

CENTRIFUGAL CLARIFICATION OF MOLASSES

HW BERNHARDT

Sugar Milling Research Institute, University of Natal, Durban, 4041 South Africa

Abstract

The compositions of the various organic and inorganic species in cane molasses show wide variations. Centrifugation can be used to remove suspended solid particles. The bulk of these are precipitated calcium compounds. Removal of calcium by precipitation and subsequent centrifugation can be enhanced by the addition of sulphuric acid. The effects of dilution, temperature, and acid addition on the efficiency of calcium removal by centrifugation are described. A relatively simple procedure to determine the optimal molasses pretreatment method for maximum calcium removal is presented.

Introduction

The main motivation for undertaking the work described in this report is to develop a process for making a product similar to high test molasses (HTM) from final cane molasses. Essentially the process comprises pretreatment involving centrifugal clarification of the final molasses, inversion of the sucrose in the treated molasses, separation of the invert-rich fraction by ion exclusion and evaporation of this purified invert stream. The concentrated invert syrup, which has a composition similar to HTM, is to be used as a feedstock for speciality fermentations. A preliminary economic analysis (Bernhardt, 1996) shows that the process has economic potential. A list of the major processing steps is given in Figure 1.

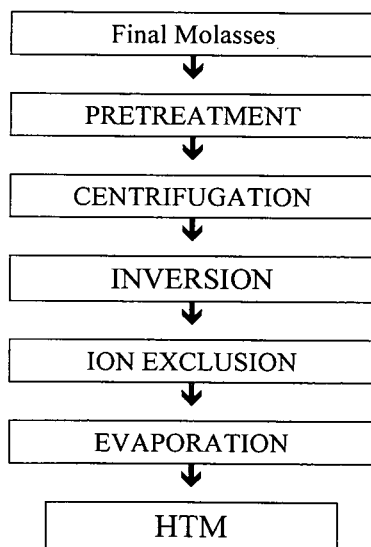


Figure 1. Major processing steps involved in making HTM from final molasses.

Apart from sugars (mainly sucrose, glucose and fructose), final molasses contains a variety of chemical constituents including cations such as Ca, Mg and K, anions like sulphates, phosphates and chlorides, and a variety of organic components such as acids, colour bodies and several degradation products. Ca ions, in particular, form insoluble complexes with many other chemical species normally present in molasses and these complexes give rise to numerous downstream processing problems such as fouling of evaporators, reducing the effectiveness of sugar separation techniques like ion exclusion and adversely affecting fermentation processes. An important aspect of the pretreatment therefore involves maximising the removal of Ca ions.

Several methods of removing Ca ions have been investigated by Davis *et al.* (1997). The investigation showed that centrifugation of suitably diluted final molasses acidified with sulphuric acid gives the best removal. The sulphate ions from sulphuric acid lead to a precipitation of sparingly soluble Ca salts. Centrifugation as a means of removing solid ash constituents from molasses has been in use for many years. Different authors recommend different ways of pretreating the molasses prior to centrifugation (Thompson, 1993; Davis *et al.*, 1997). Because of the variability of the composition of cane molasses a single method of pretreatment will not give optimal Ca removal for every type of molasses. This work describes a systematic attempt at determining the optimal pretreatment method for a given batch of cane molasses.

Theoretical aspects

The Stokes formula for settling velocity,

$$v = \frac{d_p^2 g (\rho - \rho_p)}{18 \eta}$$

calculates the velocity v of settling of solid particles suspended in a liquid under the influence of gravity. It forms the basis on which quantitative comparisons of centrifugation efficiencies are made. The formula indicates that the pertinent variables are particle diameter d_p , density difference $(\rho - \rho_p)$ between the mother liquor and the solid particles, and liquor viscosity η . Particle diameter is influenced by precipitation speed (reaction kinetics) and crystallisation properties of the precipitate. Viscosity is affected by composition, temperature and fluid concentration. Liquor density depends on the composition, concentration, and temperature while particle density is a property of the precipitate which is not likely to vary significantly under different conditions. Gravitational acceleration is represented by the symbol g .

The *measurement* of centrifugation efficiency also deserves some comment. Thompson (1993) used the mass of oven-

dried sludge generated by laboratory centrifugation as a means of comparing the effectiveness of industrial scale centrifugation. Drying the sludge is time consuming which is a disadvantage if results are needed quickly. On the other hand, determination of wet sludge mass (or volume) is inconclusive because the dry solid content of sludge can vary from about 60 to 40% and its relative density is variable. The criteria used to judge centrifugation efficiencies are described in the section on Methods.

Fundamental considerations

The optimum molasses pretreatment and centrifugation procedure endeavours to satisfy the following conditions:

- adequate Ca removal
- minimum energy consumption
- minimum utility consumption (water, electricity)
- minimum sugar loss
- minimum chemical addition
- simplest processing steps
- cheapest processing equipment
- minimum labour requirements
- minimum waste generation
- continuous operation.

Degree of dilution, viscosity, temperature, precipitation efficiency and energy consumption are all interrelated, demonstrating the complexity of the process. The more viscous, the slower the degree of settling, i.e. the lower the centrifugal separation of solids. Dilution lowers viscosity and leads to enhanced mass transfer giving potentially better precipitation, but excessive dilution tends to increase the amount of dissolved Ca, i.e. decrease the potential amount of precipitated Ca. Furthermore, if heating is required, the amount of energy consumed will be higher. High temperature lowers viscosity which makes centrifugal separation of Ca more efficient but it requires greater amounts of heating energy. Prolonged high temperature exposure will result in the degradation of some of the sugars in the molasses.

It is clear that, because of the many competing factors just described, it is not possible to satisfy all the requirements for optimum molasses pretreatment and centrifugation listed above. If these factors are applied to the Davis *et al.* (1997) method of diluting the molasses with water, adding sulphuric acid and heating, while stirring for a certain length of time prior to centrifugation, then it will be desirable to dilute as little as possible, to use the minimum amount of acid, to agitate no more than is necessary for adequate precipitate formation, and to conduct the process at the lowest temperature that will give adequate precipitation and solid separation in the centrifuge.

The *method* for determining the optimum pretreatment procedure should:

- be as simple as possible
- require the minimum labour
- use inexpensive measuring equipment
- give results quickly
- be executable by ordinary laboratory technical staff.

The foregoing considerations indicate that the optimal pretreatment method represents a compromise between a number of competing criteria.

Materials and methods

The investigation was carried out at two levels. Most of the method development work was conducted on a benchtop laboratory centrifuge (Hettich Universal) using 10 ml graduated tapered tubes which fit snugly into the cylindrical metal pockets of the centrifuge head. The head can accommodate eight tubes at a time. The speed of rotation of the centrifuge is 3 500 rpm and it generates 250 g at the tube tip. The automatic timer of the centrifuge was set at 10 minutes for all of the tests. Larger scale centrifugation tests were done on a fixed bowl Alfa Laval disc-stack centrifuge (type MAB 104B-20) which has a rotation speed of 1 500 rpm.

Samples of final molasses from UC, ML, MS and SZ were used. The range of compositions represented by these samples, as indicated in Table 1, was considered adequate for the purposes of the investigation. Molasses dilution was carried out using ordinary tap water, and industrial grade sulphuric acid of 98% purity was used for acidification. All molasses, water and acid measurements were done by mass. The measure that was used to gauge pretreatment effectiveness was Ca content determined by atomic absorption (AA) spectroscopy. Approximate visual indicators of pretreatment efficiency were the quantities of sludge generated which, for laboratory centrifugation, were judged on volume using the graduated centrifuge tubes, whereas for the pilot scale centrifugations the amount of wet sludge removed from the solid bowl was weighed.

Table 1. Composition of molasses samples used.

Source	Brix (°)	Sulphated ash (%)	Ca (ppm)	Mg (ppm)	K (ppm)
UC	82,20	14,03	6 000	3 200	36 000
MS	80,60	15,81	5 509	4 040	34 154
ML	82,05	16,47	6 960	5 200	44 000
SZ	79,85	13,97	3 451	4 577	41 901

In order to compare changes brought about by different treatments, these changes were related to the starting brix of the molasses. A more accurate measure of comparison would have been dry solids. Since the determination of dry solids for molasses is far more cumbersome and time consuming than that of brix, it was decided that the discrepancy between dry solids and brix values did not materially affect the validity of the conclusions. Typical corresponding brix and dry solid measurements for three undiluted and two diluted molasses samples are shown in Table 2.

Table 2. Corresponding brix and dry solid values for molasses samples.

Dry solids %	77,96	77,89	77,81	60,50	60,80
Brix °	82,30	82,25	82,40	63,99	63,47

The investigation attempted to assess quantitatively the effects of dilution, acid addition, temperature, degree of agitation, kinetics and centrifuge type on Ca removal.

Results and discussion

Precision of Ca determinations

Since Ca removal is the main purpose of the pretreatment, Ca content is the most appropriate indicator of pretreatment effectiveness. In order to ascertain what constitutes a significant difference in values it is necessary to have an idea of the precision of the analysis. Using 91 samples that were analysed twice, the second time after storing the samples in a freezer for approximately three months, the average of the relative standard deviations (RSDs) obtained for the Ca analyses was close to 10%. This indicates that the determination of Ca in molasses by AA is not highly precise.

Chemical composition of precipitate

Since precipitation is produced by the addition of sulphuric acid, one would expect, because of the low solubility of calcium sulphate (solubility constant at 25°C is $2,45 \times 10^{-5}$), a significant proportion of the precipitate to be made up of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum). Analytical data, however, indicated that this is not the case. Samples of centrifuge sludge were submitted for X-ray fluorescence (XRF) analysis and X-ray diffraction (XRD). XRF analyses the quantities of elements in a sample while XRD gives information on the chemical nature of crystals. A typical molasses sludge XRF analysis profile is shown in Table 3 and the XRD data of the same sample are shown in Table 4.

Table 3. Typical XRF analysis of molasses sludge (%).

Constituent	Ash	Whole sample
SiO ₂	3,50	2,24
Al ₂ O ₃	0,44	0,28
Fe ₂ O ₃	0,38	0,24
MnO	0,06	0,04
MgO	3,62	2,32
CaO	30,06	19,25
Na ₂ O	0,27	0,17
K ₂ O	52,15	33,40
TiO ₂	0,05	0,04
P ₂ O ₅	1,33	0,85
Subtotal	91,86	58,83
Loss on ignition 1 000°C	35,95	35,95
Subtotal		94,78
S% (in sulphate)		2,06
Cl ppm		7 668

Table 3 indicates that the major elemental constituents are Ca and K (CaO 30,06% and K₂O 52,15% of the ash values, respectively). This is consistent with the finding (given in Table 4) that the major inorganic constituent is syngenite [$\text{CaK}_2(\text{SO}_4)_2$]. If CaSO_4 were the predominant component then CaO would exceed the other components by far in the XRF analysis. It is also interesting to note the relatively low value of MgO, indicating that not much Mg precipitates. The

presence of high molecular weight compounds such as colour bodies, which are likely to become entrained with the syngenite crystals during centrifugation, is to be expected. The quantity of organic compounds in the sludge is indicated by the loss on ignition (LOI) figure of the analysis. The XRD analysis (Table 4), which identifies the crystalline phases, singles out syngenite [$\text{CaK}_2(\text{SO}_4)_2$] as the major component. It also mentions that amorphous materials (organic compounds and silica) are present. Another compound that has been identified as a minor constituent of molasses sludge (not reported in Table 4) is gorgeyite [$\text{Ca}_5\text{K}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$]. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is not listed as a significant component and only traces have been identified by the XRD analysis.

Table 4. XRD results for molasses sludge.

Constituent	Presence
Syngenite	major
Amorphous materials (organic compounds/silica)	present
Ca oxalate	none

Effects of temperature and viscosity

Viscosity and temperature of molasses are closely linked, as shown in Table 5 which gives details of viscosity measurements using two different measuring elements (cone and plate, and spindle) on a sample of molasses from MS diluted to 65°Bx. Although there is a discrepancy between the absolute values of the corresponding measurements of the two methods, the inverse relationship between viscosity and temperature is clear.

Table 5. Viscosity data of 65° Bx molasses from MS.

Temperature (°C)	Viscosity (cP)	
	Spindle	Cone and plate
25	565	244
35	225	199
45	91,5	149
55	64,6	95,7
65	56,5	85,3
75	53,4	-

The influence of temperature on centrifugation efficiency is shown in Table 6. For UC molasses the Ca removal at high temperature is superior to that at lower temperature, but for ML molasses the difference is insignificant. The results indicate that an improvement in centrifugation efficiency can be expected, but the effect does not appear to be dramatic.

Table 6. Effect of temperature on centrifugation efficiency.

Source	Brix (°)	pH	Temperature (°C)	Ca removal (%)
UC	45,0	2,38	25	54,8
			60	63,6
ML	50,0	1,88	24	92,2
			73	91,3

Temperature affects viscosity, which in turn impacts on centrifugation efficiency. However, it is also known that the solubility of certain calcium salts (gypsum in particular) is temperature dependent. It would therefore be useful to get an idea of the importance of temperature in enhancing precipitation apart from the viscosity effect. The difficulty, of course, is that the only way to measure a difference is by centrifugation which depends heavily on viscosity.

The following technique was employed to try to separate the importance of temperature only. Samples of molasses from UC and ML were diluted to 65 and 50°Bx, acidified to pH close to three with sulphuric acid and centrifuged in the laboratory centrifuge at low and high temperatures. Samples of the clarified liquid were decanted from the centrifuge tubes and analysed for calcium. The results (Ca values normalised to 82°Bx) are shown in Table 7. The reasoning behind this scheme was as follows. At the higher brix (65°) the viscosity difference between low and high temperatures is much more pronounced than at the lower brix (50°). If temperature has a significant influence on precipitation then this should operate in a similar way at the higher and the lower brix (provided the temperature differences are similar). So, at the higher brix one would expect a solubility effect (if significant) as well as a significant viscosity effect, whereas at the lower brix one would expect predominantly a solubility effect. If viscosity is the overriding mechanism then the difference between the Ca content at the high temperature, compared with the low temperature, should be greater at the higher brix. The percentage difference in the last column of Table 7 is calculated by subtracting the Ca level at the higher temperature from the corresponding level at the lower temperature, and dividing by the Ca level at the lower temperature.

Table 7. Calcium in supernatant after centrifugation at different dilutions and temperatures.

Source	Brix (°)	pH	Temperature (°C)	Ca* (ppm)	Difference (%)
UC	65	3,02	17,0	6 078	+7,6
		3,02	72,8	6 541	
	50	3,31	16,5	3 196	-22,5
		3,31	69,0	2 478	
ML	65	2,99	14,4	4 505	+23,7
		2,99	78,3	5 573	
	50	3,04	17,3	1 545	-22,9
		3,04	71,6	1 191	

* normalised to 82°Bx

The results in Table 7 are interesting, considering that all Ca data have been normalised to 82°Bx. Contrary to expectation, at the higher brix (65°), the positive difference indicates that less Ca is removed at the higher temperature. In other words, there is another phenomenon which overrides the viscosity effect. It is likely that at the higher temperature less precipitate is formed (i.e. the Ca compounds are more soluble). The negative differences at the lower (50°) brix signify a reduction in Ca content as a result of the higher temperature. This may be due to the fact that at that concentration the viscosity difference has a more marked effect on

centrifugation efficiency than at the higher concentration, or that solubility of Ca compounds is far more sensitive to temperature at lower concentrations than at higher ones. The most important deduction to be drawn is that *dilution has a very profound influence on Ca removal efficiency - far more than temperature or viscosity* because dilution from 65 to 50°Bx produced a drop of more than 50% of the Ca levels for both molasses types, irrespective of the temperature. A separate study of the effect of dilution is reported later.

Two other effects of centrifugation at elevated temperatures compared to ambient have been noticed. Samples of sludge collected from *hot* 65°Bx molasses from FX contained *no* detectable silica whereas the corresponding *cold* molasses yielded a sludge containing 4,4% silica. Furthermore, the XRF analysis of the same two samples (data not presented here) showed that sludge from the hot molasses had a much higher LOI (57,4%) than the cold (38,0%). This implies that the quantity of combustible organic constituents separated out at high temperature was significantly more than that at the lower temperature.

Effect of time and agitation

In order to assess whether precipitation of solids produced by the addition of acid is a slow or a fast reaction, two separate tests were done. In the first test molasses was heated while stirring to 75°C immediately after acid addition. One portion of this was centrifuged as soon as it had reached 75°C, and the remainder was kept hot and agitated for a further four hours before centrifuging. The volume of sludge in the bottom of the centrifuge tubes was similar in both cases, indicating no significant effect of the extended reaction time.

The second test used 65°Bx UC molasses acidified to pH 1,98. No additional heating was applied, but the temperature of the acidified molasses (due to the heat of mixing with concentrated sulphuric acid) had risen to 40°C. The Ca content of the decanted liquid after laboratory centrifugation was 4 000 ppm. The remainder of the sample was left standing at room temperature for 18 hours. Prior to centrifugation it was heated to 40°C. The Ca content of the decanted liquid was 4 197 ppm, which does not appear to be significantly different from the sample that was centrifuged without delay. Precipitation of calcium compounds in molasses therefore seems to be a very fast reaction which is complete soon after adequate mixing.

Effect of dilution

Diluting final molasses with water will reduce its viscosity, which will lead to enhanced efficiency of centrifugal separation of precipitated solids. On the other hand, increased dilution tends to dissolve more precipitated solids, so that the benefits of viscosity reduction are counteracted by the increased solution of solids and it is expected that for each type of molasses an optimal dilution exists in terms of Ca removal. The results of a laboratory investigation into the effects of dilution on Ca content for a sample of unacidified molasses from UC (pH = 5,4) are shown in Figure 2. To make a valid comparison all measured Ca values have been

normalised to the brix of the first sample (70°). The significantly reduced Ca content at dilutions around 50°Bx is partly explained by lime solubility data in sugar solutions (Chen and Chou, 1993).

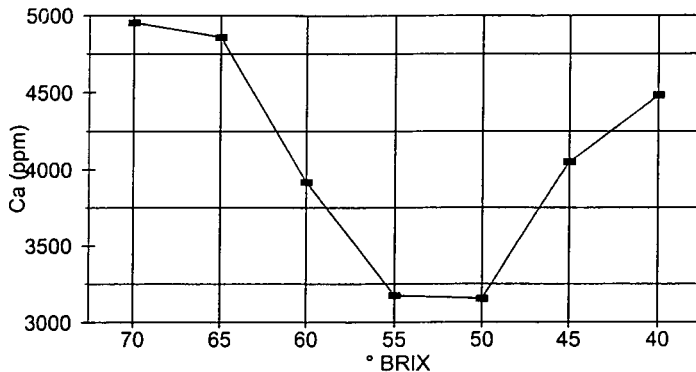


Figure 2. Ca in supernatant (normalised to 70°Bx) after centrifuging molasses diluted to various brix levels.

Since sulphuric acid promotes the precipitation of Ca compounds, a sample of UC molasses was acidified to a pH of 3,96, diluted to different brix values and centrifuged. The results are shown in Figure 3 where the Ca figures have again been normalised to 70°Bx. The shape of the curve in Figure 3 is similar to that of Figure 2 showing a clear optimum dilution in terms of Ca removal. The calcium levels in Figure 3 are approximately half of those in Figure 2, indicating the beneficial effect of acid addition. In both cases the molasses was from the same batch.

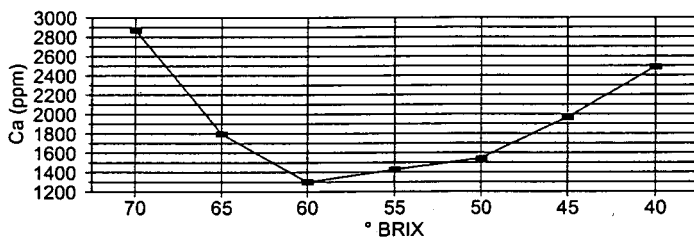


Figure 3. Effect of dilution on UC molasses acidified to pH 3,96.

Effect of sulphuric acid addition

Since dilution itself seems to be an important variable determining the degree of Ca removal, and since the optimum dilution, from the graphs in Figures 2 and 3 appears to be in the range 50 to 60°Bx, it was decided to carry out the investigation of the effect of sulphuric acid addition at 50°Bx. For the purposes of acidification, concentrated (98% purity) sulphuric acid was used to minimise the effect of added dilution. All liquid measurements were done by mass to two decimal places. Since the amount of acid actually added was so small in comparison to the total mass of liquid, no correction was made to the dilution figure. The sulphuric acid was added to 100 g aliquots of 50°Bx molasses in multiples of 1 g. After thorough stirring the pH was measured. Samples of the acidified molasses were then centrifuged in the laboratory unit and the clarified liquid in the centrifuge tubes was decanted for cation analysis. The results obtained are

given in Table 8. Apart from the Ca values, K and Mg contents are also included so that the effect of acid addition on removal of these cations is shown.

Table 8. Effect of sulphuric acid addition on Ca, K and Mg contents of 50°Bx molasses.

Source of molasses	Acid added (g)	pH	Ca (ppm)	K (ppm)	Mg (ppm)
UC	0	5,30	2 573	21 471	2 584
	1	3,95	2 252	19 685	2 559
	2	3,04	964	16 667	2 907
	3	2,00	481	17 570	2 804
	4	0,88	403	15 385	2 814
	5	0,37	362	14 961	2 756
ML	0	5,65	3 217	24 954	4 037
	1	3,89	1 858	23 600	3 800
	2	2,99	816	20 907	3 945
	3	1,66	321	20 000	3 800
	4	0,87	267	20 238	3 770
	5	0,33	206	18 327	3 984

Table 8 indicates that there is a steady and very effective decrease in the Ca content with increased acid addition (decreasing pH). A gradual decrease in the K content is also apparent which is consistent with the finding that syngenite (a Ca-K complex salt) is the main constituent of the precipitate. The Mg results do not show a consistent pattern. In fact, the accuracy of Mg analysis by atomic absorption is not very high, possible due to the interference of a number of other inorganic species. The Mg data also indicate that hardly any Mg is removed. The Ca levels as a function of pH are depicted in Figures 4 and 5.

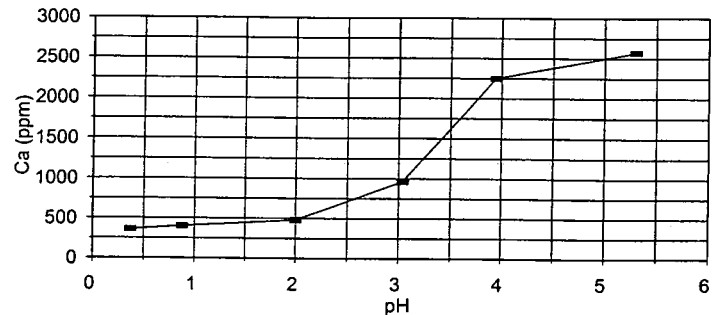


Figure 4. Effect of pH on Ca content (UC molasses).

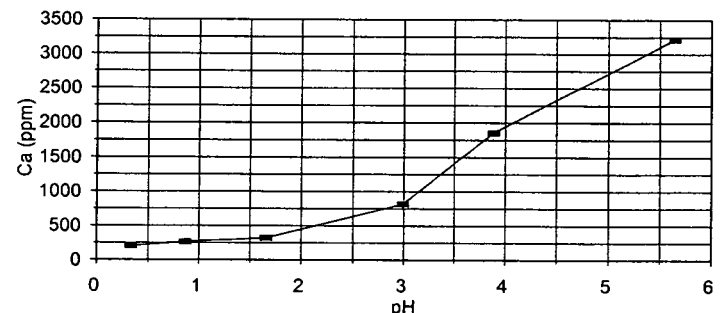


Figure 5. Effect of pH on Ca content (ML molasses).

Effect of using a different precipitant

In order to test whether the sulphate ion in sulphuric acid was the main precipitating agent a solution of ammonium sulphate in water was prepared. A saturated solution at room temperature contained 20 g ammonium sulphate in 50 g solution.

Table 9. Effect of ammonium sulphate on Ca levels.

Source	Water (g)	(NH ₄) ₂ SO ₄ solution (g)	SO ₄ ²⁻ (ppm)	Ca in supernatant (ppm)
ML	60	0	0	3 643
	50	10	17 222	2 128
	40	20	34 444	1 187
	30	30	51 666	1 634
	20	40	68 888	3 065
UC	60	0	0	3 090
	50	10	17 222	2 394
	40	20	34 444	2 629
	30	30	51 666	2 898

Tests were performed on diluted molasses–ammonium sulphate mixtures that gave approximately a 50°Bx solution. This was achieved by weighing 100 g molasses and adding the quantities of tap water and saturated ammonium sulphate solution indicated in Table 9. No pH measurements were taken which, in hindsight, was perhaps unwise. Table 9 also gives the Ca levels achieved in the supernatant by the respective mixtures after centrifugation. It is evident that the Ca levels are relatively high in comparison with those obtained using sulphuric acid, as shown in Table 8. It is clear that the addition of a soluble sulphate salt is not as effective in removing Ca as sulphuric acid. This was also apparent from the diffuse nature of the precipitate in the centrifuge tubes, and therefore the last addition of ammonium sulphate (40 g) was not performed. The reason for the greater effectiveness of sulphuric acid compared with dissolved sulphate from a salt appears to be that acid promotes the dissociation of calcium saccharate, resulting in the formation of sucrose and insoluble calcium complexes (Chen and Chou, 1993).

Effect of seeding

The rate of crystal growth in a supersaturated solution normally increases after seeding the solution with very small solid particles of the same chemical composition as the desired crop of crystals. To test whether seeding has any effect on Ca removal, half of a sample of diluted (45°Bx) molasses was seeded with molasses sludge (100 g/5 kg diluted molasses). After acidification and centrifugation, the sludge and supernatant were compared with those from the unseeded half. The dilution and acid addition had been established as yielding optimum Ca removal for that molasses according to the method described later. The results, shown in Table 10, indicate that seeding with previously generated molasses sludge does not enhance the degree of precipitation, nor of Ca removal. If seeding did improve precipitation, it could be expected that the sludge mass for the seeded portion would be considerably more than 100 g higher than for the unseeded portion, since 100 g of sludge had been added as seed. Seeding therefore appears to lead to an increase in the Ca content in the supernatant.

Table 10. Effect of seeding on sludge mass and Ca in supernatant.

Treatment	Mass of sludge (g)	Ca in supernatant (ppm)
Seeding	972	986
No seeding	952	903

Comparison of laboratory and pilot plant centrifuges

Most of the investigation described above was done with the aid of the laboratory centrifuge. The laboratory operation is a batch process where the residence time during which the liquid is exposed to the centrifugal force can be determined by the operator (in the experiments described above it was kept constant at 10 minutes), whereas in the pilot centrifuge the liquid being clarified flows through the machine continuously, despite the fact that the solids are accumulated batchwise. The separating action in a pilot size unit, which is similar to that of an industrial machine, although ultimately dependent on centrifugal force, is somewhat different to that of a laboratory unit because the flow path of the material being clarified is between a set of disks, as opposed to an unobstructed settling path in the laboratory centrifuge tubes.

The results of identical feed materials being clarified in the laboratory centrifuge and the pilot unit are given in Table 11. It is clear that, in terms of Ca removal, laboratory centrifugation was slightly more efficient than that performed by the Alfa Laval pilot unit. The last row shows that, for 45°Bx molasses, centrifugation at elevated temperature gives more effective Ca removal, similar to the 50°Bx laboratory results from Table 6.

Table 11. Calcium in supernatants after centrifuging with laboratory (tube) or pilot (disc bowl) centrifuges.

Source	Brix (°)	pH	Temperature (°C)	Laboratory Ca (ppm)	Alfa Laval Ca (ppm)
UC	45	2,56	25	769	934
ML	45	0,39	30	297	438
SZ	45	–	25	508	648
UC	45	2,38	25 60	580 519	832 560

Laboratory pretreatment optimisation test

It is clear from the foregoing description that, due to the variability in composition of cane molasses, a single pretreatment method will not result in optimal calcium removal for each type of molasses. It is therefore desirable to have a relatively simple laboratory procedure whereby, for each new batch of molasses, the optimal pretreatment method can be established quickly and reliably.

The method that is described below rests on the finding that the two most important operations determining the effectiveness of calcium removal by centrifugation are dilution and acid addition. Three dilutions of the final molasses are pre-

pared: 45, 50 and 55°Bx. Using 100 g final molasses the quantities of water that are added to achieve these are 75, 60 and 45 g respectively (assuming a starting brix of 80°). To 40 g aliquots of each of these dilutions three amounts of concentrated sulphuric acid are added: 1, 2 and 3 g. This then results in nine different combinations of dilution and acid addition. After careful stirring, subsamples of these are centrifuged in a laboratory unit for 10 minutes, and the appearance and length of the plugs of settled solids in the bottoms of the tubes are noted. The best combination of dilution and acid addition is the one which yields the longest, clearly defined, *light coloured* sediment with a *sharp upper surface*. For this tube, if the supernatant liquid is decanted, the plug of sediment remains intact. A sediment that is *darkly coloured*, and barely distinguishable from the remaining molasses mixture, although it may be much longer than a light coloured precipitate, is sub-optimal and usually indicates insufficient separation efficiency. In the latter case decanting results in losing a considerable fraction of the partially settled solids.

In order to correlate the optimum as determined by the laboratory centrifugation test described above with the Ca levels, samples from a number of tests were submitted to atomic absorption (AA) analysis. The results are shown in Figure 6. The optimum, indicated by circle on graphs, determined from visual inspection of the plug in the centrifuge tubes was in every case close to the optimum as indicated from the AA results.

Conclusions

The results of this investigation indicate that:

- The principal benefit of molasses pretreatment is the removal of a significant proportion of the calcium normally present in cane molasses.
- Dilution and sulphuric acid addition are the most effective pretreatment steps for Ca removal by centrifugation.
- High temperature does enhance Ca removal in the 50 to 55°Bx dilution range, but not at 65°Bx or higher, although its effect is not dramatic.
- Provided a suitably diluted and acidified sample of molasses has been adequately stirred, additional subsequent stirring or increased residence time before centrifugation does not appear to result in superior calcium removal.
- Sulphate ions obtained from a soluble salt are not as effective in promoting precipitation of calcium compounds in molasses as concentrated sulphuric acid.
- Due to the range of composition of South African cane molasses, a single pretreatment method will not produce optimal Ca removal for each batch of molasses.
- A laboratory centrifuge and graduated centrifuge tubes should be adequate for the determination of the optimum molasses pretreatment method.
- Pilot scale (and presumably industrial scale) centrifugation is almost as effective in centrifugal clarification of molasses as laboratory centrifugation.

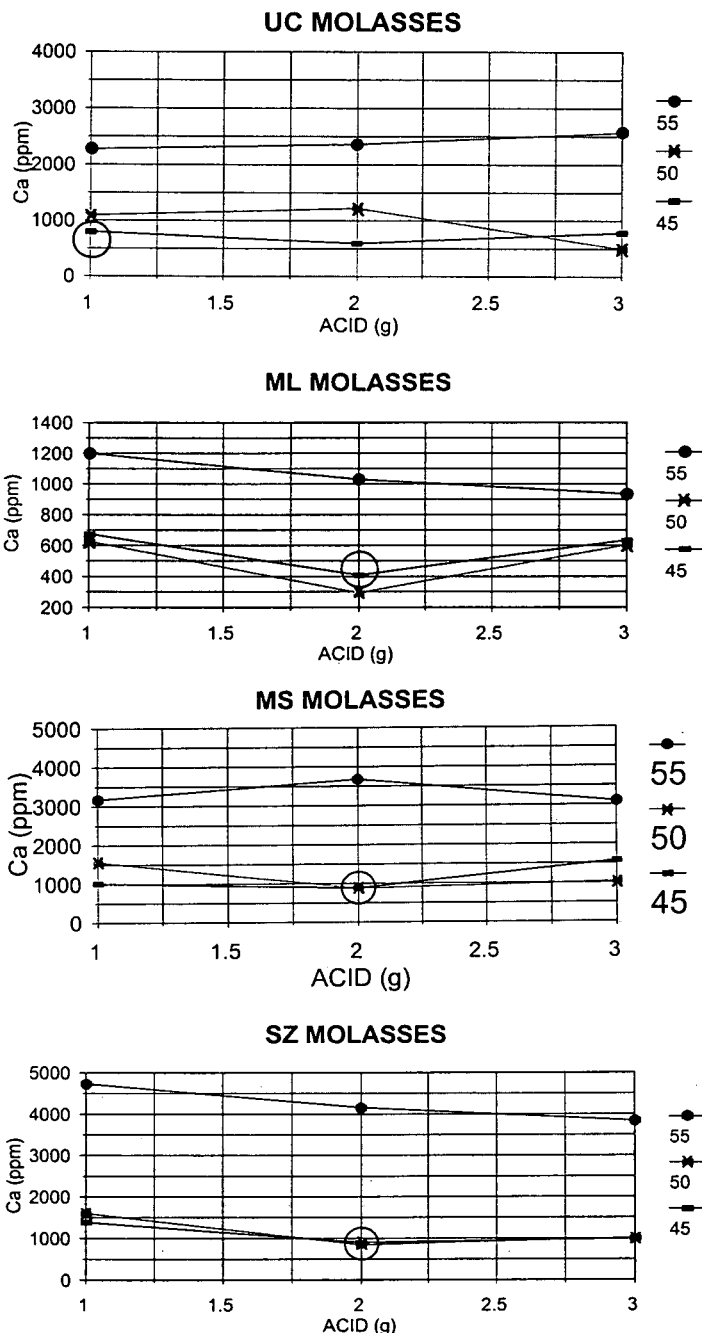


Figure 6. Results of laboratory optimisation tests.

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