Feret's diameter, also referred to as the 'maximum calliper' by Image J®, is defined as the longest distance between parallel tangents to the projected area of the particle (Anon, 2012). The use of the maximum calliper replaces the manual measurement of the longest distance across the projected crystal area, as in the initial investigations.
- The raw data was processed in Microsoft Excel® to determine the mean, median and CV, defined as the ratio of standard deviation to mean.

Determining the minimum number crystal size measurements

Work carried out by Lionnet (1998) on C-massecuites involved determining the minimum number of crystals to be sized, based on the standard deviation of the width and length of the crystals. A similar method was employed to estimate the minimum number of crystals to be measured when assessing slurries. The length of the slurry crystals (assumed to be equal to the Feret's diameter) was measured for 20 crystals followed by increments of 20 until the standard deviation value became constant. Figure 2 illustrates the findings.

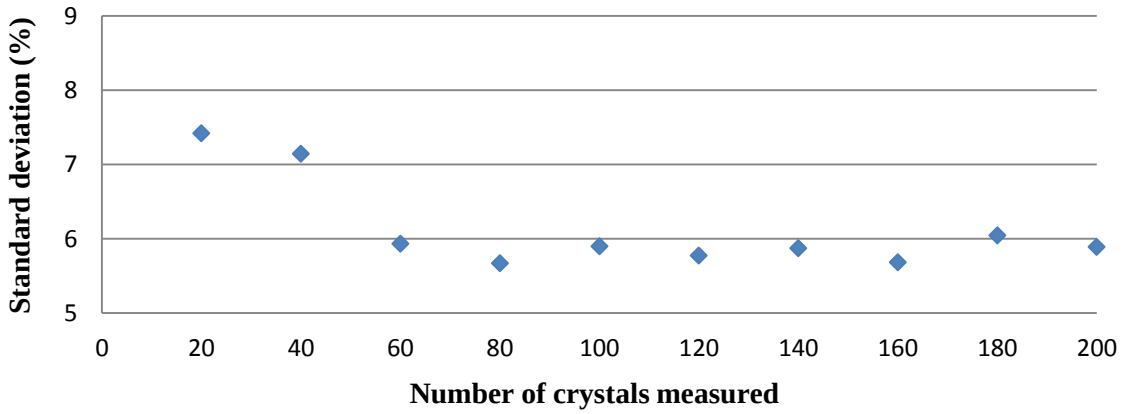

Figure 2. Standard deviations of slurry crystals as a function of sample size.

The standard deviations were determined using manual sizing of the crystals, and it is expected that an automatic sizing would not deviate substantially from the test performed. For the manual count, as can be seen in Figure 2, the standard deviation became constant after 60 crystals were counted and a sample size of at least 100 crystals was thought necessary for any slurry evaluations. For the Image J® analyses proposed, more than 1000 crystals are analysed for every image taken (usually three images per analysis).

Repeatability

Repeatability in sampling from the ball-mill contents and then the subsequent sampling from the sub-sample were tested as illustrated in Figure 3. The results of the measurements are shown in Table 1. Differences in means were tested using the Student's t-test, and differences in variances were tested using the F-test, both at a 95% confidence interval, between samples 1a, 1b and 1c, and between 1a-c combined, and samples 2 and 3, with the results shown in Appendix 2, Tables A2-1 to A2-4. There were no significant differences in means between

any pair of tests, apart from between 1abc and 2, and in some cases the differences in variances were significant at the 95% confidence level. However, as can be seen in Table 1, the actual differences were very small, and thus it was concluded that the sampling, sub-sampling and analysis procedures with Image J® are repeatable.

Having shown repeatability of the image software and sampling technique, evaluation of the various factory slurries involved only a single analysis.

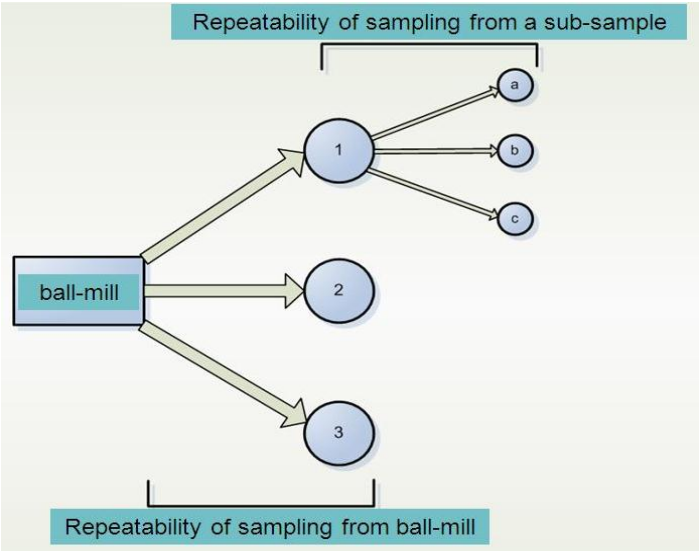

Figure 3. The method used to evaluate repeatability in sampling (analysis of 1-3), sub-sampling (analysis of a-c) and the use of the Image J® technique.

Table 1. Repeatability test results.

Slurry quality parameters	Sample 1			Sample 1abc combined	Sample 2	Sample 3
	a	b	c			
Mean (μm)	9.05	9.23	9.26	9.18	9.52	9.27
σ (standard deviation)	6.72	6.76	6.67	6.72	6.50	6.55
CV (%)	74.29	73.20	71.98	73.18	68.33	70.68

Settled volume of slurry

The settled volume (V_{ST}) of slurry crystals was obtained by pouring 500 mL of a well mixed sample into a volumetric cylinder followed by reading off the settled volume of crystals after approximately six hours or once all crystals had settled.

Crystal density

An estimate of the crystal density may be obtained by utilising the CSD data and the settled volume of crystals. Image J® additionally provides the minimum Feret's diameter which is the shortest distance between parallel tangents across the particle projected area. It is assumed that the maximum and minimum Feret's diameters are the mean length and width of a crystal respectively (Faria *et al.*, 2003). Furthermore, from general microscope observations, it is assumed that the crystals are fairly flat; hence it will be assumed that the width of the crystal

is equal to the height of the crystal. The volume of a single crystal may be estimated, as in the CSD analyses of C-massecuite (personal communication[1]), by Equation 1.

$$V_C = L \times W^2 \qquad \text{Equation 1}$$

where L = length of the crystals (μm)
W = width of the crystals (μm)
V_C = volume of a single crystal (μm^3).

Therefore the mean crystal volume, given the CSD data, may be determined by Equation 2.

$$V_m = \frac{\sum_{i=1}^{n} V_{Ci}}{n} \qquad \text{Equation 2}$$

where V_m = the arithmetic mean volume (μm^3)
n = the number of crystals analysed.

The settled volume of slurry crystals (V_{ST}) was comprised of the volume of the crystals alone, and the organic solvent volume occupying the voids present between the settled crystals. The volume fraction of the abovementioned voids is critical in determining the crystal density which will be observed later on; however, the void fraction is directly dependent on the bulk density of the slurry crystals. The bulk density was determined experimentally by measuring the settled volume of a known mass of slurry crystals in an organic solvent, as in the procedure which follows.

Approximately 250 g of slurry from each mill was centrifuged for 15 minutes at 1500 rpm, followed by decanting of the solvent. The paste-like crystals were dried at 105°C for approximately four hours. After one hour of drying, the slurry-cake was gently separated into individual smaller crystals using a pestle (referred to as 'conditioning'). When drying was complete, the crystals were further conditioned so that no agglomerates could be felt. A fixed mass of slurry (20 g) was deposited into a 250 mL volumetric cylinder that initially was filled to the 150 mL mark with saturated colourless methylated spirits, followed by additional methylated spirits to the 250 mL mark. The crystals were allowed to settle freely for 16 hours to obtain a settled volume of crystals. It is assumed that the density of the colourless methylated spirits is approximately the same as the density of the organic solvent used by the individual mills.

The bulk density (ρ_b) of the slurry crystals from the above experiments was determined by simply dividing the known mass of crystals by the volume obtained after 16 hours of settling (Appendix 3). According to Fogler (2006), the voidage percentage can be determined by Equation 3.

$$\phi = \left(1 - \frac{\rho_b}{\rho_c}\right) \times 100 \qquad \text{Equation 3}$$

where ϕ = voidage (%)
ρ_b = bulk density of slurry crystals (g/cm^3)
ρ_c = sucrose crystal density = 1.5862 g/cm^3 (Sugartech, 2012).

[1]Dr Richard Simpson, Sugar Milling Research Institute NPC, Durban, South Africa

The settled volume of crystals obtained from 500 mL of slurry can be used to determine the no-void volume. The number of crystals may be determined by Equation 4.

$$N_C = \frac{V_{ST} \times \phi}{V_m} \qquad \text{Equation 4}$$

where N_C = total number of crystals
V_{ST} = settled volume crystals in 500 mL of slurry (μm^3).

The crystal density (nuclei/mL slurry) of slurry can be determined using Equation 5.

$$\frac{N_C}{V_T} \qquad \text{Equation 5}$$

where V_T (mL) is the total volume of slurry used to determine the settled volume of crystals (500 mL).

Duration of slurry assessment tests
Once the mill staff have become familiar with the methodology involved in assessing slurry quality as suggested, it can be estimated that the test duration will be as follows:

- Sampling and subsampling (25 minutes)
- Taking of photomicrographs (5 minutes)
- Image J® processing (10 minutes).

Thus, in about 40 minutes, a slurry quality can be assessed with regards to its CSD, mean size, CV and habit. For the habit (or shape) of the crystal, a simple classification system or comment can be used, e.g. Class 1 = regular, well-formed crystals, Class 2 = defaced crystals, and so forth.

In order to determine the crystal density, a duration of five minutes is estimated for data processing once the settled volume is known (the settled volume determination is dependent on the crystal mean size and could span from three to six hours). However, it is envisaged that this test would not be done routinely.

Assessment of South African ball-milled slurries

Factories that participated in the survey of Madho *et al.* (2010) were approached to send through to the SMRI entire batches of slurry as prepared by their standard techniques. These samples were then assessed using the methods developed, the results of which appear in Table 2. Photomicrographs of the slurries appear in Appendix 4. Further to this, Mill 6, which was the only mill to adhere strictly to the SASTA Laboratory Manual method, was also requested to mill their slurry at various durations to determine the effect of grinding time on slurry quality. Also reported in Table 2 is the number of crystals per cubic metre of massecuite – this value was calculated from the crystal densities determined and from slurry usage per cubic metre of massecuite as reported by Madho *et al*. (2010).

Table 2. Slurry assessment results.

Mill	Milling time (h)	Mean size (µm)	Median (µm)	Standard deviation	CV (%)	Crystal density (nuclei/mL slurry)	No. crystals/m^3 massecuite
Mill 1	12	9.4	7.8	6.8	72.5	2.40×10^8	1.44×10^{12}
Mill 2	12	8.7	7.2	6.2	71.1	3.02×10^8	1.81×10^{12}
Mill 3	24	9.0	7.3	6.7	74.3	2.67×10^8	1.60×10^{12}
Mill 4	4	7.9	6.5	5.7	71.8	4.06×10^8	5.68×10^{12}
Mill 5	12	6.7	6.2	3.4	50.4	8.58×10^8	9.44×10^{12}
Mill 6	4	6.9	6.2	4.0	57.9	5.78×10^8	n/a
Mill 6	8	6.0	5.5	3.1	51.7	9.91×10^8	n/a
Mill 6*	12	5.8	5.5	3.0	51.5	1.07×10^9	6.44×10^{12}
Mill 6	16	5.6	5.0	2.9	51.8	1.38×10^9	n/a
Mill 6	24	5.5	5.2	2.7	49.6	1.43×10^9	n/a
Mill 7	12	6.9	5.8	4.6	67.0	5.83×10^8	1.22×10^{12}
Mill 8	4	9.2	7.4	6.9	75.2	1.95×10^8	6.25×10^{12}
Mill 9	12	7.2	6.3	4.2	57.9	4.75×10^8	2.28×10^{12}
Mill 10	24	5.9	5.4	3.0	50.9	8.42×10^8	1.01×10^{13}

*Standard milling time for Mill 6. Slurries produced with other milling times were not used for pan boiling at Mill 6; hence no massecuite crystal counts are available.

Discussion

Effect of ball-milling time on CSD

Derived from the results of Table 2, Figure 4 shows the effect of ball-milling time on the mean size and CV of Mill 6 slurry.

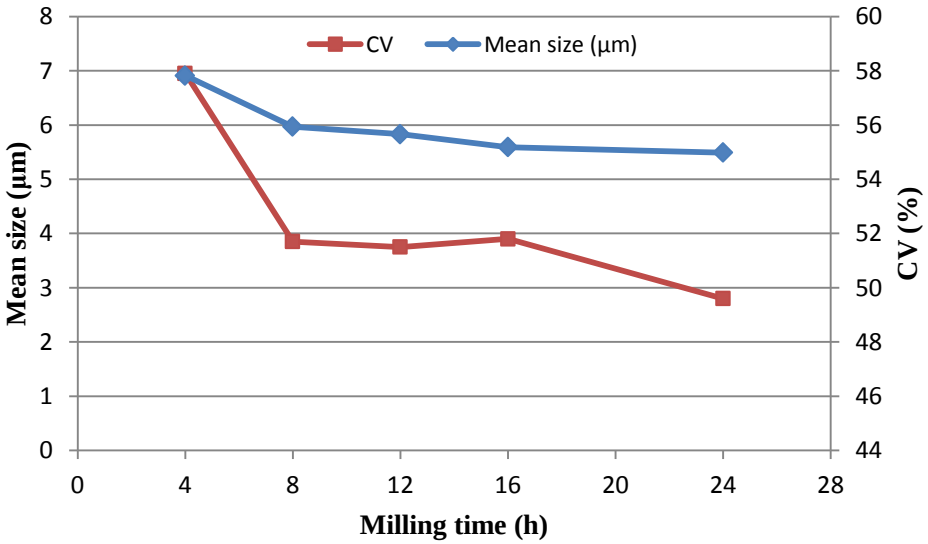

Figure 4. Effect of ball-milling time on mean size and coefficient of variance (CV) of the South African Sugar Technologists' Association prescribed method of slurry preparation.

From Figure 4 it can be seen that there is a rapid drop in mean size and CV from a ball-milling time of four to eight hours. However, after eight hours there was little effect on the mean size and CV. This implies that, for the SASTA method of slurry preparation, the grinding time could be dropped from the prescribed 12 hours to eight hours, as there are no

substantial gains to be made from the extra milling in terms of the quality of the slurry produced.

CSDs of various factory slurries

Table 2 shows that, of the routine methods, Mill 5 slurry had the lowest size variation (CV=50.4%), other than the Mill 6 trial at 24 hours (CV=49.6%), with a mean size of 6.7 µm, and that the slurry from Mill 8 had the highest size variation (75.2%) with a mean crystal size of 9.2 µm. It is fairly likely that the latter is as a result of the short ball-milling time, as Mill 4 (CV=71.8%) shared a close size variation for the same ball-milling time.

Comparison of the effects of the various factors is difficult as a result of the wide range in variation in all factors, leading to multiple combinations (Appendix 1). However, by using some data exploratory techniques, it appears in general that the sugar:solvent ratio has the largest influence on the quality of the slurry in terms of mean size, standard deviation, CV and crystal density, with the four mills showing the poorest values of these parameters being those four with the highest sugar:solvent ratios. This can be explained by considering the mechanism of ball-milling, where a high charge to liquid ratio leads to poor movement and a cushioning effect, which reduces the impact of the balls on the crystals and hence the efficiency of milling (Coulson and Richardson, 1978).

The second most significant effect appears to be time of milling, as may be expected, and as confirmed by the Mill 6 trials reported above. However, the data suggest that when the sugar:solvent ratio is high, longer milling times do not substantially improve the results (Mill 3, for example). It is important to note that longer milling times do not just reduce the mean size, but also improve the standard deviation and the CV. This may be explained mechanistically by the stochastic nature of ball-milling, as, the longer milling takes place, the higher the probability that the larger crystals will have been impacted and reduced in size. It should furthermore be noted that the longer milling times will not continue to decrease the mean size (as seen in Figure 4) as the latter is largely a function of the ball size, with smaller balls being required to reduce the mean size further (Coulson and Richardson, 1978).

It has already been established that Mill 6 slurry is prepared using the prescribed method (12 h) and results from Table 2 indicate that its size variation (CV=51.5%) is similar to Mill 5 quality slurry (CV=50.4%), deemed to have the best CV in the survey. It is thus evident that, for mills to improve on their CV of the slurry produced, the time of grinding and the ratio of the mass of sugar to volume of solvent used are critical.

An oversight in Madho *et al*. (2010) and also in this paper is that the diameter of the steel balls used, the size of the ball-mill and the speed of the ball-mill rotation were not included in the survey. It is suggested that these factors be considered in any further studies.

Crystal density and number of crystals used in a cubic metre of massecuite

From Table 2 and Figure 5 it can be observed, as is expected, that the larger mean crystal sizes yield lower crystal densities (number of crystals per mL of slurry) and *vice versa*. Mills 5, 6 and 10, which produced the highest crystal densities, also introduced the most crystals per given volume of massecuite (see Table 2).

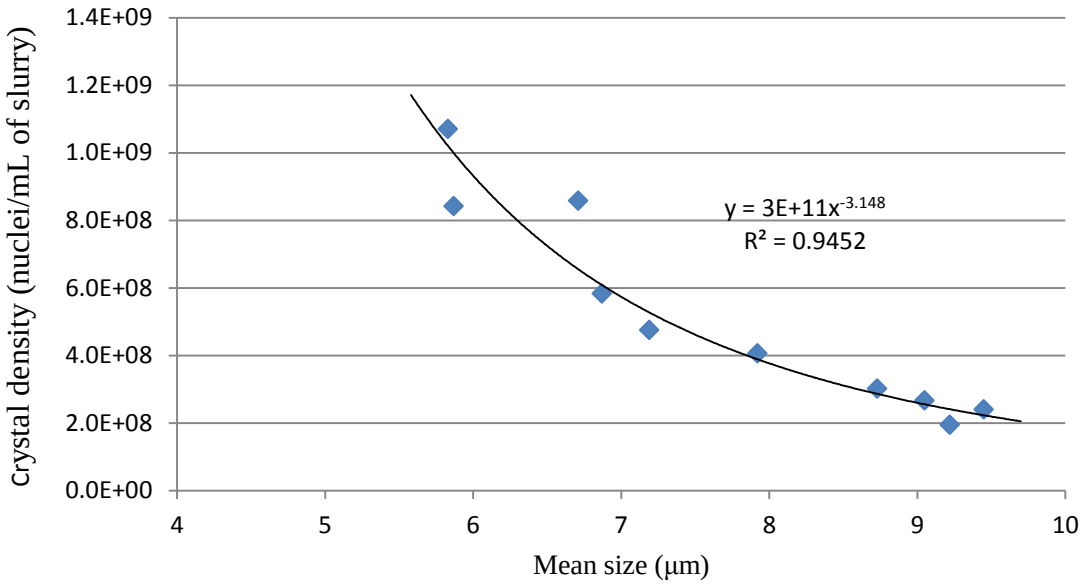

Figure 5. Relationship between slurry mean crystal size and crystal density for some South African mills, with logarithmic trend line.

Crystal habit

The larger crystals (>20 µm) present in slurries displayed shapes that were longitudinal, oval and, in most cases, irregular. The smaller crystals (<10 µm) were difficult to examine; however, their edges were rounded and they appeared as circular dots. The photomicrographs of the various slurries can be obtained in Appendix 4; however, the large number of finer crystals may not easily be seen at this resolution.

Conclusions

A repeatable image analysis technique using simple microscopy and image analysis has been developed to quantify the quality of factory slurry. The SASTA method of slurry preparation as implemented at Mill 6 produced crystals that had a mean size of about 5.8 µm, a CV of about 51.5% and a crystal density of approximately 1.07 x 10^9 nuclei per mL of slurry. This slurry, together with two others, distinguished themselves from the rest of the slurries examined as they had low CVs (the highest CV examined was 75.2% and the lowest 50.4%) which may be as a result of the grinding time and sugar:solvent ratio used.

Future work

Without conditioning it is generally accepted that a large CSD in slurry would lead to large CSDs in the seed, massecuite and sugar produced, and hence an ideal seed should have a narrow CSD or CV. However, the effect of the mean size of the slurry crystals has not, to the knowledge of the authors, been documented. Future work on slurries will utilise the SMRI's pilot vacuum pans to evaluate the practical implications of the slurry mean crystal size. Sugar mills willing to partake in this exercise are encouraged to contact the SMRI.

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Amatikulu, Darnall, Felixton, Komati, Malalane, Eston, Noodsberg, Sezela, Umzimkulu and Umfolozi sugar mills for the provision of slurry samples and preparation details. A special thanks goes to Kavitha Bachu from Wirsam (Durban) for allowing the use of various microscope parts on loan.

REFERENCES

Anon (1985). *Laboratory Manual for South African Sugar Factories*. South African Sugar Technologists' Association, 3rd Edition, Mount Edgecombe, South Africa. pp 160-162.

Anon (2012). Image J®: Image Processing and Analysis in Java. http://rsbweb.nih.gov/ij/index.html [accessed January 2012].

Badley JGH (1957). The production of footings by the full seeding method. *Proc British West Indies Sug Technol* pp 133-135.

Coulson JM and Richardson JF (1978). *Chemical Engineering*, Volume 2: Unit Operations. 3rd Edition, Pergamon Press, Oxford, UK. p 77.

Faria N, Pons MN, Feyo de Azavedo S, Rocha F and Vivier H (2003). Quantification of the morphology of sucrose crystals by image analysis. *Powder Technology* 133: 55-67.

Fogler HS (2006). *Elements of Chemical Reaction Engineering*. Prentice Hall, 4th Edition, New Jersey, USA. p 179.

Horiba Scientific (2012). A guidebook to particle size analysis. http://www.horiba.com/fileadmin/uploads/Scientific/Documents/PSA/PSA_Guidebook.pdf [accessed March 2012].

Lionnet GRE (1998). The incorporation of impurities into sucrose crystals during the crystallisation process. PhD Thesis, University of Natal, Durban, South Africa. pp 33-35.

Love DJ, Peacock SD and Schumann GT (2004). Quantification of crystal conglomerates using image analysis. *Proc S Afr Sug Technol Ass* 78: 531-542.

Madho S, Muir BM and Hlongwane M (2010*).* A survey of slurry preparation at usage at South African sugar factories. Technical Note No. 27/10 (RC), Sugar Milling Research Institute, Durban, South Africa. 4 pp.

Sugartech (2012). Density of sugar factory products. http://www.sugartech.co.za/density/index.php [accessed March 2012].

Tinke AP, Vanhoutte K, Vanhoutte F, De Smet M and De Winter H (2005). Laser diffractometry and image analysis as a supportive analytical tool in the pharmaceutical development of immediate release direct compression formulations. *International Journal of Pharmaceutics* 4: 88.

Trottier R, Dhodapkar S and Wood S (2010). Particle sizing across the CPI: This survey of modern measurement technologies demonstrates how selection criteria vary by application. *Chemical Engineering* 4: 62-63.

van der Poel PW, de Schutter MAM, Bleyenberg CC and van Heeschvelde PMT (1985). A new approach to full seeding. *La Sucrerie Belge* 103: 15-24.

van der Poel PW, Schinech H and Schwartz T (1998). *Sugar Technology: Beet and Cane Sugar Manufacture.* Verlag Dr Albert Bartens, Berlin, Germany. 665 pp.

APPENDIX 1.
Some of the slurry preparation methods used in South Africa.

The results of the survey from Madho *et al*. (2010) were updated and are as follows:

Mill no.	Mass of sugar used (g)	Volume of solvent used (L)	Sugar:solvent (g/L)	No. of balls in mill	Duration of milling (h)	Final slurry volume (L)
SASTA method	**800**	**2.0**	**400**	**2500**	**12**	**6.0**
Mill 1	2500	2.0	1250	2500	12	6.0
Mill 2	2500	2.0	1250	2500	12	6.0
Mill 3	2500	2.0	1250	2500	24	6.0
Mill 4	8500	14.0	607	4240	4	14.0
Mill 5	2500	6.0	417	2000	12	11.0
Mill 6	**800**	**2.0**	**400**	**2500**	**12**	**6.0**
Mill 7	1500	1.9	789	2500	12	2.1
Mill 8	1500	1.6	938	2500	4	3.2
Mill 9	1500	3.6	417	1500	12	4.8
Mill 10	1600	4.0	400	2500	24	12.0

APPENDIX 2.
Repeatability tests results.

The results of the t-tests for samples 1a, b and c are shown in Table A2-1 and results of F-tests for samples 1a, b and c are shown in Table A2-2. The results of the t-tests for samples 1a, b and c combined, 2 and 3 are shown in Table A2-3 and results of F-tests for samples 1a, b and c combined, 2 and 3 are shown in Table A2-4.

Table A2-1. Results of t-test for samples 1a, b and c.

Comparison	**1a vs 1b**		**1a vs 1c**		**1b vs 1c**	
Sample	**1a**	**1b**	**1a**	**1c**	**1b**	**1c**
Mean	9.05	9.23	9.05	9.26	9.23	9.26
Variance	45.19	45.67	45.19	44.4	45.69	44.44
Observations	4066	4827	4066	3754	4827	3754
df	8891		7818		8579	
Hypothesized mean	0		0		0	
t stat	**-1.29**		**-1.40**		**-0.18**	
P(T<=t) two-tail	0.20		0.16		0.85	
t Critical two-tail	1.96		1.96		1.96	

Table A2-2. Results of F-test for samples 1a, b and c.

Comparison	**1a vs 1b**		**1a vs 1c**		**1b vs 1c**	
Sample	**1a**	**1b**	**1a**	**1c**	**1b**	**1c**
Mean	9.05	9.23	9.05	9.26	9.23	9.26
Variance	45.19	45.67	45.19	44.4	45.69	44.44
Observations	4066	4827	4066	3754	4827	3754
df	4065	4826	4065	3753	4826	3753
F	**1.01**		**1.02**		**1.03**	
P(F<=f) one-tail	0.36		0.30		0.19	
F Critical one-tail	1.05		1.05		1.05	

Table A2-3. Results of t-test for samples 1a, b and c combined, 2 and 3.

Comparison	**1abc vs 2**		**1abc vs 3**		**2 vs 3**	
Sample	**1abc**	**2**	**1abc**	**3**	**2**	**3**
Mean	9.18	9.52	9.18	9.27	9.52	9.27
Variance	45.16	42.28	45.16	42.91	42.29	42.91
Observations	12647	3001	12647	4044	3001	4044
df	15646		16689		7043	
Hypothesized mean	0		0		0	
t stat	**-2.46**		**-0.70**		**1.58**	
P(T<=t) two-tail	0.01		0.48		0.11	
t Critical two-tail	1.96		1.96		1.96	

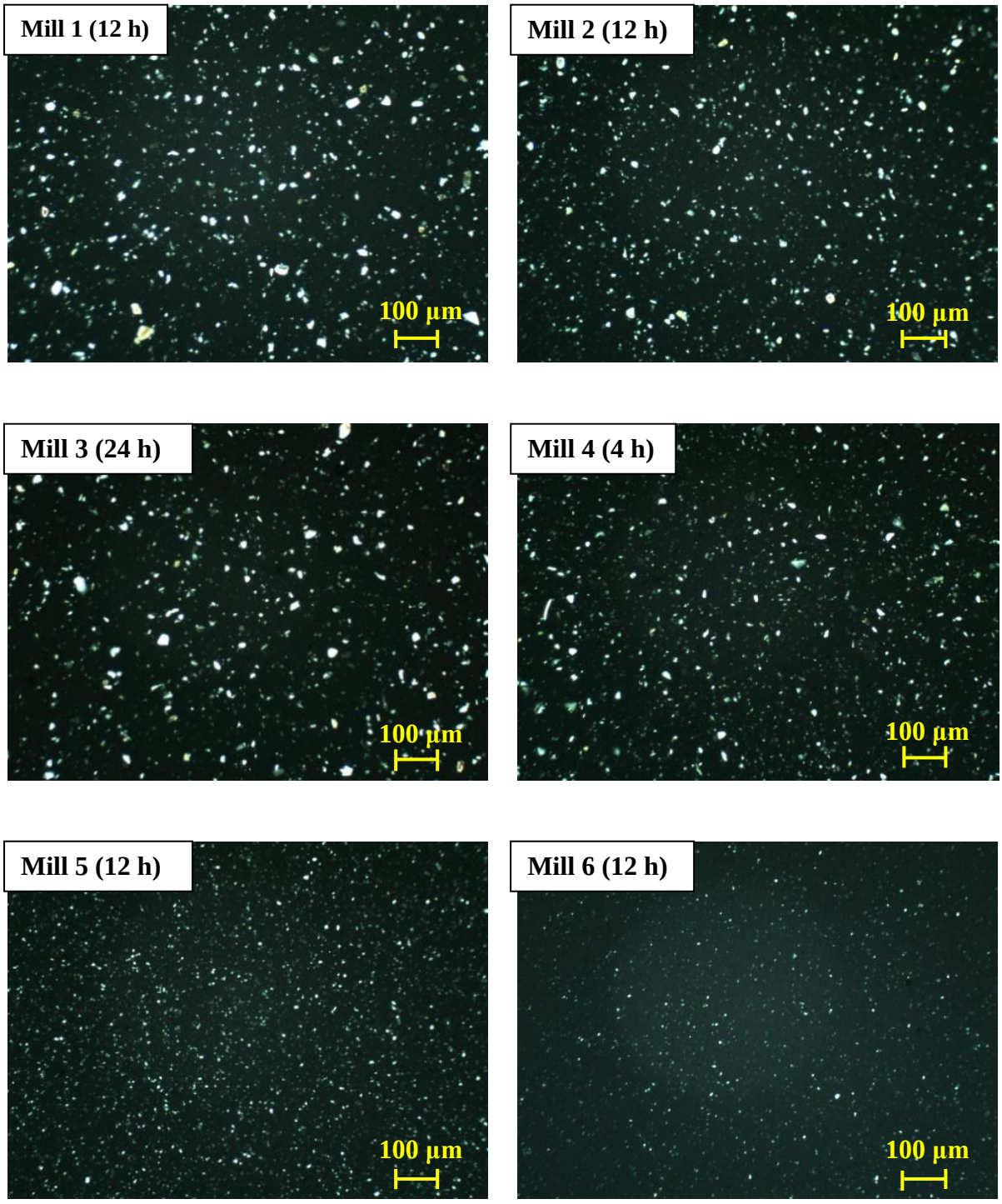
Table A2-4. Results of F-test for samples 1a, b and c combined, 2 and 3.

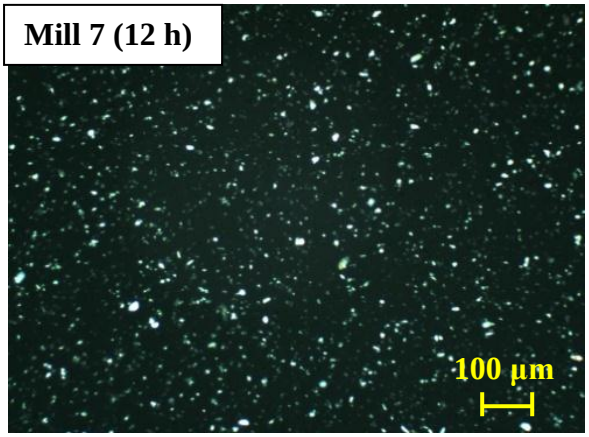
Comparison	**1abc vs 2**		**1abc vs 3**		**2 vs 3**	
Sample	**1abc**	**2**	**1abc**	**3**	**2**	**3**
Mean	9.18	9.52	9.18	9.27	9.52	9.27
Variance	45.16	42.28	45.16	42.91	42.29	42.91
Observations	12647	3001	12647	4044	3001	4044
df	12646	3000	12646	4043	3000	4043
F	**1.07**		**1.05**		**1.01**	
P(F<=f) one-tail	0.01		0.02		0.34	
F Critical one-tail	1.06		1.04		1.06	

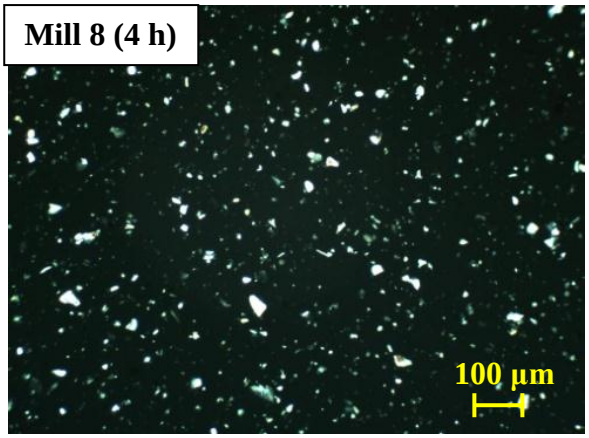
APPENDIX 3.
Bulk densities of various South African slurries.

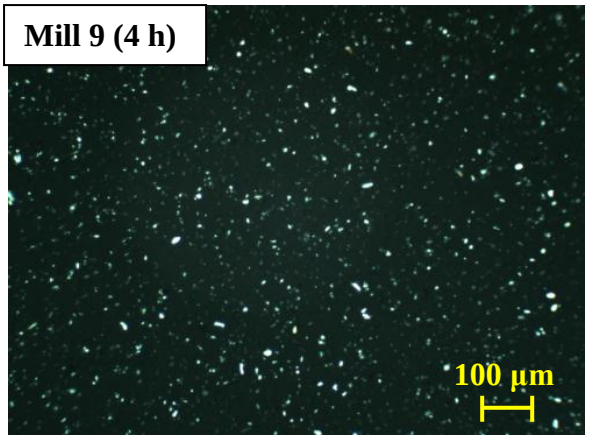
Mill	**Milling time (h)**	**ρ_b (bulk density) (g/mL)**
Mill 1	12	0.492
Mill 2	12	0.497
Mill 3	24	0.535
Mill 4	4	0.473
Mill 5	12	0.417
Mill 6	4	0.469
Mill 6	8	0.432
Mill 6	12	0.439
Mill 6	16	0.439
Mill 6	24	0.439
Mill 7	12	0.442
Mill 8	4	0.520
Mill 9	12	0.460
Mill 10	24	0.379

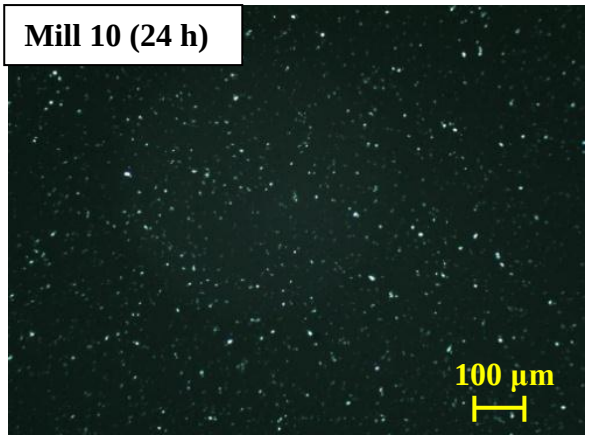
APPENDIX 4.
Photomicrographs of some South African ball-milled slurries.




Mill 7 (12 h)
100 µm


Mill 8 (4 h)
100 µm


Mill 9 (4 h)
100 µm


Mill 10 (24 h)
100 µm